Sonntag / Van Wylen

INTRODUCTION TO THERMODYNAMICS

CLASSICAL AND STATISTICAL

Third Edition

USEFUL FORMULAE

$V = (1-x)V_f + x V_g$

$h = (1-x)h_f + x h_f$

$u = u_f + x u_{fg}$

$u = (1-x)u_f + x u_g$

$+Q \equiv$ heat transferred to the system

$+W \equiv$ work done by the system

$Q = \Delta u + W$

$\Delta u^{(\text{const. sp. a})} = m C_{v_0} (T_2 - T_1)$

$P_r = \frac{P}{P_c} \quad T_r = \frac{T}{T_c}$ — for compress table

$V = \frac{\vec{F}}{m}$

$h = u + PV$

$x = \frac{v - v_f}{v_g - v_f}$

$P = P_0 + \frac{F}{A}$

$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$Q = (U_2 - U_1) + \frac{m(v_2^2 - v_1^2)}{2} + mg(z_2 - z_1) + W$

TEMP IS CONSTANT:

$\int P dV = P_1 V_1 \ln \frac{V_2}{V_1}$ or $\frac{P_1}{P_2}$

$(P_1 V_1 = P_2 V_2)$

POLYTROPIC PROCESS

$PV^n = \text{constant}$:

$\int P dV = \frac{P_2 V_2 - P_1 V_1}{1 - n}$

PRESSURE IS CONSTANT:

$\int P dv = P(V_2 - V_1)$

MASS FLOW RATE

$\dot{m} = \frac{AV}{v}$

$q + h_i + \frac{V_i^2}{2} + g z_i = h_e + \frac{V_e^2}{2} + g z_e + w$

THERMAL EFFICENCY OF CARNOT CYCLE:

$1 - \frac{T_L}{T_H} = \eta$

WORK OF CARNOT:

$W = \eta Q_H = \eta T_H \Delta S_H$

REVERSABLE PROCESS:

$W = mRT \ln \frac{V_2}{V_1}$

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PREFACE

In this third edition we have retained the basic objective of the previous editions: to present a comprehensive and rigorous treatment of thermodynamics while retaining an engineering perspective and, in so doing, to provide a textbook that offers considerable flexibility for the inclusion of material on statistical thermodynamics. It is clear that engineers of the twenty-first century will find increasing applications of phenomena and devices based on atomic-scale principles, and some introduction and incorporation of such approaches to problems will be an important part of their educational experience.

We have deliberately directed our presentation to students. New concepts and definitions are presented in the context in which they are first relevant. The first thermodynamic properties to be defined (Chapter 2) are those that can be readily measured: pressure, specific volume, and temperature. In Chapter 3 tables of thermodynamic properties are introduced, but only in regard to these measurable properties. Internal energy and enthalpy are introduced in connection with the first law, entropy in connection with the second law, and the Helmholtz and Gibbs functions in the section on availability. Many 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 provide some progression in difficulty.

We have presented the subject matter so that there are several arrangements by which the material can be covered, both within the classical section, Chapters 1 to 14, and within the statistical section, Chapters 15 to 18. This has been done not only for the amount of material from each part to be studied, but also for the sequence in which the topics may be taken up.

The principal changes of our philosophy and direction in this edition are twofold: an increased awareness and emphasis on environmental issues and concerns throughout the text and in the text problems; and a recognition of the steadily growing use of computers in the study of thermodynamics and also in the solution of thermodynamic problems. The use of computers is reflected in our inclusion of the entire appendix material on classical thermodynamics, Tables A.1 through A.16, on computer disks, and also in the inclusion there of FORTRAN subroutines for the properties of substances listed in these tables, Tables A.1 through A.6, A.11, A.12, and A.14. This allows a considerable flexibility for studying many problems in thermodynamics in terms of the variable quantities involved, and for creating many new design-oriented problems as well. There are of course many other changes in detail in the new edition, but the general organization and order of text material remains the same as in the previous edition.

Throughout the book we have attempted to maintain an engineering perspective, particularly in the choice of examples and problems. One of the major changes from the previous edition is in the problems. Although a number of the earlier problems have been retained, most are new or have been significantly revised. A number of new problems requiring a computer-based solution have been added throughout the book, beginning in Chapter 2, so that instructors who wish to incorporate these problems into the course may do so at any time throughout the term. Several different classes of applications of thermodynamics are introduced in the first chapter, and these then serve as a basis for many of the problems in later chapters. We have retained a chapter on cycles (Chapter 10) because we find that many students enjoy this subject, and it can also serve to strengthen effectively the student's understanding of the first and second laws of thermodynamics, and to introduce him or her to engineering design and practice. Many of the computer-related problems are in this chapter, as are problems concerning a number of modern and relevant applications: heat pumps, cogeneration, topping and bottoming cycles, two-stage systems, combined cycles, and many others. We have also included comments and problems that relate thermodynamics to environmental concerns, as mentioned earlier.

There has been a general updating of text material, definitions, and thermodynamic data, in an effort to remain consistent with current practice in the field. For example, the new temperature scale, ITS-90, is included in Chapter 2, a conceptual approach to the introduction of thermodynamic tables has been presented in Chapter 3, and new ideal-gas tables consistent with the most recent JANAF tables are introduced in Chapter 5, as well as new air tables that are consistent with these tables. In addition, new analysis and the correlation between thermodynamic and ideal-gas temperature scales are included in Chapter 7, a simplified account of developments concerning thermodynamic irreversibility and availability is presented in Chapter 9, more accurate three-parameter generalized correlations are introduced into Chapter 12, and thermochemical properties and equilibrium constants are made internally consistent with the earlier-mentioned gas tables. Applications of statistical thermodynamics in Chapter 18 have been shortened somewhat, and the appendix tables and data have been thoroughly revised and extended.

In regard to the symbols used in this text, we were guided by two considerations. First, we have used the symbols commonly found in the general literature of both classical and statistical thermodynamics; second, we have tried to maintain a consistency of symbols throughout the book. In a limited number of cases, we have used a given symbol for more than one purpose. We believe, however, that the context will clarify the meaning of these symbols.

Our philosophy regarding units in this edition has been to organize the book so that the course or sequence can be taught entirely in SI units (Le Système International d'Unités). Thus, all the text examples are in SI units, as are the complete problem sets and the thermodynamic tables. In recognition, however, of the continuing need for engineering graduates to be familiar with English Engineering units, we have included an introduction to this system in Chapter 2. We have also repeated a sufficient number of problems and tables in these units, which should allow for suitable practice for those who wish to use these units. For dealing with English units, there is the problem of distinguishing between force and mass

units. The symbols lbf and lbm have been used for pound force and pound mass to emphasize this distinction in the English system. Such symbols as lbf/in.^{2} have been used for pressure (rather than psi) and ft^3/lbm for specific volume (rather than cu ft/lb) in order to stress the fundamental units involved in the various parameters. The force–mass conversion constant g_c is treated as being implicit, to enable equations including kinetic or potential energy terms to be handled in a consistent manner with regard to units. In dealing with SI units, we have commonly used the basic units for pressure (pascal) and volume (cubic meter), although we have used the liter extensively as a convenient volume unit. Others may wish to use the bar more extensively as the pressure unit, and we trust that such flexibility in these units will present no particular difficulties to the student. Concerning the extensive properties, a lowercase letter (v, u, h, s) designates the property per unit mass (either pound mass or kilogram); an uppercase letter (V, U, H, S) the property for the entire system; a lowercase letter with a bar ($\bar{v}$, $\bar{u}$, $\bar{h}$, $\bar{s}$) the property per unit mole (either the pound mole or lb mol, or the kilogram mole or kmol, in this text); and an uppercase letter with a bar ($\overline{V}$, $\overline{U}$, $\overline{H}$, $\overline{S}$) the partial molal property in a mixture. Following this pattern, we have found it convenient to designate the total heat transfer as Q, the heat transfer per unit mass of the system as q, the total work as W, and the work per unit mass of the system as w.

Furthermore, we represent the rate of flow across a system boundary or control surface by a dot over the given quantity. Thus, $\dot{Q}$ represents a rate of heat transfer across the system boundary; $\dot{W}$ the rate at which work crosses the system boundary (that is, the power); and $\dot{m}$ the mass rate of flow across a control surface ($\dot{n}$ is used when the mass rate of flow is expressed in moles per unit time). We realize that we have departed from the usual mathematical use of a dotted symbol, in which the dotted symbol typically refers to a derivative with respect to time. However, we have used the dotted symbol to indicate only a flow of heat and work across a system boundary and a flow of heat, work, and mass across a control surface, and not in any other context. We believe that these designations have contributed to a simple and consistent use of symbols for this book.

As was stated at the beginning of this preface to the third edition, the authors believe that an introduction to contemporary applications concerning atomic-scale phenomena and devices is crucial to today's engineering education. With this view in mind, the last four chapters of the book have been written and organized so that the subject of statistical thermodynamics can be introduced in one of several ways, at different depths of coverage.

The minimum coverage includes the development of an understanding of the important basic concepts of thermodynamic equilibrium and of entropy and can reasonably be achieved in four class periods. This minimum coverage would include Sections 15.1 to 15.4, 16.1, 16.5, and 17.1 to 17.3.

The next level of coverage, in two additional class periods, applies to the properties of monatomic gases and includes the additional material of Sections 15.5 and 15.6, 17.5, 18.1 and 18.2, and 18.4. A greater depth of understanding can be achieved by taking additional time to include some or all of Sections 15.8, 16.2 to 16.4, 17.4, and 18.3.

Beyond the basic coverage just discussed, the remainder of the material in this part of the text consists of special applications for those who wish to spend additional time on this subject. These topics include Maxwell–Boltzmann velocity

distribution and free molecular flow (Sections 18.5 and 18.6), diatomic gases (15.7 and 18.7), polyatomic gas (18.8), electron gas (18.9), gas mixtures (18.10), and chemical reactions (18.11). These topics are independent of one another and can be chosen as desired.

We 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 us during the writing of this edition, as it was with the earlier editions of the book. Several secretaries have aided us immeasurably throughout, and we acknowledge this assistance with many thanks. Both undergraduate and graduate students have been of particular assistance, for their perceptive questions have often caused us 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. We must single out two graduate students at the University of Michigan who have been of particular help with this project, especially in the development of the computer programs, former doctoral student Dr. Young Moo Park and current doctoral student Mr. Kyoung Kuhn Park. We appreciate their many valuable contributions to this material. Finally, for each of us, the encouragement and patience of our wives and families have been indispensable, and have made this time of writing pleasant and enjoyable, in spite of the pressures of the project.

Our hope is 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.

Ann Arbor, Michigan
June 1990

Richard E. Sonntag
Gordon J. Van Wylen

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SYMBOLS

a	acceleration
a, A	specific Helmholtz function and total Helmholtz function
AF	air–fuel ratio
c	velocity of light
C_p	constant-pressure specific heat
C_v	constant-volume specific heat
C_{p0}	zero-pressure, constant-pressure specific heat
C_{v0}	zero-pressure, constant-volume specific heat
d	electron state symbol
D	total dissociation energy
D	atomic term symbol
D_0	observed dissociation energy
e	electron charge
e, E	specific energy and total energy
f	electron state symbol
f	fugacity
$\bar{f}_i$	fugacity of component i in a mixture
F	force
F	atomic term symbol
FA	fuel–air ratio
g	acceleration due to gravity
g, G	specific Gibbs function and total Gibbs function
g_c	a constant that relates force, mass, length, and time
$\mathbf{g}_j$	jth energy level degeneracy
h	Planck's constant
h, H	specific enthalpy and total enthalpy
i	electrical current
I	irreversibility
I	moment of inertia
$\mathbf{j}$	molecular rotational quantum number
$\mathbf{J}$	atomic total angular momentum number
k	specific heat ratio: C_p/C_v
k	Boltzmann constant
$\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z$	x-, y-, z-directional translation quantum numbers
K	equilibrium constant
KE	kinetic energy
$\mathbf{l}$	electron azimuthal quantum number
L	length

lw, LW	lost work per unit mass and total lost work
m	mass
$\dot{m}$	mass rate of flow
$\mathbf{m}_l$	electron magnetic quantum number
$\mathbf{m}_s$	electron spin quantum number
m_r	molecular reduced mass
M	molecular weight
mf	mass fraction
$\mathbf{n}$	electron principal quantum number
n	number of moles
n	polytropic exponent
N	number of particles
N_0	Avogadro's number
p	electron state symbol
P	mathematical probability
P	atomic term symbol
P	pressure
P_i	partial pressure of component i in a mixture
PE	potential energy
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	radius
r_e	molecular equilibrium separation
R	gas constant
$\overline{R}$	universal gas constant
s	electron state symbol
s, S	specific entropy and total entropy
S	atomic term symbol
t	time
T	temperature
u, U	specific internal energy and total internal energy
u_{v0}	zero-point energy per mole
$\mathbf{v}$	molecular vibration quantum number
v, V	specific volume and total volume
vf	volume fraction
$\mathbf{V}$	velocity
w	thermodynamic probability—number of microstates
w, W	work per unit mass and total work
$\dot{W}$	rate of work, or power
w_{rev}	reversible work between two states assuming heat transfer with surroundings
x	quality
x	liquid-phase or solid-phase mole fraction
y	vapor-phase mole fraction
Z	partition function

Z	elevation
Z	compressibility factor
Z	electrical charge

SCRIPT LETTERS

$\mathscr{A}$	area
$\mathscr{C}$	number of components
${}_N\mathscr{C}_M$	combinations of N, M at a time
$\mathscr{E}$	electrical potential
$\mathscr{H}$	magnetic field intensity
$\mathscr{M}$	magnetization
$\mathscr{P}$	number of phases
${}_N\mathscr{P}_M$	permutations of N, M at a time
$\mathscr{S}$	surface tension
$\mathscr{T}$	tension
$\mathscr{V}$	variance
$\mathscr{Z}$	nuclear charge

GREEK LETTERS

α	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
η	efficiency
μ	chemical potential
μ_J	Joule–Thomson coefficient
ν	stoichiometric coefficient
ρ	density
ϕ	relative humidity
ϕ	availability for a system
ψ	availability associated with a steady-state, steady-flow process
ω	humidity ratio or specific humidity

SUBSCRIPTS

c	property at the critical point
c.v.	control volume
e	electronic
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	energy state
i	state of a substance entering a control volume
i	property of saturated solid
ig	difference in property for saturated vapor and saturated solid
j	energy level
mp	most probable (equilibrium)
n	nuclear
r	reduced property
r	relative value
r	rotation
s	isentropic process
t	translation
v	vibration
0	property of the surroundings

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
L	liquid phase
S	solid phase
V	vapor phase

1

SOME INTRODUCTORY COMMENTS

In the course of our study of thermodynamics, a number of the examples and problems presented refer to processes that occur in equipment such as a steam power plant, a fuel cell, a vapor-compression refrigerator, a thermoelectric cooler, a rocket engine, and an air separation plant. In this introductory chapter a brief description of this equipment is given. There are at least two reasons for including such a chapter. First, many students have had limited contact with such equipment, and the solution of problems will be more meaningful when they have some familiarity with the actual processes and the equipment. Second, this chapter will provide an introduction to thermodynamics, including the use of certain terms (which will be more formally defined in later chapters), some of the problems to which thermodynamics can be applied, and some of the things that have been accomplished, at least in part, from the application of thermodynamics.

Thermodynamics is relevant to many other processes than those cited in this chapter. It is basic to the study of materials, chemical reactions, and plasmas. The student should bear in mind that this chapter is only a brief and necessarily very incomplete introduction to the subject of thermodynamics.

1.1 THE SIMPLE STEAM POWER PLANT

A schematic diagram of a simple steam power plant is shown in Fig. 1.1. High-pressure superheated steam leaves the boiler, which is also referred to as a steam generator, and enters the turbine. The steam expands in the turbine and, in doing so, does work, which enables the turbine to drive the electric generator. The low-pressure steam leaves the turbine and enters the condenser, where heat is transferred from the steam (causing it to condense) to the cooling water. Because large quantities of cooling water are required, power plants are frequently located near rivers or lakes. This transfer of heat to the water in lakes and rivers leads to the thermal pollution problem, which has been studied extensively in recent years. During our study of thermodynamics we will gain an understanding of why this heat transfer is necessary and how it can be minimized. When the supply of cooling water is limited, a cooling tower may be used. In the cooling tower some of the cooling water evaporates in such a way that it lowers the temperature of the water that remains as a liquid.

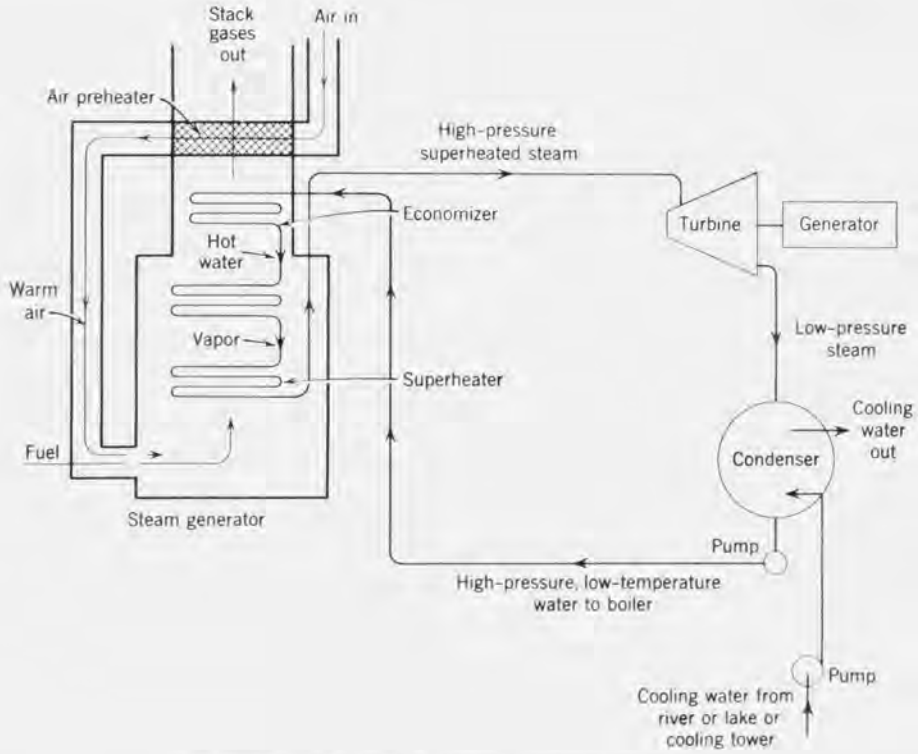


FIGURE 1.1 Schematic diagram of a steam power plant.

The pressure of the condensate leaving the condenser is increased in the pump and thus enables the condensate to flow into the steam generator. In many steam generators an economizer is used. An economizer is simply a heat exchanger in which heat is transferred from the products of combustion (just before they leave the steam generator) to the condensate. The temperature of the condensate is increased, but no evaporation takes place. In other sections of the steam generator, heat is transferred from the products of combustion to the water, causing it to evaporate. The temperature at which evaporation occurs is called the saturation temperature. The steam then flows through another heat exchanger, known as a superheater, where the temperature of the steam is increased well above the saturation temperature.

In many power plants the air that is used for combustion is preheated in the air preheater by transferring heat from the stack gases as they are leaving the furnace. This air is then mixed with fuel—which might be coal, fuel oil, natural gas, or other combustible material—and combustion takes place in the furnace. As the products of combustion pass through the furnace, heat is transferred to the water in the superheater, the boiler, the economizer, and to the air in the air preheater. The products of combustion from power plants are discharged to the atmosphere, which is one of the facets of the air pollution problem we now face.

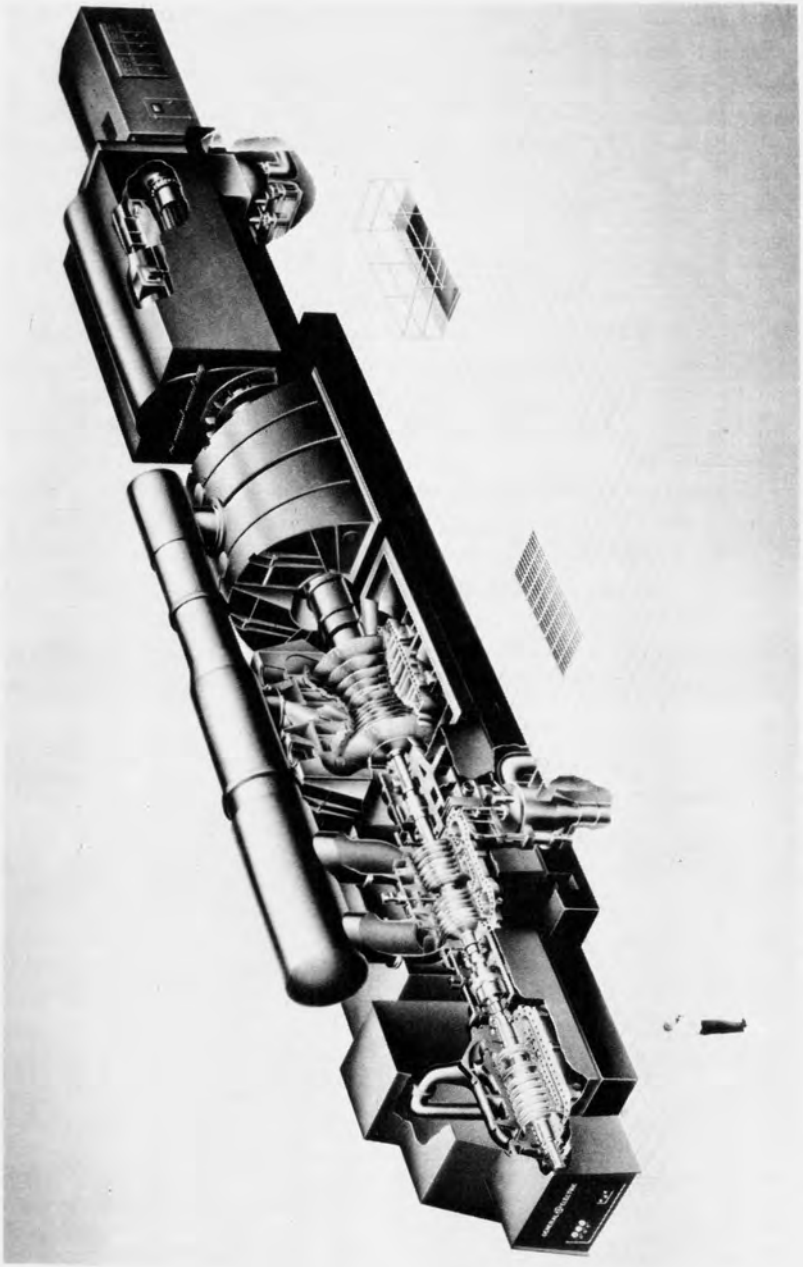


FIGURE 1.2 A large steam turbine. (Courtesy General Electric Co.)

A large power plant has many other pieces of equipment, some of which will be considered in later chapters.

Figure 1.2 shows a steam turbine and the generator that it drives. Steam turbines vary in capacity from less than 10 kilowatts to more than 1 000 000 kilowatts.

Figure 1.3 shows a cutaway view of a condenser. The steam enters at the top and the condensate is collected in the hot well at the bottom while the cooling water flows through the tubes. A large condenser has a tremendous number of tubes, as shown in Fig. 1.3.

Figure 1.4 shows a large steam generator. The flow of air and products of combustion are indicated. The condensate, also called the boiler feedwater, enters at the economizer inlet, and the superheated steam leaves at the superheater outlet.

The number of operating nuclear power plants has increased substantially in recent years. In these power plants the reactor replaces the steam generator of the conventional power plant, and the radioactive fuel elements replace the coal, oil, or natural gas.

There are several different reactor designs in current use. One of these is the boiling-water reactor, such as the system shown in Fig. 1.5. In other nuclear power plants a secondary fluid circulates from the reactor to the steam generator, where heat is transferred from the secondary fluid to the water, which in turn goes through a conventional steam cycle. Safety considerations and the necessity to keep the turbine, condenser, and related equipment from becoming radioactive are always major considerations in the design and operation of a nuclear power plant.

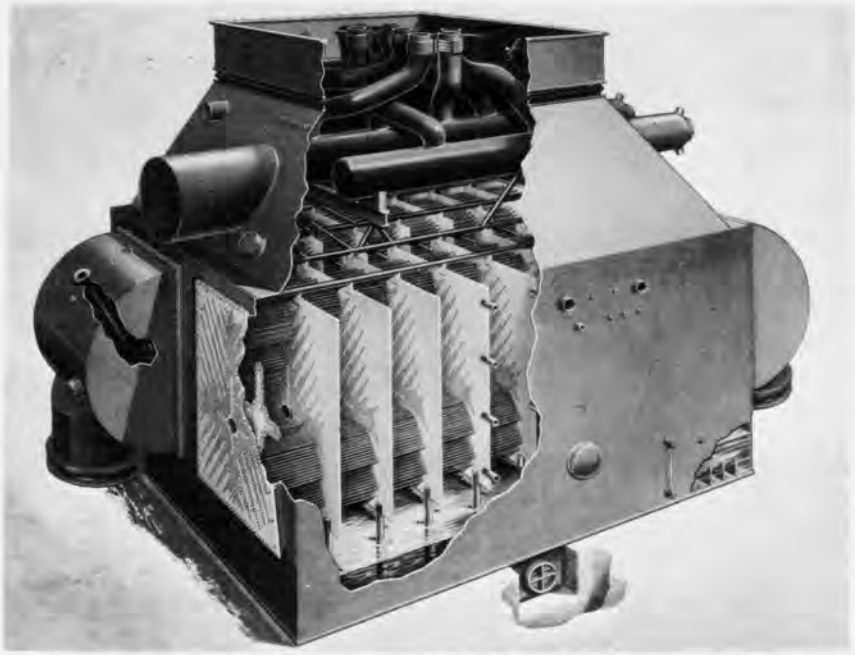


FIGURE 1.3 A condenser used in a large power plant (Courtesy Westinghouse Electric Corp.).

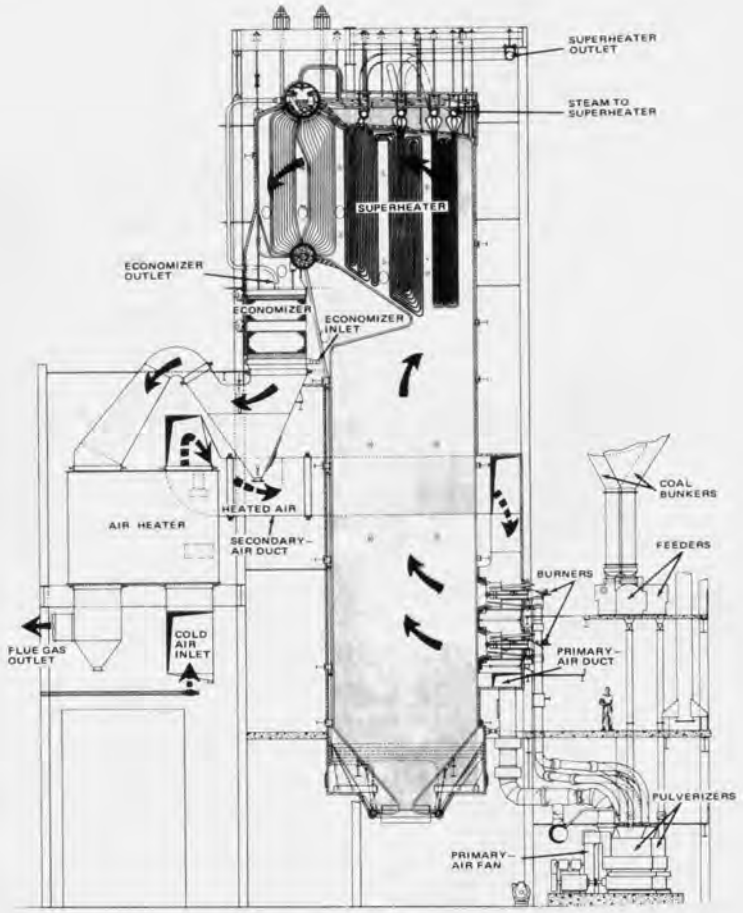


FIGURE 1.4 A large steam generator (Courtesy Babcock and Wilcox Co.).

1.2 FUEL CELLS

When a conventional power plant is viewed as a whole, as shown in Fig. 1.6, fuel and air enter the power plant and products of combustion leave the unit. There is also a transfer of heat to the cooling water, and work is done in the form of the electrical energy leaving the power plant. The overall objective of a power plant is to convert the availability (to do work) of the fuel into work (in the form of electrical energy) in the most efficient manner, taking into consideration cost, space, safety, and environmental concerns.

We might well ask whether all the equipment in the power plant, such as the steam generator, the turbine, the condenser, and the pump, is necessary. Is it possible to produce electrical energy from the fuel in a more direct manner?

The fuel cell accomplishes this objective. Figure 1.7 shows a schematic arrangement of a fuel cell of the ion-exchange membrane type. In this fuel cell hydrogen

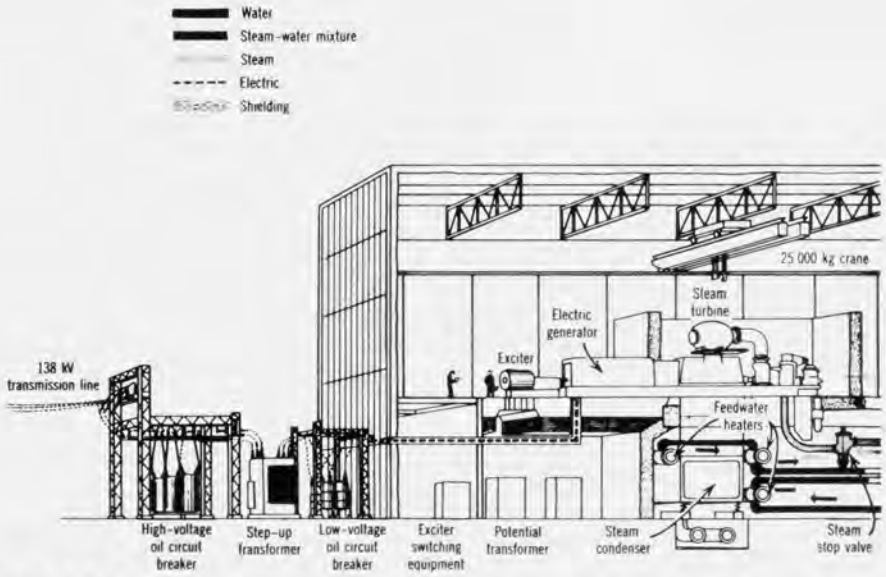


FIGURE 1.5 Schematic diagram of the Big Rock Point nuclear plant of Consumers Power Company at Charlevoix, Michigan (Courtesy Consumers Power Company).

and oxygen react to form water. Let us consider the general features of the operation of this type of fuel cell.

The flow of electrons in the external circuit is from anode to cathode. Hydrogen enters at the anode side, and oxygen enters at the cathode side. At the surface of the ion-exchange membrane the hydrogen is ionized according to the reaction

$$2H_2 \rightarrow 4H^+ + 4e^-$$

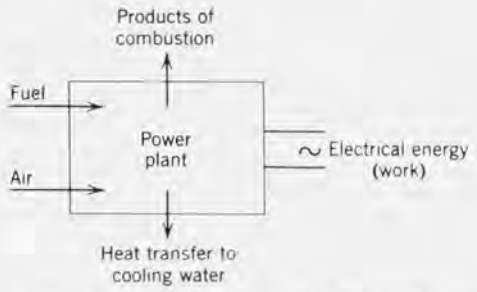
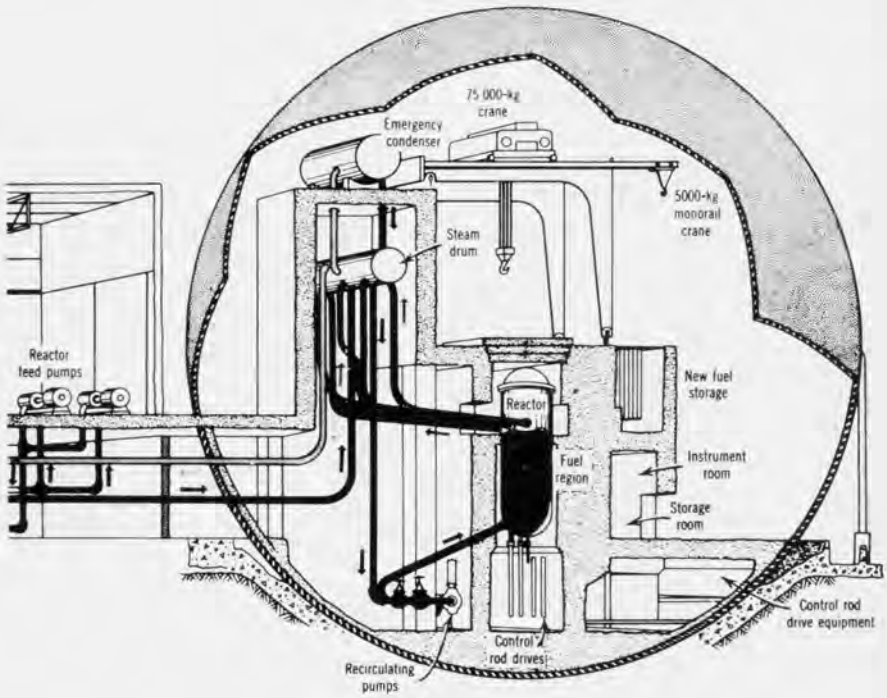


FIGURE 1.6 Schematic diagram of a power plant.



The electrons flow through the external circuit and the hydrogen ions flow through the membrane to the cathode, where the following reaction takes place.

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O$$

There is a potential difference between the anode and cathode, and thus there is a flow of electricity through a potential difference; this, in thermodynamic terms, is called work. There may also be a transfer of heat between the fuel cell and the surroundings.

At the present time the fuel used in fuel cells is usually either hydrogen or a mixture of gaseous hydrocarbons and hydrogen. The oxidizer is usually oxygen. However, current development is directed toward the production of fuel cells that use hydrocarbon fuels and air. Although the conventional (or nuclear) steam power plant is still used in large-scale power-generating systems, and conventional piston engines and gas turbines are still used in most transportation power systems, the fuel cell may eventually become a serious competitor. The fuel cell is already being used to produce power for space and other special applications.

Thermodynamics plays a vital role in the analysis, development, and design of all power-producing systems, including reciprocating internal-combustion engines and gas turbines. Considerations such as the increase of efficiency, improved design optimum operating conditions, environmental pollution, and alternate methods of power generation involve, among other factors, the careful application of the fundamentals of thermodynamics.

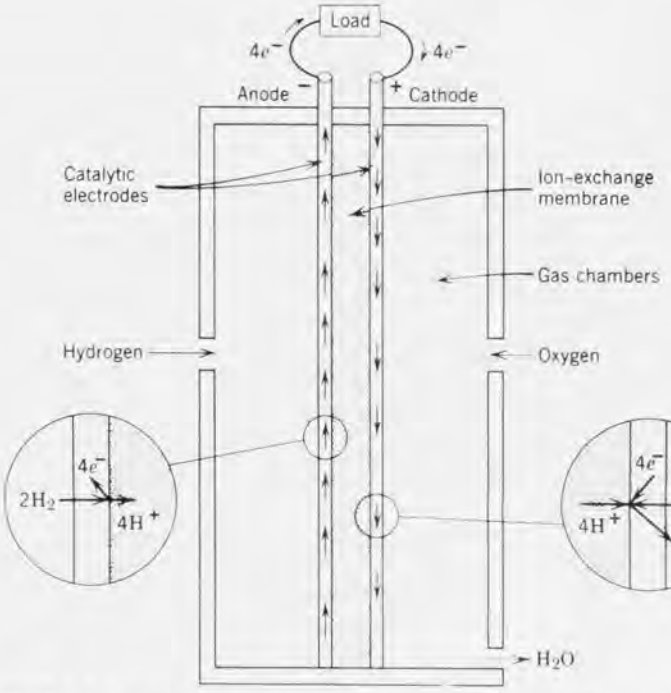


FIGURE 1.7 Schematic arrangement of an ion-exchange membrane type of fuel cell.

1.3 THE VAPOR-COMPRESSION REFRIGERATION CYCLE

A simple vapor-compression refrigeration cycle is shown schematically in Fig. 1.8. The refrigerant enters the compressor as a slightly superheated vapor at a low pressure. It then leaves the compressor and enters the condenser as a vapor at some elevated pressure, where the refrigerant is condensed as heat is transferred to cooling water or to the surroundings. The refrigerant then leaves the condenser as a high-pressure liquid. The pressure of the liquid is decreased as it flows through the expansion valve and, as a result, some of the liquid flashes into cold vapor. The remaining liquid, now at a low pressure and temperature, is vaporized in the evaporator as heat is transferred from the refrigerated space. This vapor then reenters the compressor.

In a typical home refrigerator the compressor is located in the rear near the bottom of the unit. The compressors are usually hermetically sealed, that is, the motor and compressor are mounted in a sealed housing, and the electric leads for the motor pass through this housing. This seal prevents leakage of the refrigerant. The condenser is also located at the back of the refrigerator and is arranged so that the air in the room flows past the condenser by natural convection. The expansion valve takes the form of a long capillary tube, and the evaporator is located around the outside of the freezing compartment inside the refrigerator.

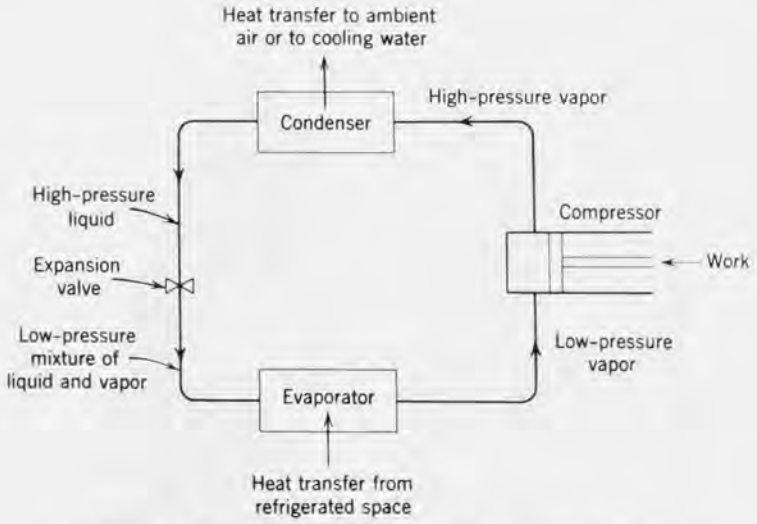


FIGURE 1.8 Schematic diagram of a simple refrigeration cycle.

Figure 1.9 shows a large centrifugal unit that is used to provide refrigeration for an air-conditioning unit. In this unit, water is cooled and then circulated to provide cooling where needed.

1.4 THE THERMOELECTRIC REFRIGERATOR

We may well ask the same question about the vapor-compression refrigerator that we asked about the steam power plant—is it possible to accomplish our objective in a more direct manner? Is it possible, in the case of a refrigerator, to use the electrical energy (which goes to the electric motor that drives the compressor) to produce cooling in a more direct manner, and to avoid the cost of the compressor, condenser, evaporator, and all the related piping?

The thermoelectric refrigerator is such a device. This is shown schematically in Fig. 1.10. The thermoelectric device, like the conventional thermocouple, uses two dissimilar materials. There are two junctions between these two materials in a thermoelectric refrigerator. One is located in the refrigerated space and the other in ambient surroundings. When a potential difference is applied, as indicated, the temperature of the junction located in the refrigerated space will decrease and the temperature of the other junction will increase. Under steady-state operating conditions, heat will be transferred from the refrigerated space to the cold junction. The other junction will be at a temperature above the ambient, and heat will be transferred from the junction to the surroundings.

A thermoelectric device can also be used to generate power by replacing the refrigerated space with a body that is at a temperature above the ambient. Such a system is shown in Fig. 1.11.

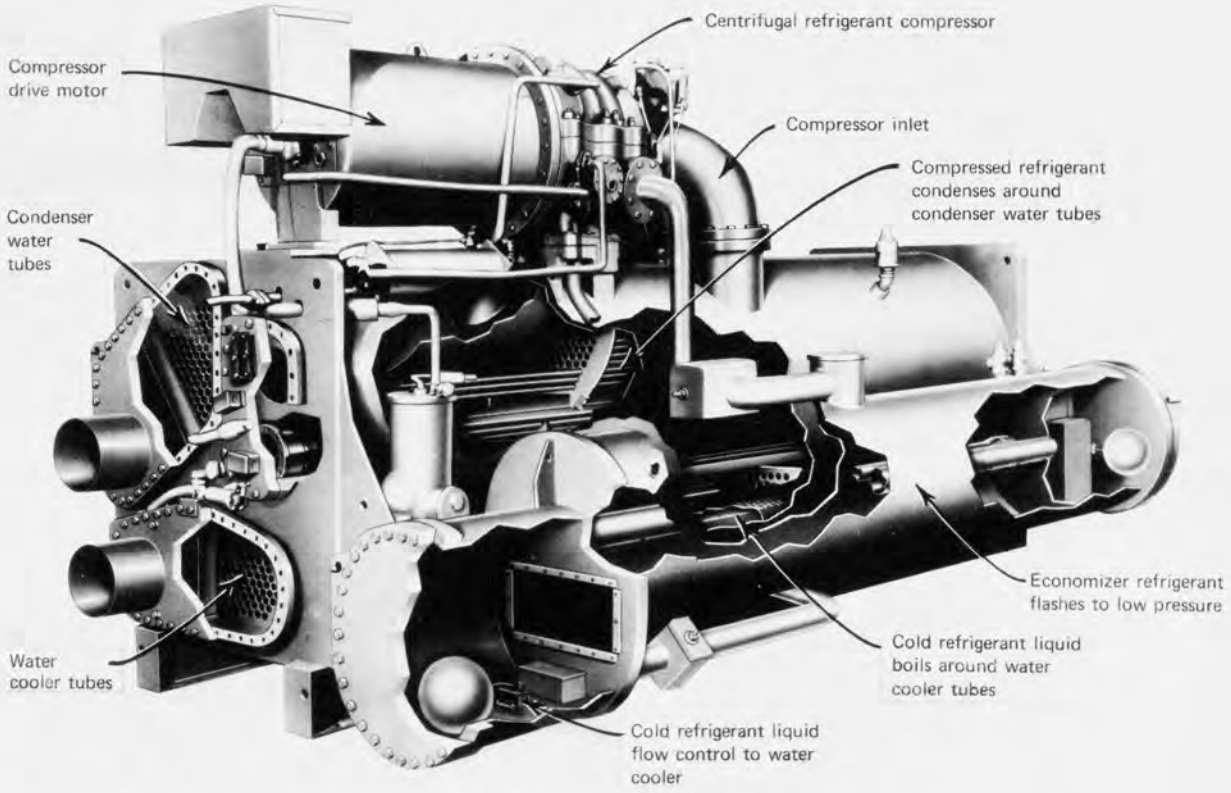


FIGURE 1.9 A refrigeration unit for an air-conditioning system (Courtesy Carrier Air Conditioning Co.)

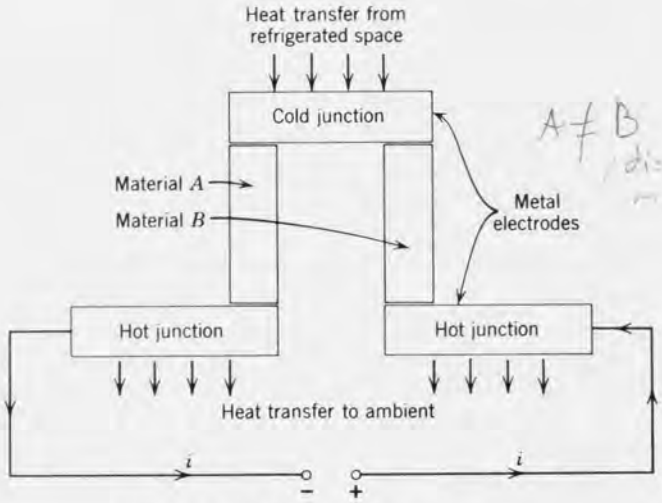


FIGURE 1.10 A thermoelectric refrigerator.

The thermoelectric refrigerator cannot yet compete economically with the conventional vapor-compression units. However, in certain special applications, the thermoelectric refrigerator is already in use and, in view of research and development efforts under way in this field, it is quite possible that thermoelectric refrigerators will be much more extensively used in the future.

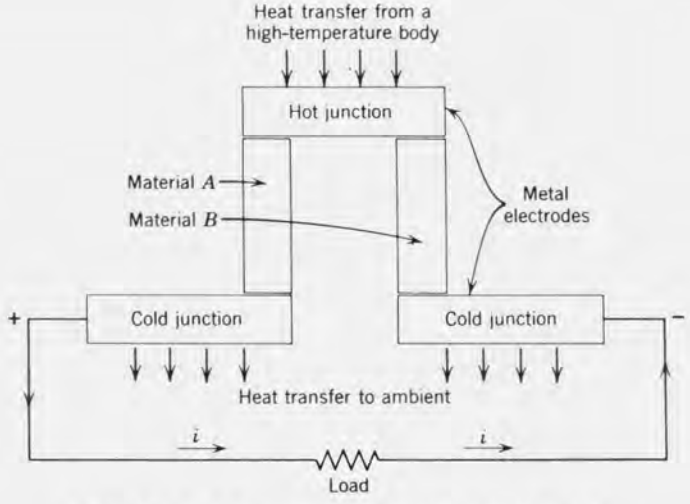


FIGURE 1.11 A thermoelectric power generation device.

1.5 THE AIR SEPARATION PLANT

One process of great industrial significance is the air separation plant, in which air is separated into its various components. The oxygen, nitrogen, argon, and rare gases so produced are used extensively in various industrial, research, space, and consumer goods applications. The air separation plant can be considered an example from two major fields, the chemical process industry and cryogenics. Cryogenics is a term applied to technology, processes, and research at very low temperatures (in general, below 150 K). In both chemical processing and cryogenics, thermodynamics is basic to an understanding of many phenomena that occur and to the design and development of processes and equipment.

A number of different designs of air separation plants have been developed. Consider Fig. 1.12, which shows a somewhat simplified sketch of a type of plant that is frequently used. Air from the atmosphere is compressed to a pressure of 2 to 3 megapascals. It is then purified, particularly to remove carbon dioxide (which would plug the flow passages as it solidifies when the air is cooled to its liquefaction temperature). The air is then compressed to a pressure of 15 to 20 megapascals, cooled to the ambient temperature in the aftercooler, and dried to remove the water vapor (which would also plug the flow passages as it freezes).

The basic refrigeration in the liquefaction process is provided by two different processes. In one process the air in the expansion engine expands. During this

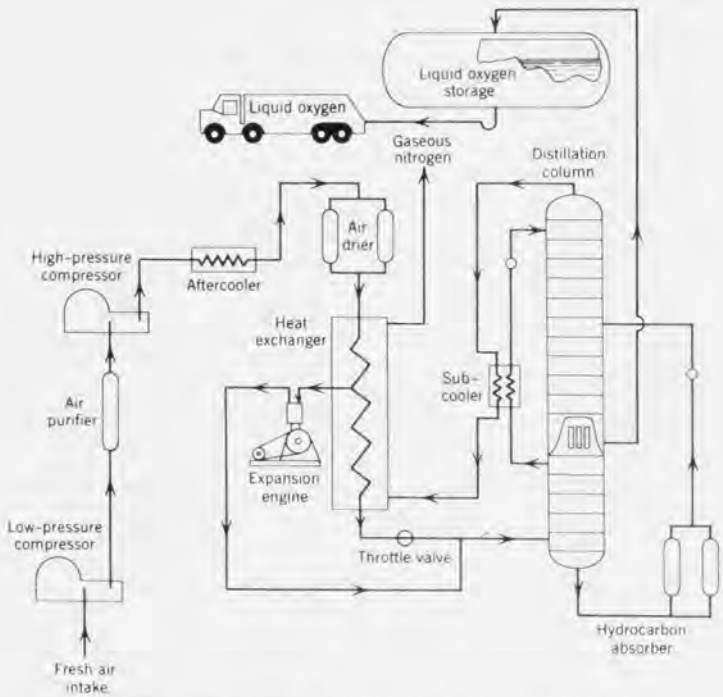


FIGURE 1.12 A simplified diagram of a liquid oxygen plant.

process the air does work and as a result the temperature of the air is reduced. In the other refrigeration process air passes through a throttle valve that is so designed and so located that there is a substantial drop in the pressure of the air and, associated with this, a substantial drop in the temperature of the air.

As shown in Fig. 1.12, the dry, high-pressure air enters a heat exchanger. The air temperature drops as it flows through the heat exchanger. At some intermediate point in the heat exchanger, part of the air is bled off and flows through the expansion engine. The remaining air flows through the rest of the heat exchanger and through the throttle valve. The two streams join (both are at the pressure of 0.5 to 1 megapascal) and enter the bottom of the distillation column, which is referred to as the high-pressure column. The function of the distillation column is to separate the air into its various components, principally oxygen and nitrogen. Two streams of different composition flow from the high-pressure column through throttle valves to the upper column (also called the low-pressure column). One of these streams is an oxygen-rich liquid that flows from the bottom of the lower column and the other is a nitrogen-rich stream that flows through the subcooler. The separation is completed in the upper column. Liquid oxygen leaves from the bottom of the upper column and gaseous nitrogen from the top of the column. The nitrogen gas flows through the subcooler and the main heat exchanger. It is the transfer of heat to this cold nitrogen gas that causes the high-pressure air entering the heat exchanger to become cooler.

Not only is a thermodynamic analysis essential to the design of the system as a whole, but essentially every component of such a system, including the compressors, the expansion engine, the purifiers and driers, and the distillation column, operates according to the principles of thermodynamics. In this separation process we are also concerned with the thermodynamic properties of mixtures and the principles and procedures by which these mixtures can be separated. This is the type of problem encountered in the refining of petroleum and many other chemical processes. It should also be noted that cryogenics is particularly relevant to many aspects of the space program, and a thorough knowledge of thermodynamics is essential for creative and effective work in cryogenics.

1.6 THE CHEMICAL ROCKET ENGINE

The advent of missiles and satellites brought to prominence the use of the rocket engine as a propulsion power plant. Chemical rocket engines may be classified as either liquid propellant or solid propellant, according to the fuel used.

Figure 1.13 shows a simplified schematic diagram of a liquid propellant rocket. The oxidizer and fuel are pumped through the injector plate into the combustion chamber where combustion takes place at high pressure. The high-pressure, high-temperature products of combustion expand as they flow through the nozzle, and as a result they leave the nozzle with a high velocity. The momentum change associated with this increase in velocity gives rise to the forward thrust on the vehicle.

The oxidizer and fuel must be pumped into the combustion chamber, and some auxiliary power plant is necessary to drive the pumps. In a large rocket this auxiliary

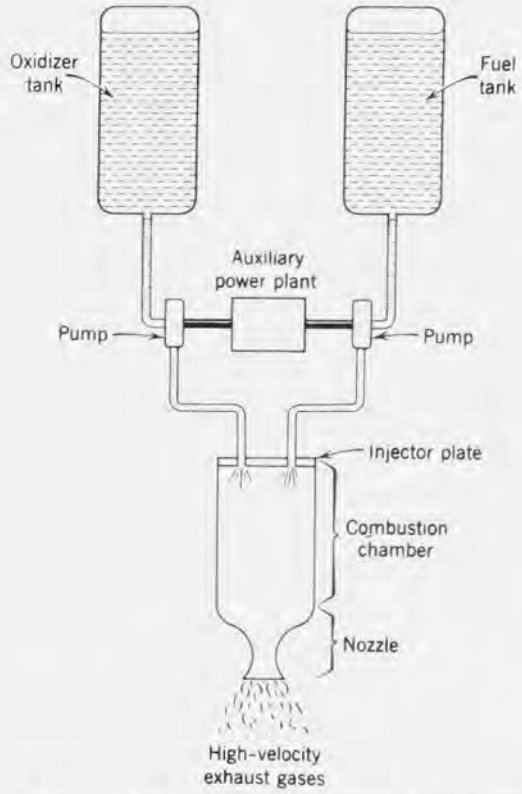


FIGURE 1.13 Simplified schematic diagram of a liquid-propellant rocket engine.

power plant must be very reliable and have a relatively high power output, yet it must be light in weight. The oxidizer and fuel tanks occupy the largest part of the volume of an actual rocket, and the range and payload of a rocket are determined largely by the amount of oxidizer and fuel that can be carried. Many different fuels and oxidizers have been considered and tested, and much effort has gone into the development of fuels and oxidizers that will give a higher thrust per unit mass rate of flow of reactants. Liquid oxygen is frequently used as the oxidizer in liquid-propellant rockets, and liquid hydrogen is frequently used as the fuel.

Much work has also been done on solid-propellant rockets. They have been very successfully used for jet-assisted takeoffs of airplanes, military missiles, and space vehicles. They are much simpler in both the basic equipment required for operation and the logistic problems involved in their use, but they are more difficult to control.

1.7 ENVIRONMENTAL ISSUES

In the first six sections of this chapter, we have introduced and discussed a number of devices, each of which produces certain effects for the use and convenience of humankind. For example, the construction and operation of the steam power plant

creates electricity, which is so deeply entrenched in our society that we take its ready availability for granted. In recent years, however, it has become increasingly apparent that we need to consider seriously the effects of such an operation on our environment. Combustion of hydrocarbon fuels releases carbon dioxide into the atmosphere, where its concentration is increasing. Carbon dioxide, as well as other gases, absorbs infrared radiation from the surface of the earth, holding it close to the planet and creating the "greenhouse effect", which in turn is believed to cause global warming and critical climatic changes around the earth. Power plant combustion, particularly of coal, releases sulfur dioxide, which is absorbed in clouds and later falls as acid rain in many areas. Refrigeration and air-conditioning systems, as well as other industrial processes, use certain chlorofluorocarbons that eventually find their way to the upper atmosphere and destroy the protective ozone layer.

These are only some of the many environmental problems caused by our efforts to produce goods and effects intended to improve our way of life. During our study of thermodynamics, which is the science of the conversion of energy from one form to another, we must continue to reflect on these issues. We must consider how we can eliminate or at least minimize damaging effects, as well as use our natural resources efficiently and responsibly.

2

SOME CONCEPTS AND DEFINITIONS

One excellent definition of thermodynamics is that it is the science of energy and entropy. Since we have not yet defined these terms, an alternate definition in already familiar terms is: thermodynamics is the science that deals with heat and work and these properties of substances that bear a relation to heat and work. Like all sciences, the basis of thermodynamics is experimental observation. In thermodynamics these findings have been formalized into certain basic laws, which are known as the first, second, and third laws of thermodynamics. In addition to these laws, the zeroth law of thermodynamics, which in the logical development of thermodynamics precedes the first law, has been set forth.

In the chapters that follow, we will present these laws and the thermodynamic properties related to these laws, and apply them to a number of representative examples. The objective of the student should be to gain both a thorough understanding of the fundamentals and an ability to apply these fundamentals to thermodynamic problems. The examples and problems further this twofold objective. It is not necessary for the student to memorize numerous equations, for problems are best solved by the application of the definitions and laws of thermodynamics. In this chapter some concepts and definitions basic to thermodynamics are presented.

2.1 THE THERMODYNAMIC SYSTEM AND THE CONTROL VOLUME

A thermodynamic system is defined as a quantity of matter of fixed mass and identity on which attention is focused for study. Everything external to the system is the surroundings, and the system is separated from the surroundings by the system boundaries. These boundaries may be either movable or fixed.

In Fig. 2.1 the gas in the cylinder is considered the system. If a Bunsen burner is placed under the cylinder, the temperature of the gas will increase and the piston will rise. As the piston rises, the boundary of the system moves. As we will see later, heat and work cross the boundary of the system during this process, but the matter that comprises the system can always be identified.

An isolated system is one that is not influenced in any way by the surroundings. This means that no heat or work cross the boundary of the system.

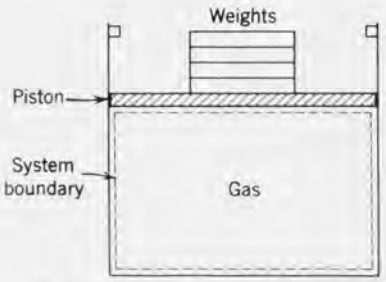


FIGURE 2.1 Example of a system.

In many cases a thermodynamic analysis must be made of a device, such as an air compressor, which has a flow of mass into it, out of it, or both, as shown schematically in Fig. 2.2. The procedure followed in such an analysis is to specify a control volume that surrounds the device under consideration. The surface of this control volume is referred to as a control surface. Mass, as well as heat and work (and momentum), can flow across the control surface.

Thus, a system is defined when dealing with a fixed quantity of mass, and a control volume is specified when a flow of mass is to be analyzed. The difference in these two approaches is considered in detail in Chapter 6. The terms closed system and open system are sometimes used as the equivalent of the terms system (fixed mass) and control volume (involving a flow of mass). The procedure that will be followed in the presentation of the first and second laws of thermodynamics is first to present these laws for a system and then to make the necessary transformations to apply them to a control volume.

2.2 MACROSCOPIC VERSUS MICROSCOPIC POINT OF VIEW

An investigation into the behavior of a system may be undertaken from either a microscopic or a 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

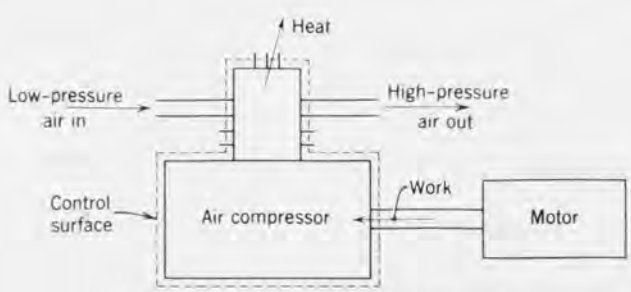


FIGURE 2.2 Example of a control volume.

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 large digital computer, this is a quite 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 approach 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 known as kinetic theory and statistical mechanics.

The other approach that reduces the number of variables to a few that can be handled is 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 not concerned with the action of the individual molecules but with the time-averaged force on a given area, which can be measured by a pressure gage. In fact, these macroscopic observations are completely independent of our assumptions regarding the nature of matter.

The theory and development of thermodynamics in this book will be presented from both the macroscopic and the microscopic points of view. Chapters 3 through 14 cover the principles and a number of applications of classical thermodynamics; Chapters 15 through 18 constitute an introduction to the subject of statistical thermodynamics.

A few remarks should be made regarding the continuum. From the macroscopic view, we are always concerned with volumes that are very large compared to molecular dimensions and, therefore, with systems that contain many molecules. Because we are not concerned with the behavior of individual molecules, we can treat the substance as being continuous, disregarding the action of individual molecules; this is called a continuum. The concept of a continuum, 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, and goes hand in hand with the macroscopic view.

2.3 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 that 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, and 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 properties. 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 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 comprises the system in Fig. 2.1 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 a 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.

2.4 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. 2.3 is removed, the piston rises and a change in state occurs, for the pressure decreases and the specific volume increases. The path of the succession of states through which the system passes is called the process.

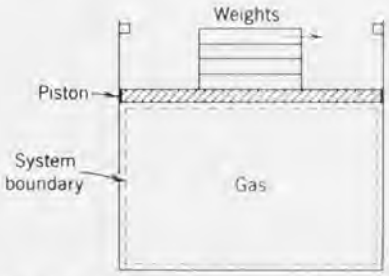


FIGURE 2.3 Example of a system that may undergo a quasiequilibrium process.

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. 2.3, mechanical equilibrium does not exist, and as a result the piston is moved upward until mechanical equilibrium is again 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 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. 2.3 are small and are taken off one by one, the process could be considered quasi-equilibrium. On the other hand, if all the weights were removed at once, the piston would rise rapidly until it hit 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 this process. An isothermal process is a constant-temperature process, an isobaric (sometimes called isopiestic) 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 text the term cycle will refer to a thermodynamic "cycle" unless otherwise designated.

2.5 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. The relation between force and mass is often a difficult matter for students, and 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 one-year period is called the mean solar day, and the mean solar second is 1/86 400 of the mean solar day. (The measurement of the earth's rotation is sometimes made relative to a fixed star, in which case the period is called a sidereal 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-13 atoms to resonate 9 192 631 770 cycles in a cesium resonator.

For periods of time less than a second, the prefixes milli, micro, nano, or pico, as listed in Table 2.1, 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 2.1 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). For many years the accepted standard was the International Prototype Meter, the distance between two marks on a platinum–iridium bar under certain prescribed conditions. This bar is maintained at the International Bureau of Weights and Measures, Sevres, France. In 1960, the CGPM adopted a definition of the

TABLE 2.1 *Unit Prefixes*

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

meter as a length equal to 1 650 763.73 wavelengths in a vacuum of the orange-red line of krypton-86. Then in 1983, the CGPM 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, and may be atoms, molecules, electrons, ions, or other particles or specific groups. For example, one mole of diatomic oxygen, having a molecular weight of 32 (compared to 12 for carbon), is 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 weight. In this text, 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 weight, 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:

$$F = ma$$

The unit of force is the newton (N), which by definition is the force required to accelerate a mass of one kilogram at the rate of one meter per second per second.

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

It is worth noting that SI units derived from proper nouns use capital letters for symbols; others use the 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 has been 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 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 weight 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 concept of force is not defined from Newton's second law, but is instead established as an independent quantity. Thus, for this system, unlike other systems of units, a conversion constant g_c is necessary in Newton's second law. The unit for force is defined in terms of an experimental procedure as follows. Let the standard pound mass be suspended in the earth's gravitational field at a location where the acceleration due to gravity is 32.1740 ft/s^2. The force with which the standard pound mass is attracted to the earth (the buoyant effects of the atmosphere on the standard pound mass must also be standardized) is defined as the unit for force and is termed a pound force (lbf). We must be careful to distinguish between a lbm and a lbf, and we do not use the term pound alone. Since we have independently defined the units for force, mass, length, and time, we have the relation, from Newton's second law,

$$F = \frac{ma}{g_c}$$

or

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

or

$$g_c = 32.174 \frac{\text{lbm ft}}{\text{lbf s}^2}$$

Note that the conversion constant g_c has both a numerical value and dimensions. We also note that for gravitational accelerations that are not too different from the standard value (32.174 ft/s^2 or 9.806 65 m/s^2), the lbf is approximately numerically equal to the lbm. This is the reason that people often drop the designation, which can lead to confusion and inconsistencies. To illustrate, let us calculate the force due to gravity on a one-pound mass at a location where the acceleration due to gravity is 32.14 ft/s^2 (about 10 000 ft above sea level).

$$F = \frac{ma}{g_c} = \frac{1 \text{ lbm} \times 32.14 \text{ ft/s}^2}{32.174 \text{ lbm ft/lbf s}^2}$$
$$= 0.999 \text{ lbf}$$

We further note that the pound force could very well have been defined as

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

in a manner analogous to that for the newton in the SI system. It follows that

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

Comparing this with the conversion constant g_c, we have

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

Since a pure number can be substituted into an equation at any point, we can therefore substitute this unit conversion constant g_c as necessary. Throughout the remainder of this text, we will follow this philosophy, and will not include the constant g_c explicitly in our equations, even when our attention is focused on the English Engineering system of units.

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 a body weighs so much, we mean that this is the force with which it is attracted to the earth (or some other body), that is, the product of its mass and the local gravitational acceleration. The mass of a substance remains constant with elevation, but its weight varies with elevation.

2.6 ENERGY

One of the very important concepts in a study of thermodynamics is the concept of energy. Energy is a fundamental concept, such as mass or force and, as is often the case with such concepts, is very difficult to define. Energy has been defined as the capability to produce an effect. Fortunately the word "energy" and the basic concept that this word represents are familiar to us in everyday usage, and a precise definition is not essential at this point.

It is important to note that energy can be stored within a system and can be transferred (as heat, for example) from one system to another. In our study of statistical thermodynamics we will examine, from a molecular view, the ways in which energy can be stored. Because it is helpful in a study of classical thermodynamics to have some notion of how this energy is stored, a brief introduction is presented here.

Consider as a system a certain gas at a given pressure and temperature contained within a tank or pressure vessel. When considered from the molecular view, we identify three general forms of energy.

1. Intermolecular potential energy, which is associated with the forces between molecules.
2. Molecular kinetic energy, which is associated with the translational velocity of individual molecules.
3. Intramolecular energy (that within the individual molecules), which is associated with the molecular and atomic structure and related forces.

The first of these forms of energy, the intermolecular potential energy, depends on the magnitude of the intermolecular forces and the position the molecules have relative to each other at any instant of time. It is impossible to determine accurately the magnitude of this energy because we do not know either the exact configuration and orientation of the molecules at any time, or the exact intermolecular potential

function. However, there are two situations for which we can make good approximations. The first situation is at low or moderate densities. In this case the molecules are relatively widely spaced, so that only two-molecule or two- and three-molecule interactions contribute to the potential energy. At these low and moderate densities, techniques are available for determining, with reasonable accuracy, the potential energy of a system composed of reasonably simple molecules. The second situation is at very low densities; under these conditions the average intermolecular distance between molecules is so large that the potential energy may be assumed to be zero. Consequently, we have in this case a system of independent particles (an ideal gas) and, therefore, from a statistical point of view, we are able to concentrate our efforts on evaluating the molecular translational and internal energies.

The translational energy, which depends only on the mass and velocities of the molecules, is determined by using the equations of mechanics—either quantum or classical.

The intramolecular internal energy is more difficult to evaluate because, in general, it may result from a number of contributions. Consider a simple monatomic gas such as helium. Each molecule consists of a helium atom. Such an atom possesses electronic energy as a result of both orbital angular momentum of the electrons about the nucleus and angular momentum of the electrons spinning on their axes. The electronic energy is commonly very small compared with the translational energies. (Atoms also possess nuclear energy, which, except in the case of nuclear reactions, is constant. We are not concerned with nuclear energy at this time.) When we consider more complex molecules, such as those comprised of two or three atoms, additional factors must be considered. In addition to having electronic energy, a molecule can rotate about its center of gravity and thus have rotational energy. Furthermore, the atoms may vibrate with respect to each other and have vibrational energy. In some situations there may be an interaction between the rotational and vibrational modes of energy.

In the evaluation of the energy of a molecule, reference is often made to the degree of freedom, f, for these energy modes. For a monatomic molecule, such as helium, $f = 3$, and this represents the three directions, x, y, and z in which the molecule can move. For a diatomic molecule, such as oxygen, $f = 6$. Three of these are the translation of the molecule as a whole in the x, y, and z directions, and two are for rotation. The reason why there are only two modes of rotational energy is evident from Fig. 2.4, where we take the origin of the coordinate system at the

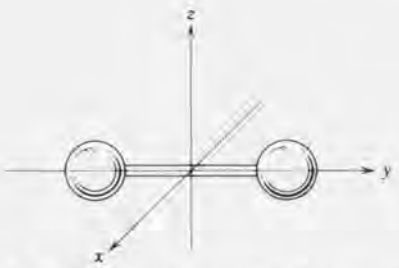


FIGURE 2.4 The coordinate system for a diatomic molecule

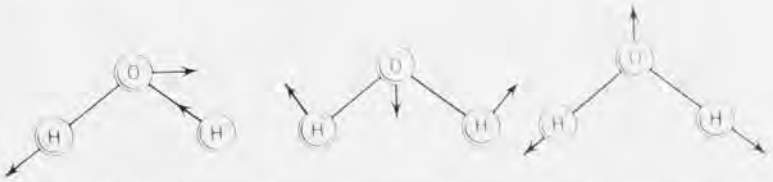


FIGURE 2.5 The three principal vibrational modes for the water molecule.

center of gravity of the molecule, and the y-axis along the molecule's internuclear axis. The molecule will then have an appreciable moment of inertia about the x-axis and the z-axis, but not about the y-axis. The sixth degree of freedom of the molecule is vibration, which relates to stretching of the bond joining the atoms.

For a more complex molecule such as H_2O, there are additional vibrational degrees of freedom. Figure 2.5 shows a model of the H_2O molecule. From this diagram it is evident that there are three vibrational degrees of freedom. It is also possible to have rotational energy about all three axes. Thus, for the H_2O molecule, there are nine degrees of freedom ($f = 9$), three translational, three rotational, and three vibrational.

This general discussion can be summarized by referring to Fig. 2.6. Let heat be transferred to the water. During this process the temperature of the liquid and vapor (steam) will increase, and eventually all the liquid will become vapor. From the macroscopic view we are concerned only with the energy that is transferred as heat, the change in properties, such as temperature and pressure, and the total amount of energy (relative to some base) that the H_2O contains at any instant. Thus, questions about how energy is stored in the H_2O do not concern us. From a microscopic viewpoint we are concerned about the way in which energy is stored

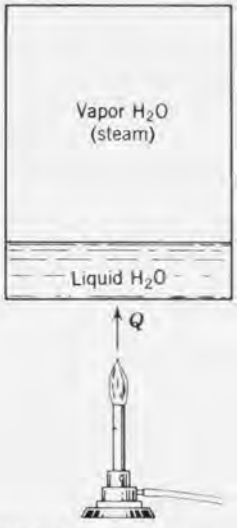


FIGURE 2.6 Heat transfer to water.

in the molecules. We might be interested in developing a model of the molecule so that we could predict the amount of energy required to change the temperature a given amount. There is an obvious relation between the macroscopic or classical and the microscopic or statistical points of view, and this book has been designed to give both and to relate them to each other. Many of these considerations will relate to the matter of energy.

2.7 SPECIFIC VOLUME

The specific volume of a substance is defined as the volume per unit mass, and is given the symbol v. The density of a substance is defined as the mass per unit volume, and is therefore the reciprocal of the specific volume. Density is designated by the symbol ρ. Specific volume and density are intensive properties.

The specific volume of a system in a gravitational field may vary from point to point. For example, if the atmosphere is considered a system, the specific volume increases as the elevation increases. Therefore, the definition of specific volume involves the specific volume of a substance at a point in a system.

Consider a small volume δV of a system, and let the mass be designated δm. The specific volume is defined by the relation

$$v = \lim_{\delta V \to \delta V'} \frac{\delta V}{\delta m}$$

where $\delta V'$ is the smallest volume for which the system can be considered a continuum.

Thus, in a given system, we should speak of the specific volume or density at a point in the system, and recognize that this may vary with elevation. However, most of the systems that we consider are relatively small, and the change in specific volume with elevation is not significant. Therefore, we can speak of one value of specific volume or density for the entire system.

In this text, the specific volume and density will be given either on a mass or on a mole basis. A bar over the symbol (lowercase) will be used to designate the property on a mole basis. Thus, $\bar{v}$ will designate molal specific volume and $\bar{\rho}$ will designate the molal density. In SI units, those for specific volume are m^3/kg and m^3/mol (or $m^3/kmol$); for density the corresponding units are kg/m^3 and mol/m^3 (or $kmol/m^3$). In English units, those for specific volume are ft^3/lbm and $ft^3/lb\,mol$; the corresponding units for density are lbm/ft^3 and $lb\,mol/ft^3$.

Although the SI unit for volume is the cubic meter, a commonly used volume unit is the liter (L), which is a special name given to a volume of 0.001 cubic meters, that is, $1\ L = 10^{-3}\ m^3$. $\frac{1\ L}{10^{-3}\ m^3} = 1$

2.8 PRESSURE

When dealing with liquids and gases, we ordinarily speak of pressure; for solids we speak of stresses. The pressure in a fluid at rest at a given point is the same in all directions, and we define pressure as the normal component of force per unit

area. More specifically, if $\delta\mathscr{A}$ is a small area, $\delta\mathscr{A}'$ the smallest area over which we can consider the fluid a continuum, and δF_n the component of force normal to $\delta\mathscr{A}$, we define pressure, P, as

$$P = \lim_{\delta\mathscr{A} \to \delta\mathscr{A}'} \frac{\delta F_n}{\delta\mathscr{A}}$$

The pressure P at a point in a fluid in equilibrium is the same in all directions. In a viscous fluid in motion, the variation in the state of stress with orientation becomes an important consideration. These considerations are beyond the scope of this book, and we will consider pressure only in terms of a fluid in equilibrium.

The unit for pressure in the International System is the force of one newton acting on a square meter area, which is called the pascal (Pa). That is,

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

In general, the unit for pressure that is consistent with the English units is pounds force per square foot (lbf/ft^2). On the other hand, in common parlance and general experimental work, pressures are often measured in pounds force per square inch (lbf/in.^{2}). Therefore, the student should be careful in numerical calculations to introduce the conversion 144 in.^{2} = 1 ft^2 as necessary.

Two other units, not part of the International System, continue to be widely used. These are the bar, where

$$1 \text{ bar} = 10^5 \text{ Pa} = 0.1 \text{ MPa}$$

and the standard atmosphere, where

$$1 \text{ atm} = 101\,325 \text{ Pa} = 14.696 \text{ lbf/in.}^2$$

which is slightly larger than the bar. In this text, we will normally use the SI unit, the pascal, and especially the multiples of kilopascal and megapascal. The bar will be utilized often in the examples and problems, but the atmosphere will not be used, except in specifying certain reference points.

In most thermodynamic investigations we are concerned with absolute pressure. Most pressure and vacuum gages, however, read the difference between the absolute pressure and the atmospheric pressure existing at the gage. This is referred to as gage pressure. This is shown graphically in Fig. 2.7, and the following examples illustrate the principles. Pressures below atmospheric and slightly above atmospheric, and pressure differences (for example, across an orifice in a pipe) are frequently measured with a manometer, which contains water, mercury, alcohol, oil, or other fluids. From the principles of hydrostatics one concludes that for a difference in level of L meters, the pressure difference in pascals is calculated by the relation

$$\Delta P = \rho L g$$

where ρ is the density of the fluid, and g is the local acceleration due to gravity. The accepted standard value for gravitational acceleration is

$$g = 9.806\,65 \text{ m/s}^2 = 32.174 \text{ ft/s}^2$$

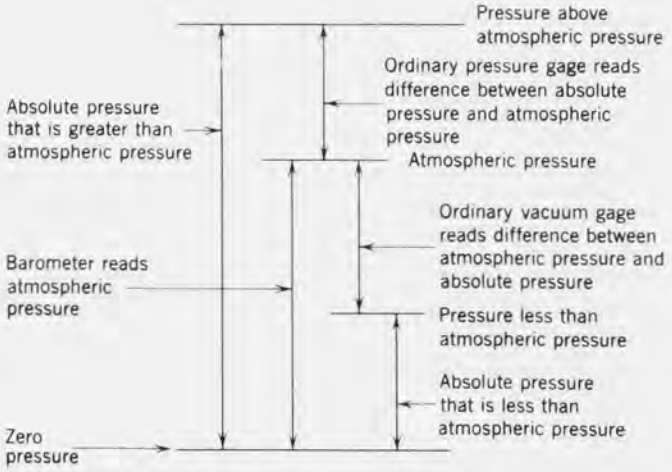


FIGURE 2.7 Illustration of terms used in pressure measurement.

but the value varies with location and elevation. The use of a manometer is illustrated in Fig. 2.8.

For distinguishing between absolute and gage pressure in this text, the term pascal or lbf/in.^{2} will always refer to absolute pressure. Any gage pressure will be indicated as such.

2.9 EQUALITY OF TEMPERATURE

Although temperature is a familiar property, an exact definition of it is difficult. We are aware of "temperature" first of all as a sense of hotness or coldness when we touch an object. We also learn early that when a hot body and a cold body are brought into contact, the hot body becomes cooler and the cold body becomes warmer. If these bodies remain in contact for some time, they usually appear to have the same hotness or coldness. However, we also realize that our sense of hotness or coldness is very unreliable. Sometimes very cold bodies may seem hot,

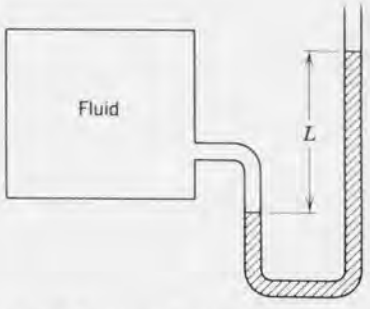


FIGURE 2.8 Example of pressure measurement using a column of fluid.

and bodies of different materials that are at the same temperature appear to be at different temperatures.

Because of these difficulties in defining temperature, we define equality of temperature. Consider two blocks of copper, one hot and the other cold, each of which is in contact with a mercury-in-glass thermometer. If these two blocks of copper are brought into thermal communication, we observe that the electrical resistance of the hot block decreases with time and that of the cold block increases with time. After a period of time has elapsed, however, no further changes in resistance are observed. Similarly, when the blocks are first brought in thermal communication, the length of a side of the hot block decreases with time, but the length of a side of the cold block increases with time. After a period of time, no further change in length of either of the blocks is perceived. In addition, the mercury column of the thermometer in the hot block drops at first and that in the cold block rises, but after a period of time no further changes in height are observed. We may say, therefore, that two bodies have equality of temperature if, when they are in thermal communication, no change in any observable property occurs.

2.10 THE ZEROTH LAW OF THERMODYNAMICS

Now consider the same two blocks of copper and another thermometer. Let one block of copper be brought into contact with the thermometer until equality of temperature is established, and then remove it. Then let the second block of copper be brought into contact with the thermometer. Suppose that no change in the mercury level of the thermometer occurs during this operation with the second block. We then can say that both blocks are in thermal equilibrium with the given thermometer.

The zeroth law of thermodynamics states that when two bodies have equality of temperature with a third body, they in turn have equality of temperature with each other. This seems very obvious to us because we are so familiar with this experiment. Because the principle is not derivable from other laws, and because it precedes the first and second laws of thermodynamics in the logical presentation of thermodynamics, it is called the zeroth law of thermodynamics. This law is really the basis of temperature measurement. Every time a body has equality of temperature with the thermometer, we can say that the body has the temperature we read on the thermometer. The problem remains how to relate temperatures that we might read on different mercury thermometers or obtain from different temperature-measuring devices, such as thermocouples and resistance thermometers. This observation suggests the need for a standard scale for temperature measurements.

2.11 TEMPERATURE SCALES

Two scales are commonly used for measuring temperature, namely the Fahrenheit (after Gabriel Fahrenheit, 1686–1736) and the Celsius. The Celsius scale was formerly called the centigrade scale but is now designated the Celsius scale after Anders Celsius (1701–1744), the Swedish astronomer who devised this scale.

The Fahrenheit temperature scale is used with the English Engineering system of units, and the Celsius scale with the SI unit system. Until 1954 both of these scales were based on two fixed, easily duplicated points—the ice point and the steam point. The temperature of the ice point is defined as the temperature of a mixture of ice and water that is in equilibrium with saturated air at a pressure of 1 atm. The temperature of the steam point is the temperature of water and steam, which are in equilibrium at a pressure of 1 atm. On the Fahrenheit scale these two points are assigned the numbers 32 and 212, respectively, and on the Celsius scale the points are 0 and 100, respectively. Why Fahrenheit chose these numbers is an interesting story. In searching for an easily reproducible point, Fahrenheit selected the temperature of the human body and assigned it the number 96. He assigned the number 0 to the temperature of a certain mixture of salt, ice, and salt solution. On this scale the ice point was approximately 32. When this scale was slightly revised and fixed in terms of the ice point and steam point, the normal temperature of the human body was found to be 98.6 F.

In this text the symbols F and °C will denote the Fahrenheit and Celsius scales, respectively. The symbol T will refer to temperature on all temperature scales.

At the tenth CGPM in 1954, the Celsius scale was redefined in terms of a single fixed point and the ideal-gas temperature scale. The single fixed point is the triple point of water (the state in which the solid, liquid, and vapor phases of water exist together in equilibrium). The magnitude of the degree is defined in terms of the ideal-gas temperature scale, which is discussed in Chapter 7. The essential features of this new scale are a single fixed point and a definition of the magnitude of the degree. The triple point of water is assigned the value 0.01°C. On this scale the steam point is experimentally found to be 100.00°C. Thus, there is essential agreement between the old and new temperature scales.

We have not yet considered an absolute scale of temperature. The possibility of such a scale comes from the second law of thermodynamics and is discussed in Chapter 7. On the basis of the second law of thermodynamics, a temperature scale that is independent of any thermometric substance can be defined. This absolute scale is usually referred to as the thermodynamic scale of temperature. However, it is very complicated to use this scale directly, and therefore, a more practical scale, the International Temperature Scale, which closely represents the thermodynamic scale, has been adopted.

The absolute scale related to the Celsius scale is the Kelvin scale (after William Thomson, 1824–1907, who is also known as Lord Kelvin), and is designated K (without the degree symbol). The relation between these scales is

$$K = {}^{\circ}C + 273.15$$

In 1967, the CGPM defined the kelvin as 1/273.16 of the temperature at the triple point of water. The Celsius scale is now defined by this equation instead of by its earlier definition.

The absolute scale related to the Fahrenheit scale is the Rankine scale and is designated R. The relation between these scales is

$$R = F + 459.67$$

2.12 THE INTERNATIONAL TEMPERATURE SCALE OF 1990

In 1989 the International Committee on Weights and Measures adopted a revised International Temperature Scale of 1990, the ITS-90, which is described below. This scale, similar to earlier ones of 1927, 1948, and 1968, has been refined, extended in range, and made to conform more closely to the thermodynamic temperature scale. It is based on a number of fixed and easily reproducible points that are assigned definite numerical values of temperature, and on specified formulas relating temperature to the readings on certain temperature-measuring instruments for the purpose of interpolation between the defining fixed points. These defining points and a summary of the interpolation techniques are listed here for the sake of completeness, although the student will have limited need for them at this time.

The defining fixed-point temperatures in International Kelvin Temperatures are:

^{3}He and ^{4}He	VP	3 to 5
e-H_2	TP	13.8033
e-H_2 (or He)	VP (or CVGT)	≈17
e-H_2 (or He)	VP (or CVGT)	≈20.3
Ne	TP	24.5561
O_2	TP	54.3584
Ar	TP	83.8058
Hg	TP	234.3156
H_2O	TP	273.16
Ga	MP	302.9146
In	FP	429.7485
Sn	FP	505.078
Zn	FP	692.677
Al	FP	933.473
Ag	FP	1234.93
Au	FP	1337.33
Cu	FP	1357.77

VP indicates vapor pressure point; CVGT indicates constant volume gas thermometer point; TP indicates triple point (equilibrium temperature at which the solid, liquid and vapor phases coexist); FP indicates freezing point and MP indicates melting point (the FP and the MP are equilibrium temperatures at which the solid and liquid phases coexist under a pressure of 101 325 Pa, one standard atmosphere). The isotopic composition is that naturally occurring.

The means available for measurement and interpolation lead to a division of the temperature scale into four general ranges.

1. The range from 0.65 to 5.0 K is based on vapor pressure measurements for ^{3}He and ^{4}He, the latter divided into two parts. Each has a specified 12-term equation for the vapor-pressure as a function of temperature.
2. The range from 3.0 to 24.5561 K is based on measurements using a helium constant-volume gas thermometer, which has been calibrated at three points: one point in the range from 3 to 5 K, based on helium vapor pressure mea-

surements; one at the triple point of equilibrium-hydrogen; and one at the triple point of neon.

3. The range from 13.8033 to 1234.93 K is based on fixed points in the table and on measurements of resistance ratios of certain platinum resistance thermometers calibrated at specified sets of the fixed points, and using equations and corrections in each of four subranges of temperature. There are also alternatives for further subdividing these ranges.
4. The range above 1234.93 K is based on measurements of the intensity of visible-spectrum radiation compared with that of the same wavelength at the freezing point of either silver, gold, or copper, and on Planck's equation for blackbody radiation.

PROBLEMS

2.1 A mass of 25 kg is accelerated steadily at the rate of 20 m/s^2. What force is required?

2.2 Two kilomoles of diatomic nitrogen gas are enclosed in a container. A force of 1 kN accelerates this system. Neglecting the mass of the container, what is the acceleration?

2.2E Two pound moles of diatomic nitrogen gas are enclosed in a container. A force of 1000 lbf now accelerates this system. Neglecting the mass of the container, what is the acceleration?

2.3 The "standard" acceleration (at sea level and 45 degrees latitude) due to gravity is 9.806 65 m/s^2. Calculate the force due to "standard" gravity acting on a mass of 50 kg.

2.4 With what force is a mass of 100 kg attracted to the earth at a location where the gravitational acceleration is 9.65 m/s^2?

2.5 Gravitational acceleration on the surface of the moon is approximately one-sixth that on the surface of the earth. A 1-kg mass is "weighed" with a beam balance on the surface of the moon. What is the expected reading? If this mass is weighed with a spring scale that reads correctly for standard gravity on earth (see Problem 2.3), what is the reading?

2.6 One means of inducing an artificial gravity inside an orbiting space station is by rotating the station. If a gravity of 2 m/s^2 is induced in this manner, how much would a man who weighs 75 kg on earth weigh inside the space station?

2.7 A 25-kg steel tank having a volume capacity of 250 L is filled with liquid water. What force is needed to accelerate this combined system at a rate of 2 m/s^2? Assume that the density of the water is 1000 kg/m^3.

2.7E A 50-lbm steel tank having a volume capacity of 10 ft^3 is filled with liquid water. What force is needed to accelerate this combined system at a rate of 5 ft/s^2? Assume that the density of the water is 62.4 lbm/ft^3.

2.8 A gas is contained in a vertical cylinder fitted with a piston, as shown in Fig. 2.9. Atmospheric pressure outside is 1 bar, and the piston diameter is 100 mm. What is the mass of the piston if the gas pressure inside is 110 kPa? Assume standard gravitational acceleration.

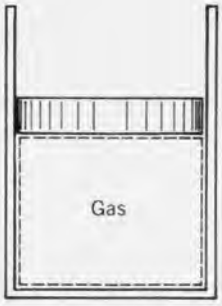


FIGURE 2.9 Sketch for Problem 2.8.

2.9 A mercury barometer used to read the local ambient pressure has a column height of 740 mm. What is the ambient pressure in kPa, assuming that the density of mercury is 13 600 kg/m^3?

2.10 The reading on a pressure gage is 1.65 MPa, and the local barometer reading is 94 kPa. Calculate the absolute pressure.

2.10E The reading on a pressure gage is 245 lbf/in.^{2} and the local barometer reading is 14.3 lbf/in.^{2}. Calculate the absolute pressure.

2.11 The height of a mercury manometer column used to measure a vacuum is 700 mm, and the local barometer reading is 95 kPa. Calculate the absolute pressure (see Problem 2.9).

2.12 A cylinder is fitted with a piston restrained by a spring, as shown in Fig. 2.10. The spring is fully extended (exerting no force) when the piston rests on the bottom of the cylinder. It exerts a force that is linear with distance moved as the piston rises after the air supply line valve is opened. At the state shown in the figure, the pressure inside the cylinder is 300 kPa and the volume is 0.5 L. The piston diameter is 100 mm, its mass is 5 kg, and ambient pressure outside the cylinder is 100 kPa. Additional air is admitted from the supply line, causing the piston to rise another 20 mm. What is the pressure inside the cylinder at this point?

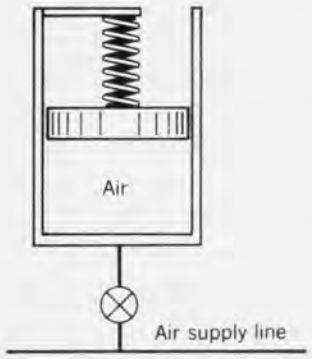


FIGURE 2.10 Sketch for Problem 2.12.

2.13 Consider a manometer containing a fluid with a density of 800 kg/m^3. What is the pressure difference if the difference in height of the two columns is 100 mm? What is the column height difference if this same pressure difference is measured by a manometer containing mercury (see Problem 2.9)?

2.14 A mercury column measures a pressure difference of 150 kPa in a piece of experimental apparatus located outdoors. The minimum temperature at this location in winter is -15°C and the maximum temperature in the summer is 35°C. What is the difference in height of the mercury column in summer compared to the height in winter when measuring the given pressure difference? Assume standard gravitational acceleration. The following data are given for the density of mercury.

T, °C	Density kg/m^3
-10	13 620
10	13 570
30	13 521

2.15 A piece of experimental apparatus is located in an airplane flying at 20 000 m, where $g = 9.75$ m/s^2. The air flow in this apparatus is measured by determining the pressure drop across an orifice with a mercury manometer. The manometer level difference reading is 250 mm, and the local temperature is -10°C (see Problem 2.14). What is the pressure drop in kPa?

2.16 The level of the water in an enclosed water tank is 40 m above ground level. The pressure in the air space above the water is 120 kPa, and the density of the water is 1000 kg/m^3. What is the water pressure at ground level?

2.16E The level of the water in an enclosed water tank is 125 ft above ground level. The pressure in the air space above the water is 18 lbf/in.^{2}, and the density of the water is 62.4 lbm/ft^3. What is the water pressure at ground level?

2.17 Two cylinders A and B are connected by a piston of two different diameters, as shown in Fig. 2.11. Cylinder B contains a gas. Cylinder A contains oil pumped up to a pressure of 300 kPa by a hydraulic pump. The mass of the piston is 10 kg. Calculate the gas pressure in cylinder B.

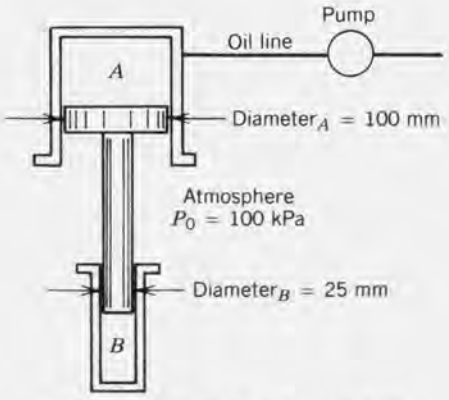


FIGURE 2.11 Sketch for Problem 2.17.

2.18 Using the freezing and boiling point temperatures for water for the Celsius and Fahrenheit scales, develop a conversion formula for the two scales. At what temperature do the two scales have the same numerical value? What is the conversion formula between the Kelvin and Rankine temperature scales?

2.19 A particular platinum versus rhodium–platinum thermocouple is to be calibrated and used in the temperature range described as range 3 in the discussion of the IPTS-68 in Section 2.12. During calibration, the thermocouple EMF readings in microvolts are 5552, 9147, and 10 333 at the freezing points of antimony, silver, and gold, respectively. Assuming a polynomial relation of the form

$$\text{EMF} = C_0 + C_1 T + C_2 T^2$$

determine the temperature at a location where this thermocouple gives a reading of 7500 microvolts.

COMPUTER PROBLEM

2.1C Write a computer program to solve the thermocouple calibration problem discussed in Problem 2.19. Any three sets of calibration readings can be given, and the result is a polynomial equation with specified coefficients that can be used at any temperature in the calibrated range.

3

PROPERTIES OF A PURE SUBSTANCE

In the previous chapter we considered three familiar properties of a substance—specific volume, pressure, and temperature. We now turn our attention to pure substances and consider some of the phases in which a pure substance may exist, the number of independent properties a pure substance may have, and methods of presenting thermodynamic properties.

3.1 THE PURE SUBSTANCE

A pure substance is one that has a homogeneous and invariable chemical composition. It may exist in more than one phase, but the chemical composition is the same in all phases. Thus, liquid water, a mixture of liquid water and water vapor (steam), and a mixture of ice and liquid water are all pure substances; every phase has the same chemical composition. On the other hand, a mixture of liquid air and gaseous air is not a pure substance, because the composition of the liquid phase is different from that of the vapor phase.

Sometimes a mixture of gases, such as air, is considered a pure substance as long as there is no change of phase. Strictly speaking, this is not true. As we will see later, we should say that a mixture of gases such as air exhibits some of the characteristics of a pure substance as long as there is no change of phase.

In this text the emphasis will be on simple compressible substances. This term designates substances whose surface effects, magnetic effects, and electrical effects are insignificant when dealing with the substances. On the other hand, changes in volume, such as those associated with the expansion of a gas in a cylinder, are very important. Reference will be made, however, to other substances for which surface, magnetic, and electrical effects are important. We will refer to a system consisting of a simple compressible substance as a simple compressible system.

3.2 VAPOR–LIQUID–SOLID-PHASE EQUILIBRIUM IN A PURE SUBSTANCE

Consider as a system 1 kg of water contained in the piston–cylinder arrangement shown in Fig. 3.1*a*. Suppose that the piston and weight maintain a pressure of

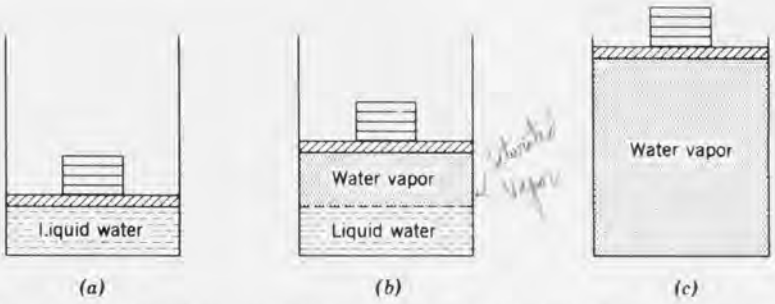


FIGURE 3.1 Constant-pressure change from liquid to vapor phase for a pure substance.

0.1 MPa in the cylinder, and that the initial temperature is 20°C. As heat is transferred to the water, the temperature increases appreciably, the specific volume increases slightly, and the pressure remains constant. When the temperature reaches 99.6°C, additional heat transfer results in a change of phase, as indicated in Fig. 3.1*b*. That is, some of the liquid becomes vapor, and during this process both the temperature and pressure remain constant, but the specific volume increases considerably. When the last drop of liquid has vaporized, further transfer of heat results in an increase in both temperature and specific volume of the vapor, as shown in Fig. 3.1*c*.

The term saturation temperature designates the temperature at which vaporization takes place at a given pressure. This pressure is called the saturation pressure for the given temperature. Thus, for water at 99.6°C the saturation pressure is 0.1 MPa, and for water at 0.1 MPa the saturation temperature is 99.6°C. For a pure substance there is a definite relation between saturation pressure and saturation temperature. A typical curve, called the vapor-pressure curve, is shown in Figure 3.2.

If a substance exists as liquid at the saturation temperature and pressure, it is called saturated liquid. If the temperature of the liquid is lower than the saturation temperature for the existing pressure, it is called either a subcooled liquid (implying that the temperature is lower than the saturation temperature for the given pressure) or a compressed liquid (implying that the pressure is greater than the saturation pressure for the given temperature). Either term may be used, but the latter term will be used in this text.

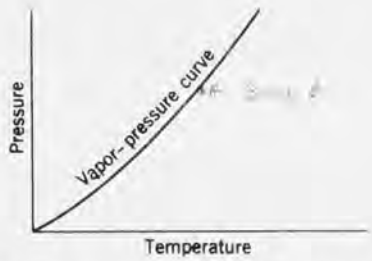


FIGURE 3.2 Vapor-pressure curve of a pure substance.

When a substance exists as part liquid and part vapor at the saturation temperature, its quality is defined as the ratio of the mass of vapor to the total mass. Thus, in Fig. 3.1*b*, if the mass of the vapor is 0.2 kg and the mass of the liquid is 0.8 kg, the quality is 0.2 or 20 percent. The quality may be considered an intensive property and has the symbol x. Quality has meaning only when the substance is in a saturated state, that is, at saturation pressure and temperature.

If a substance exists as vapor at the saturation temperature, it is called saturated vapor. (Sometimes the term dry saturated vapor is used to emphasize that the quality is 100 percent.) When the vapor is at a temperature greater than the saturation temperature, it is said to exist as superheated vapor. The pressure and temperature of superheated vapor are independent properties, since the temperature may increase while the pressure remains constant. Actually, the substances we call gases are highly superheated vapors.

Consider Fig. 3.1 again. Let us plot on the temperature–volume diagram of Fig. 3.3 the constant-pressure line that represents the states through which the water passes as it is heated from the initial state of 0.1 MPa and 20°C. Let state *A* represent the initial state, *B* the saturated-liquid state (99.6°C), and line *AB* the process in which the liquid is heated from the initial temperature to the saturation temperature. Point *C* is the saturated-vapor state, and line *BC* is the constant-temperature process in which the change of phase from liquid to vapor occurs. Line *CD* represents the process in which the steam is superheated at constant pressure. Temperature and volume both increase during this process.

Now let the process take place at a constant pressure of 1 MPa, starting from an initial temperature of 20°C. Point *E* represents the initial state, in which the specific volume is slightly less than that at 0.1 MPa and 20°C. Vaporization begins at point *F*, where the temperature is 179.9°C. Point *G* is the saturated-vapor state, and line *GH* the constant-pressure process in which the steam is superheated.

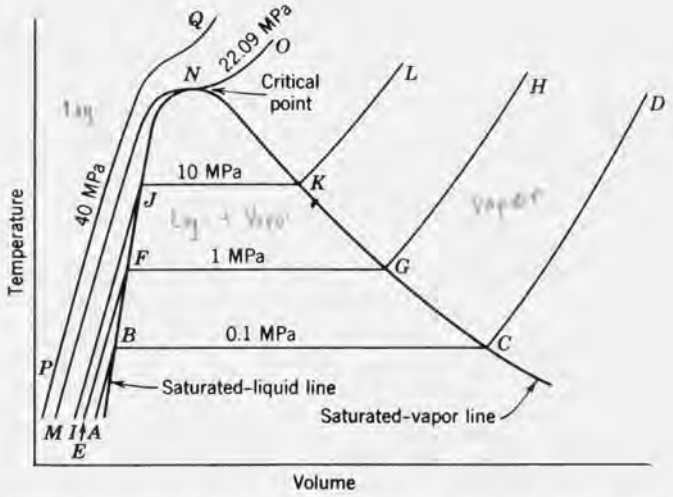


FIGURE 3.3 Temperature–volume diagram for water showing liquid and vapor phases (not to scale).

In a similar manner, a constant pressure of 10 MPa is represented by line *IJKL*, for which the saturation temperature is 311.1°C.

At a pressure of 22.09 MPa, represented by line *MNO*, we find, however, that there is no constant-temperature vaporization process. Instead, point *N* is a point of inflection with a zero slope. This point is called the critical point. At the critical point the saturated-liquid and saturated-vapor states are identical. The temperature, pressure, and specific volume at the critical point are called the critical temperature, critical pressure, and critical volume. The critical-point data for some substances are given in Table 3.1. More extensive data are given in Table A.7 in the Appendix.

A constant-pressure process at a pressure greater than the critical pressure is represented by line *PQ*. If water at 40 MPa, 20°C, is heated in a constant-pressure process in a cylinder as shown in Fig. 3.1, there will never be two phases present and the state shown in Fig. 3.1*b* will never exist. Rather, there will be a continuous change in density and at all times there will be only one phase present. The question then is when do we have a liquid and when do we have a vapor? The answer is that this is not a valid question at supercritical pressures. We simply term the substance a fluid. However, rather arbitrarily, at temperatures below the critical temperature we usually refer to it as a compressed liquid and at temperatures above the critical temperature as a superheated vapor. It should be emphasized, however, that at pressures above the critical pressure we never have a liquid and vapor phase of a pure substance existing in equilibrium.

In Fig. 3.3 line *NJFB* represents the saturated-liquid line and line *NKGC* represents the saturated-vapor line.

Let us consider another experiment with the piston–cylinder arrangement. Suppose that the cylinder contains 1 kg of ice at −20°C, 100 kPa. When heat is transferred to the ice, the pressure remains constant, the specific volume increases slightly, and the temperature increases until it reaches 0°C, at which point the ice melts and the temperature remains constant. In this state the ice is called a saturated solid. For most substances the specific volume increases during this melting process, but for water the specific volume of the liquid is less than the specific volume of the solid. When all the ice has melted, a further heat transfer causes an increase in temperature of the liquid.

If the initial pressure of the ice at −20°C is 0.260 kPa, heat transfer to the ice results in an increase in temperature to −10°C. At this point, however, the ice

TABLE 3.1 Some Critical-Point Data

	Critical Temperature, °C	Critical Pressure, MPa	Critical Volume, m^3/kg
Water	374.14	22.09	0.003 155
Carbon dioxide	31.05	7.39	0.002 143
Oxygen	−118.35	5.08	0.002 438
Hydrogen	−239.85	1.30	0.032 192

TABLE 3.2 Some Solid–Liquid–Vapor Triple-Point Data

	Temperature, °C	Pressure, kPa
Hydrogen (normal)	−259	7.194
Oxygen	−219	0.15
Nitrogen	−210	12.53
Mercury	−39	0.000 000 13
Water	0.01	0.6113
Zinc	419	5.066
Silver	961	0.01
Copper	1083	0.000 079

passes directly from the solid phase to the vapor phase in the process known as sublimation. Further heat transfer results in superheating of the vapor.

Finally, consider an initial pressure of the ice of 0.6113 kPa and a temperature of −20°C. Through heat transfer let the temperature increase until it reaches 0.01°C. At this point, however, further heat transfer may cause some of the ice to become vapor and some to become liquid, for at this point it is possible to have the three phases in equilibrium. This point is called the triple point, which is defined as the state in which all three phases may be present in equilibrium. The pressure and temperature at the triple point for a number of substances are given in Table 3.2.

This whole matter is best summarized by the diagram of Fig. 3.4, which shows how the solid, liquid, and vapor phases may exist together in equilibrium. Along the sublimation line the solid and vapor phases are in equilibrium, along the fusion line the solid and liquid phases are in equilibrium, and along the vaporization line

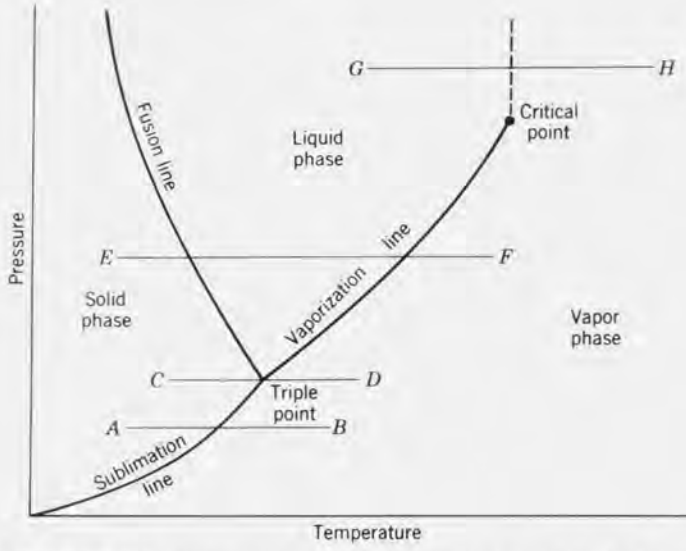


FIGURE 3.4 Pressure–temperature diagram for a substance such as water.

the liquid and vapor phases are in equilibrium. The only point at which all three phases may exist in equilibrium is the triple point. The vaporization line ends at the critical point because there is no distinct change from the liquid phase to the vapor phase above the critical point.

Consider a solid in state *A*, as shown in Fig. 3.4. When the temperature increases but the pressure (which is less than the triple-point pressure) is constant, the substance passes directly from the solid to the vapor phase. Along the constant-pressure line *EF*, the substance passes from the solid to the liquid phase at one temperature, and then from the liquid to the vapor phase at a higher temperature. Constant-pressure line *CD* passes through the triple point, and it is only at the triple point that the three phases may exist together in equilibrium. At a pressure above the critical pressure, such as *GH*, there is no sharp distinction between the liquid and vapor phases.

Although we have made these comments with rather specific reference to water (only because of our familiarity with water), all pure substances exhibit the same general behavior. However, the triple-point temperature and critical temperature vary greatly from one substance to another. For example, the critical temperature of helium, as given in Table A.7, is 5.3 K. Therefore, the absolute temperature of helium at ambient conditions is over 50 times greater than the critical temperature. On the other hand, water has a critical temperature of 374.14°C (647.29 K), and at ambient conditions the temperature of water is less than one-half the critical temperature. Most metals have a much higher critical temperature than water. When we consider the behavior of a substance in a given state, it is often helpful to think of this state in relation to the critical state or triple point. For example, if the pressure is greater than the critical pressure, it is impossible to have a liquid phase and a vapor phase in equilibrium. Or, to consider another example, the

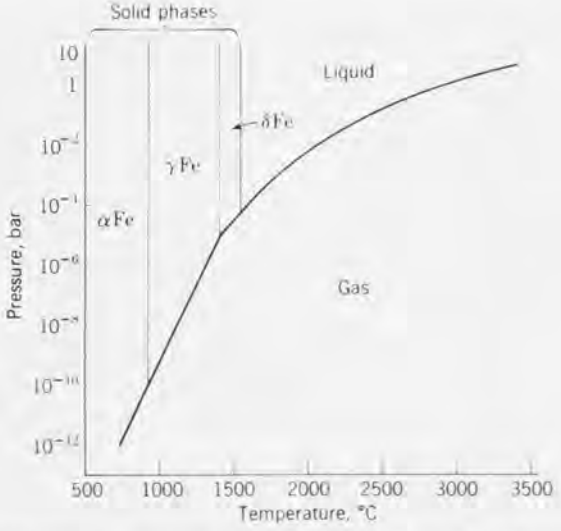


FIGURE 3.5 Estimated pressure–temperature diagram for iron (From *Phase Diagrams in Metallurgy* by F. N. Rhines, copyright 1956, McGraw-Hill Book Company; used by permission).

states at which vacuum-melting a given metal is possible can be ascertained by a consideration of the properties at the triple point. Iron at a pressure just above 5 Pa (the triple-point pressure) would melt at a temperature of about 1535°C (the triple-point temperature).

It should also be pointed out that a pure substance can exist in a number of different solid phases. A transition from one solid phase to another is called an allotropic transformation. Figure 3.5 is a pressure–temperature diagram for iron that shows three solid phases, the liquid phase, and the vapor phase. Figure 3.6 shows a number of solid phases for water. A pure substance can have a number of triple points, but only one triple point has a solid, liquid, and vapor equilibrium. Other triple points for a pure substance can have two solid phases and a liquid phase, two solid phases and a vapor phase, or three solid phases.

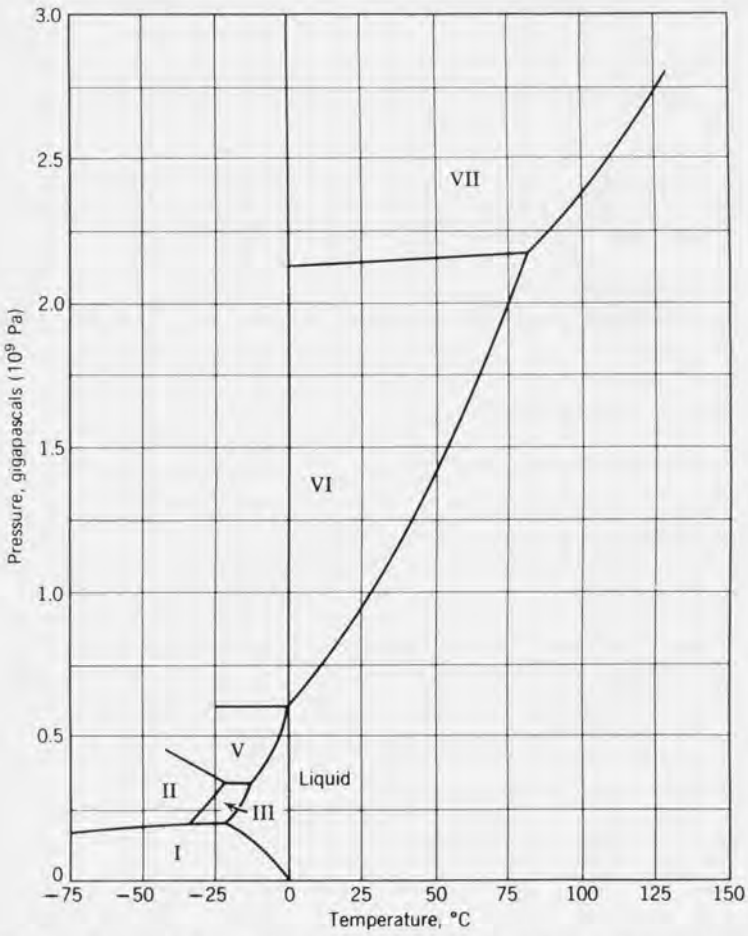


FIGURE 3.6 Phase diagram of water (Adapted from the *American Institute of Physics Handbook*, 2nd ed., 1963, McGraw-Hill).

3.3 INDEPENDENT PROPERTIES OF A PURE SUBSTANCE

One important reason for introducing the concept of a pure substance is that the state of a simple compressible pure substance (that is, a pure substance in the absence of motion, gravity, and surface, magnetic, or electrical effects) is defined by two independent properties. For example, if the specific volume and temperature of superheated steam are specified, the state of the steam is determined.

To understand the significance of the term independent property, consider the saturated-liquid and saturated-vapor states of a pure substance. These two states have the same pressure and the same temperature, but they are definitely not the same state. In a saturation state, therefore, pressure and temperature are not independent properties. Two independent properties such as pressure and specific volume or pressure and quality are required to specify a saturation state of a pure substance.

The reason for mentioning previously that a mixture of gases, such as air, has the same characteristics as a pure substance as long as only one phase is present, concerns precisely this point. The state of air, which is a mixture of gases of definite composition, is determined by specifying two properties as long as it remains in the gaseous phase. Air then can be treated as a pure substance.

3.4 EQUATIONS OF STATE FOR THE VAPOR PHASE OF A SIMPLE COMPRESSIBLE SUBSTANCE

From experimental observations it has been established that the P–$\bar{v}$–T behavior of gases at low density is closely given by the following equation of state,

$$P\bar{v} = \overline{R}T \tag{3.1}$$

where $\overline{R}$ is the universal gas constant. The value of $\overline{R}$ is

$$\overline{R} = 8.3144 \frac{\text{kN m}}{\text{kmol K}} = 8.3144 \frac{\text{kJ}}{\text{kmol } K}$$

In the English Engineering system,

$$\overline{R} = 1545 \frac{\text{ft-lbf}}{\text{lb mol } R}$$

Dividing Eq. 3.1 by M, the molecular weight, we have the equation of state on a unit mass basis,

$$\frac{P\bar{v}}{M} = \frac{\overline{R}T}{M}$$

or

$$Pv = RT \tag{3.2}$$

where

$$R = \frac{\overline{R}}{M} \tag{3.3}$$

Here R is a constant for a particular gas. The value of R for a number of substances is given in Table A.9 of the Appendix. It follows from Eqs. 3.1 and 3.2 that this equation of state can be written in terms of the total volume:

$$PV = n\bar{R}T$$
$$PV = mRT \tag{3.4}$$

It should also be noted that Eq. 3.4 can be written alternately in the form

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{3.5}$$

That is, gases at low density closely follow the well-known Boyle's and Charles' laws. Boyle and Charles, of course, based their statements on experimental observations. (Strictly speaking, neither of these statements should be called a law, since they are only approximately true and even then only under conditions of low density.)

The equation of state given by Eq. 3.1 (or Eq. 3.2) is referred to as the ideal-gas equation of state. At very low density all gases and vapors approach ideal-gas behavior, with the P–v–T relationship being given by the ideal-gas equation of state. At higher densities the behavior may deviate substantially from the ideal-gas equation of state.

Because of its simplicity, the ideal-gas equation of state is very convenient to use in thermodynamic calculations. However, two questions are now appropriate. The ideal-gas equation of state is a good approximation at low density. But what constitutes low density? Or, expressed in other words, over what range of density will the ideal-gas equation of state hold with accuracy? The second question is, how much does an actual gas at a given pressure and temperature deviate from ideal-gas behavior?

To answer both questions, we introduce the concept of the compressibility factor, Z, which is defined by the relation

$$Z = \frac{P\bar{v}}{\bar{R}T}$$

or

$$P\bar{v} = Z\bar{R}T \tag{3.6}$$

Note that for an ideal gas $Z = 1$, and the deviation of Z from unity is a measure of the deviation of the actual relation from the ideal-gas equation of state.

Figure 3.7 shows a skeleton compressibility chart for nitrogen. From this chart we make three observations. The first is that at all temperatures $Z \to 1$ as $P \to 0$. That is, as the pressure approaches zero, the P–v–T behavior closely approaches that predicted by the ideal-gas equation of state. Note also that at temperatures of 300 K and above (that is, room temperature and above) the compressibility factor is near unity up to pressures of about 10 MPa. This means that the ideal-gas equation of state can be used for nitrogen (and, as it happens, air) over this range with considerable accuracy.

Now suppose we reduce the temperature from 300 K but keep the pressure constant at 4 MPa. The density will increase, and we note a sharp decrease below

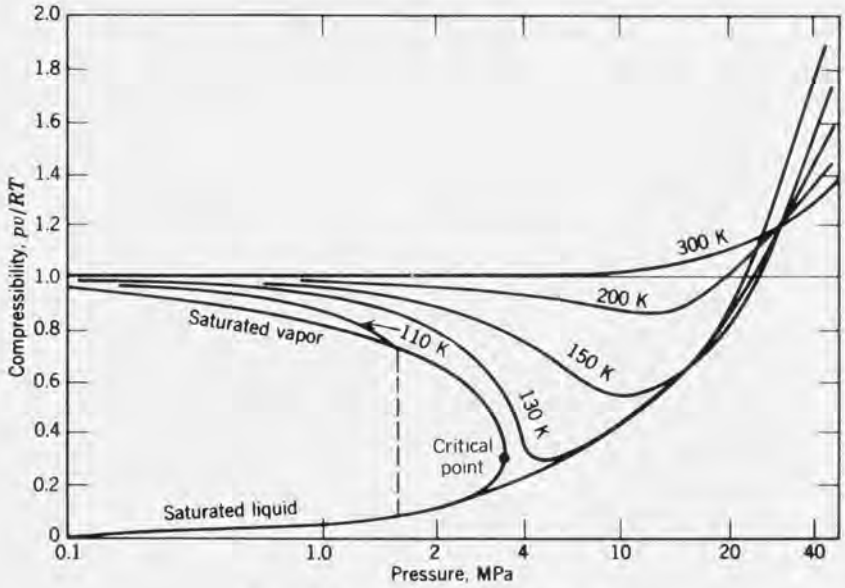


FIGURE 3.7 Compressibility of nitrogen.

unity in the value of the compressibility factor. Values of $Z < 1$ mean that the actual density is greater than would be predicted by ideal-gas behavior. The physical explanation of this is as follows. As the temperature is reduced from 300 K and the pressure remains constant at 4 MPa, the molecules are brought closer together. In this range of intermolecular distances, and at this pressure and temperature, there is an attractive force between the molecules. The lower the temperature the greater is this intermolecular attractive force. This attractive force between the molecules means that the density is greater than would be predicted by the ideal-gas behavior, which assumes no intermolecular forces. Note also from the compressibility chart that at very high densities, for pressures above 30 MPa, the compressibility factor is always greater than unity. In this range the intermolecular distances are very small, and there is a repulsive force between the molecules. This factor tends to make the density less than would otherwise be expected.

The precise nature of intermolecular forces is a rather complex matter. These forces are a function of the temperature as well as the density. The preceding discussion should be considered a qualitative analysis to assist in gaining some understanding of the ideal-gas equation of state and how the P–v–T behavior of actual gases deviates from this equation.

For other gases, the behavior of Z with respect to temperature and pressure is very similar to that of nitrogen, at least in a qualitative sense. To quantify this relation, we divide the temperature by the critical temperature of the substance, calling the result the reduced temperature, T_r. In the same manner, the pressure divided by the critical pressure is termed reduced pressure, P_r. A plot of Z versus P_r at various T_r is in reasonably close agreement quantitatively for many different gases. This plot is called a generalized compressibility chart. The basic chart for

simple spherical molecules is included in the Appendix as Fig. A.7. Corrections to this basic generalized chart value will be discussed in detail in Chapter 12. For the present, the chart will help us decide whether, in a given circumstance, it is reasonable to assume ideal-gas behavior as a model. For example, we note from the chart that if the pressure is very low (that is, $\ll P_c$), the ideal-gas model can be assumed with good accuracy, regardless of the temperature. Furthermore, at high temperatures (that is, greater than about twice T_c), the ideal-gas model can be assumed with good accuracy to pressures as high as four or five times P_c. When the temperature is less than about twice the critical temperature and the pressure is not extremely low, we are in a region, commonly termed superheated vapor, in which the deviation from ideal-gas behavior may be considerable. In this region it is preferable to use tables of thermodynamic properties or charts for a particular substance. These tables are considered in the following section.

Instead of the ideal-gas model to represent gas behavior, or even the generalized compressibility chart, which is approximate, it is desirable to have an equation of state that accurately represents the P–v–T behavior for a particular gas over the entire superheated vapor region. Such an equation is necessarily more complicated and consequently more difficult to use. Many such equations have been proposed and used to correlate the observed behavior of gases. To illustrate the nature and complexity of these equations, we present one of the best known, the Benedict–Webb–Rubin equation of state;

$$P = \frac{RT}{v} + \frac{RTB_0 - A_0 - C_0/T^2}{v^2} + \frac{RTb - a}{v^3} + \frac{a\alpha}{v^6} + \frac{c}{v^3T^2}\left(1 + \frac{\gamma}{v^2}\right)e^{-\gamma/v^2} \quad (3.7)$$

This equation contains eight empirical constants and is accurate to densities of about twice the critical density. The empirical constants for the Benedict–Webb–Rubin equation for a number of substances are given in Table 3.3.

The matter of equations of state will be discussed further in Chapter 12. Note that an equation of state that accurately describes the relation between pressure, temperature, and specific volume is rather cumbersome and that the solution requires considerable time. When we use a digital computer, it is often most convenient to determine the thermodynamic properties in a given state from such equations. However, in hand calculations, it is much more convenient to tabulate values of pressure, temperature, specific volume, and other thermodynamic properties for various substances. The Appendix includes summary tables and graphs of the thermodynamic properties of water, ammonia, chlorofluorocarbon refrigerants R-12 and R-22, nitrogen, and methane. The tables of the properties of water are usually referred to as the "steam tables" and are extracted from *Steam Tables*, by Keenan, Keyes, Hill, and Moore. The method for compiling the P–v–T data for such a table is to find an equation of state that accurately fits the experimental data, and then to solve the equation of state for the values listed in the table.

EXAMPLE 3.1

What is the mass of air contained in a room 6 m × 10 m × 4 m if the pressure is 100 kPa and the temperature is 25°C? Assume air to be an ideal gas.

TABLE 3.3 Empirical Constants for Benedict–Webb–Rubin Equation

	Units: Atmospheres, liters, moles, K.			*Gas constants:* $R = 0.082\,06$; $T = 273.15 + T(^\circ C)$				
Gas	A_0	B_0	$C_0 \cdot 10^{-6}$	a	b	$c \cdot 10^{-6}$	$\alpha \cdot 10^{3}$	$\gamma \cdot 10^{2}$
Methane	1.855 00	0.042 600	0.022 570	0.494 00	0.003 380 04	0.002 545	0.124 359	0.600
Ethylene	3.339 58	0.055 683 3	0.131 140	0.259 00	0.008 600	0.021 120	0.178 00	0.923
Ethane	4.155 56	0.062 772 4	0.179 592	0.345 16	0.011 122	0.032 767	0.243 389	1.180
Propylene	6.112 20	0.085 064 7	0.439 182	0.774 056	0.018 705 9	0.102 611	0.455 696	1.829
Propane	6.872 25	0.097 313	0.508 256	0.947 70	0.022 500	0.129 00	0.607 175	2.200
n-Butane	10.084 7	0.124 361	0.992 830	1.882 31	0.039 998 3	0.316 400	1.101 32	3.400
n-Pentane	12.179 4	0.156 751	2.121 21	4.074 80	0.066 812	0.824 17	1.810 00	4.750
n-Hexane	14.437 3	0.177 813	3.319 35	7.116 71	0.109 131	1.512 76	2.810 86	6.668 49
n-Heptane	17.520 6	0.199 005	4.745 74	10.364 75	0.151 954	2.470 00	4.356 11	9.000
Nitrogen	1.192 50	0.045 80	0.005 889 1	0.014 90	0.001 981 54	0.000 548 064	0.291 545	0.750
Oxygen	1.498 80	0.046 524	0.003 861 7	−0.040 507	−0.000 279 63	−0.000 203 76	0.008 641	0.359
Ammonia	3.789 28	0.051 646 1	0.178 567	0.103 54	0.000 719 561	0.000 157 536	0.004 651 89	1.980
Carbon dioxide	2.673 40	0.045 628	0.113 33	0.051 689	0.003 081 9	0.007 067 2	0.112 71	0.494

Sources: M. Benedict, G. Webb, and L. Rubin, *Chem. Eng. Progress*, **47**, 419 (1951) (first nine entries).
S. M. Wales, *Phase Equilibrium in Chemical Engineering*, Butterworth Publishing (1985) (last four entries).

By using Eq. 3.4 and the value of R from Table A.9, we have

$$m = \frac{PV}{RT} = \frac{100\ \text{kN/m}^2 \times 240\ \text{m}^3}{0.287\ \text{kN m/kg K} \times 298.2\ \text{K}} = 280.5\ \text{kg}$$

EXAMPLE 3.2

A tank has a volume of 0.5 m^3 and contains 10 kg of an ideal gas having a molecular weight of 24. The temperature is 25°C. What is the pressure?

The gas constant is determined first:

$$R = \frac{\overline{R}}{M} = \frac{8.3144\ \text{kN m/kmol K}}{24\ \text{kg/kmol}}$$
$$= 0.346\ 43\ \text{kN m/kg K}$$

We now solve for P:

$$P = \frac{mRT}{V} = \frac{10\ \text{kg} \times 0.346\ 43\ \text{kN m/kg K} \times 298.2\ \text{K}}{0.5\ \text{m}^3}$$
$$= 2066\ \text{kPa}$$

3.5 TABLES OF THERMODYNAMIC PROPERTIES

Tables of thermodynamic properties of many substances are available, and in general, all these tables have the same form. In this section we will refer to the steam tables. The steam tables are selected both because they are a vehicle for presenting thermodynamic tables and because steam is used extensively in power plants and industrial processes. Once the steam tables are understood, other thermodynamic tables can be readily used.

Before we introduce and discuss the actual steam tables, it is worthwhile to examine the ideas behind thermodynamic tables and to explore some of the initial difficulties that students frequently encounter. We therefore introduce these concepts on an artificial, oversimplified, and somewhat abstract basis, after which we will proceed to the actual tables. These "steam tables" actually consist of four separate tables, say A, B, C, and D, each of which is associated with a different region (phase) of the possible combinations of the two variables, T and P, as shown in Fig. 3.8. Each table is listed according to values of T and P. For each set of T and P (a state), the table contains values for four other variables, v, u, h, and s.

If the values of T and P are given, then by comparing them with the boundary values of T' and P', we are able to choose which of the four tables (A, B, C, and D) has the desired values of v, u, h, and s. Table A is the correct choice, for example, only if $T < T'$ and $P > P'$ are both true.

The principal difficulty in first learning how to use the tables is that the state may actually be specified by any two of the variables (assuming that T, P, v, u, h, and s are all independent). We then wish to find the other four variables from the appropriate table. If the two given values are not T and P, it may not be obvious which table to choose to find the other four variables. Even when we have had

experience comparing the appropriate values at the table boundaries and understand through practice in which directions the changes go, we must go through the process of finding the appropriate table each and every time.

In addition to finding the correct table, the other nuisance of everyday use of the tables is interpolation, that is, when one (or both) of the stated values is not exactly equal to a value listed in the table.

Computerized tables eliminate both of these problems, but the student nevertheless must learn to understand the significance, construction, and limitations of the tables because there will be occasions when it will be necessary to use printed tables.

Let us use this background, to introduce the actual steam tables, as presented in the Appendix, Table A.1. Table A.1 is a summary of *Steam Tables*, by Keenan, Keyes, Hill, and Moore, published in 1969 and 1978, and a revision of the original Keenan and Keyes tables first published in 1936. We will concentrate on the three properties already discussed in Chapter 2, namely T, P, and v, and note that the other properties listed in Table A.1, u, h, and s, will be discussed later. We further note that the separation of phases in terms of values of T and P is actually described by the relations illustrated in Fig. 3.4, not Fig. 3.8. The region of superheated vapor in Fig. 3.4 is given in Table A.1.3, and that of compressed liquid is given in Table A.1.4. The compressed-solid region shown in Fig. 3.4 is not listed in the Appendix. The saturated-liquid and saturated-vapor region, as seen in the T and v diagram of Fig. 3.3 (and as the vaporization line in Fig. 3.4), is listed according to the values of T in Table A.1.1 and according to the values of P (T and P are not independent in the two-phase regions) in Table A.1.2. Similarly, the saturated-solid and saturated-vapor region is listed according to T in Table A.1.5, but the saturated-solid and saturated-liquid region, the third phase boundary line shown in Fig. 3.4, is not listed in the Appendix.

In Table A.1.1, the first column after the temperature gives the corresponding saturation pressure in kilopascals or megapascals. The next two columns give specific volume in cubic meters per kilogram. The first of these columns gives the specific volume of the saturated liquid, v_f, the second column gives the specific volume of saturated vapor, v_g. The difference between these two, $v_g - v_f$, represents the increase in specific volume when the state changes from saturated liquid to saturated vapor and is designated v_{fg}.

The specific volume of a substance having a given quality can be found by using the definition of quality. Quality has already been defined as the ratio of the mass

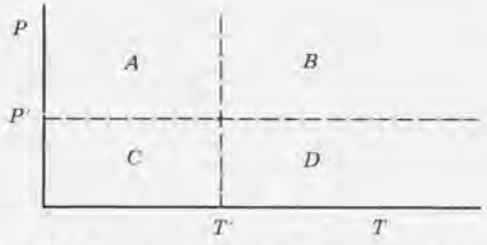


FIGURE 3.8 Schematic diagram of "steam tables" principle.

of vapor to the total mass of liquid plus vapor when a substance is in a saturation state. Let us consider a mass m having a quality x. The volume is the sum of the volume of the liquid and the volume of the vapor:

$$V = V_{\text{liq}} + V_{\text{vap}} \tag{3.8}$$

In terms of the masses, Eq. 3.8 can be written in the form

$$mv = m_{\text{liq}}v_f + m_{\text{vap}}v_g$$

Dividing by the total mass and introducing the quality x, we have

$$v = (1 - x)v_f + xv_g \tag{3.9}$$

Using the definition

$$v_{fg} = v_g - v_f$$

Equation 3.9 can then be written in the form

$$v = v_f + xv_{fg} \tag{3.10}$$

As an example, let us calculate the specific volume of saturated steam at 200°C having a quality of 70 percent. Using Eq. 3.9 gives

$$\begin{aligned} v &= 0.3(0.001\,157) + 0.7(0.127\,36) \\ &= 0.0895\ \text{m}^3/\text{kg} \end{aligned}$$

In Table A.1.2, the first column after the pressure lists the saturation temperature for each pressure. The next column lists specific volume in a manner similar to Table A.1.1. When necessary, v_{fg} can readily be found by subtracting v_f from v_g.

Table 3 of the steam tables, which is summarized in Table A.1.3, gives the properties of superheated vapor. In the superheated region, pressure and temperature are independent properties and, therefore, for each pressure a large number of temperatures is given, and for each temperature four thermodynamic properties are listed, the first one being specific volume. Thus, the specific volume of steam at a pressure of 0.5 MPa and 200°C is 0.4249 m^3/kg.

Table 4 of the steam tables, summarized in Table A.1.4, gives the properties of the compressed liquid. To demonstrate the use of this table, consider a piston and a cylinder (as shown in Fig. 3.9) that contains 1 kg of saturated-liquid water at

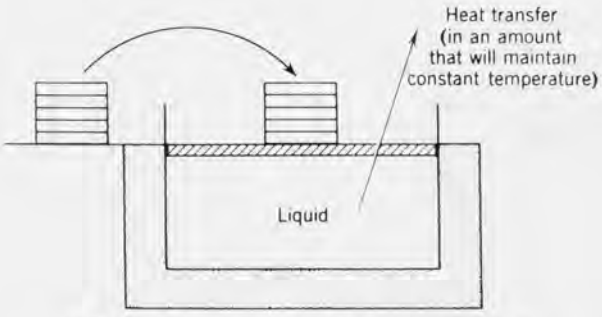


FIGURE 3.9 Illustration of compressed-liquid state.

100°C. Its properties are given in Table A.1.1, and we note that the pressure is 0.1013 MPa and the specific volume is 0.001 044 m^3/kg. Suppose the pressure is increased to 10 MPa while the temperature is held constant at 100°C by the necessary transfer of heat, Q. Since water is slightly compressible, we would expect a slight decrease in specific volume during this process. Table A.1.4 gives this specific volume as 0.001 039 m^3/kg. This is only a slight decrease, and only a small error would be made if one assumed that the volume of a compressed liquid was equal to the specific volume of the saturated liquid at the same temperature. In many situations this is the most convenient procedure, particularly when compressed-liquid data are not available.

Furthermore, because specific volume does change rapidly with temperature, care should be exercised in interpolation over the wide temperature ranges in Table A.1.4. (Sometimes it may be more accurate to use the saturated-liquid data from

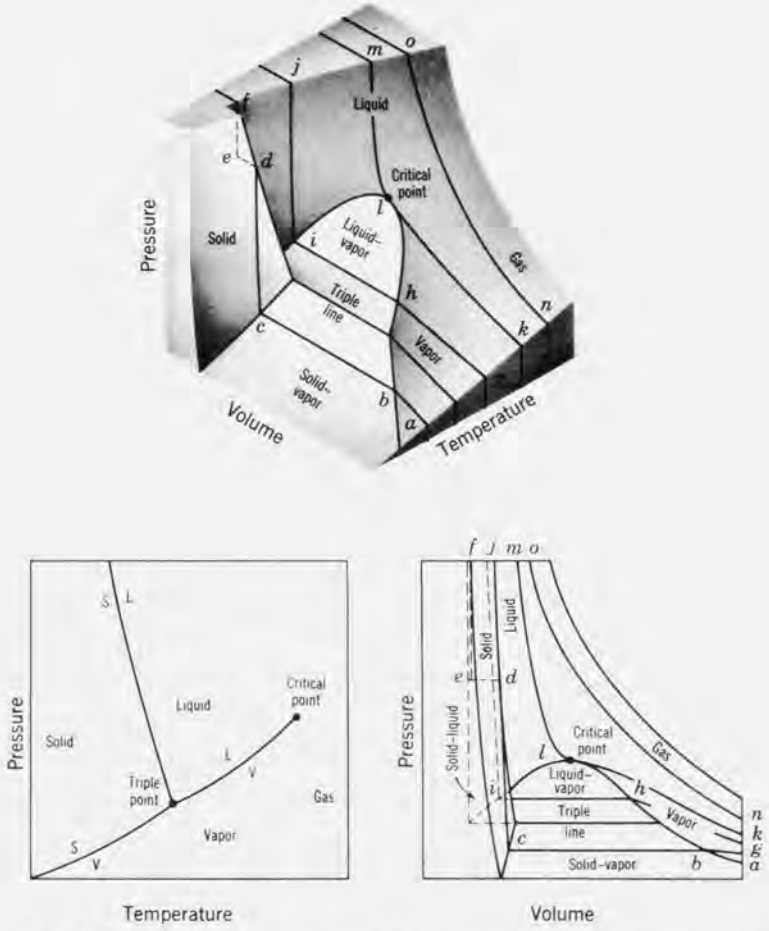


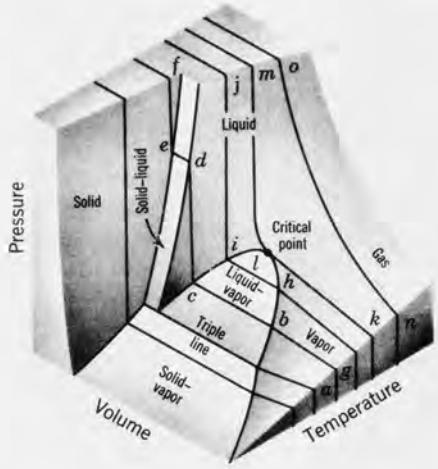
FIGURE 3.10 Pressure-volume-temperature surface for a substance that expands on freezing.

Table A.1.1 and interpolate differences between Table A.1.1, the saturated-liquid data, and Table A.1.4, the compressed-liquid data.)

Table 6 of the steam tables, which is summarized in Table A.1.5, gives the properties of saturated solid and saturated vapor that are in equilibrium. The first column gives the temperature and the second column gives the corresponding saturation pressure. As would be expected, all these pressures are less than the triple-point pressure. The next two columns give the specific volume of the saturated solid and saturated vapor (note that the tabulated value is $v_i \times 10^3$).

3.6 THERMODYNAMIC SURFACES

The matter discussed in this chapter can be well summarized by a consideration of a pressure-specific volume–temperature surface. Two such surfaces are shown in Figs. 3.10 and 3.11. Figure 3.10 shows a substance such as water in which the



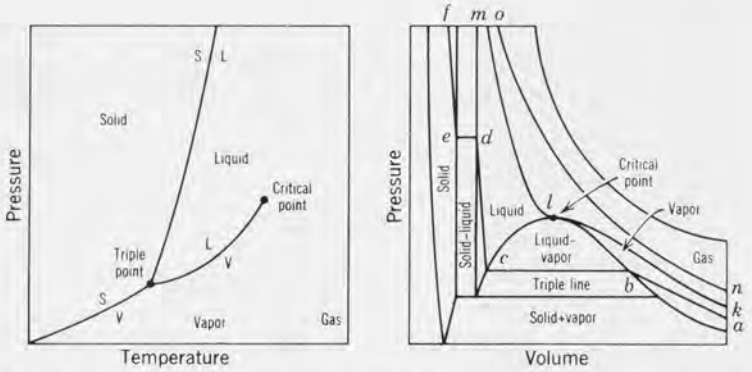


FIGURE 3.11 *Pressure-volume-temperature surface for a substance that contracts on freezing.*

specific volume increases during freezing. Figure 3.11 shows a substance in which the specific volume decreases during freezing.

In these diagrams the pressure, specific volume, and temperature are plotted on mutually perpendicular coordinates, and each possible equilibrium state is thus represented by a point on the surface. This follows directly from the fact that a pure substance has only two independent intensive properties. All points along a quasi-equilibrium process lie on the P–v–T surface, since such a process always passes through equilibrium states.

The regions of the surface that represent a single phase—the solid, liquid, and vapor phases—are indicated. These surfaces are curved. The two-phase regions—the solid–liquid, solid–vapor, and liquid–vapor regions—are ruled surfaces. By this we understand that they are made up of straight lines parallel to the specific-volume axis. This, of course, follows from the fact that in the two-phase region, lines of constant pressure are also lines of constant temperature, although the specific volume may change. The triple point actually appears as the triple line on the P–v–T surface, since the pressure and temperature of the triple point are fixed, but the specific volume may vary, depending on the proportion of each phase.

It is also of interest to note the pressure–temperature and pressure–volume projections of these surfaces. We have already considered the pressure–temperature diagram for a substance such as water. It is on this diagram that we observe the triple point. Various lines of constant temperature are shown on the pressure–volume diagram, and the corresponding constant-temperature sections are lettered identically on the P–v–T surface. The critical isotherm has a point of inflection at the critical point.

One notices that for a substance such as water, which expands on freezing, the freezing temperature decreases with an increase in pressure. For a substance that contracts on freezing, the freezing temperature increases as the pressure increases. Thus, as the pressure of vapor is increased along the constant-temperature line *abcdef* in Fig. 3.10, a substance that expands on freezing first becomes solid and then liquid. For the substance that contracts on freezing, the corresponding constant-temperature line, Fig. 3.11 indicates that as the pressure on the vapor is increased, it first becomes liquid and then solid.

EXAMPLE 3.3

A vessel having a volume of 0.4 m^3 contains 2.0 kg of a liquid water and water vapor mixture in equilibrium at a pressure of 600 kPa. Calculate

1. The volume and mass of liquid.
2. The volume and mass of vapor.

The specific volume is calculated first:

$$v = \frac{0.4}{2.0} = 0.20 \text{ m}^3/\text{kg}$$

From the steam tables (Table A.1.2),

$$v_{fg} = 0.3157 - 0.001\,101 = 0.3146$$

The quality can now be calculated using Eq. 3.10:

$$0.20 = 0.001\,101 + x\,0.3146$$
$$x = 0.6322$$

Therefore, the mass of liquid is

$$2.0(0.3678) = 0.7356 \text{ kg}$$

The mass of vapor is

$$2.0(0.6322) = 1.2644 \text{ kg}$$

The volume of liquid is

$$V_{\text{liq}} = m_{\text{liq}} v_f = 0.7356(0.001\,101) = 0.0008 \text{ m}^3$$

The volume of vapor is

$$V_{\text{vap}} = m_{\text{vap}} v_g = 1.2644(0.3157) = 0.3992 \text{ m}^3$$

EXAMPLE 3.4

A rigid vessel contains saturated ammonia vapor at 20°C. Heat is transferred to the system until the temperature reaches 40°C. What is the final pressure?

Since the volume does not change during this process, the specific volume also remains constant. From the ammonia tables, Table A.2,

$$v_1 = v_2 = 0.149\,28 \text{ m}^3/\text{kg}$$

Since v_g at 40°C is less than 0.149 28 m^3/kg, it is evident that in the final state the ammonia is superheated vapor. By interpolating between the 900- and 1000-kPa columns of Table A.2.2, we find that

$$P_2 = 936 \text{ kPa}$$

PROBLEMS

3.1 A vertical cylinder fitted with a frictionless piston contains argon gas at 100°C. The piston has a mass of 5 kg and a diameter of 100 mm, and the ambient pressure outside the cylinder is 97 kPa. If the cylinder volume is 2 L, what is the mass of argon inside?

3.2 A 40-L rigid tank that is initially evacuated is connected to an air line, as shown in Fig. 3.12. The valve is opened, and air flows into the tank until the pressure inside reaches 5 MPa, at which point the valve is closed. The temperature inside the tank is 400 K.

(a) What is the mass of air inside the tank?

(b) The tank eventually cools to room temperature, that is, 300 K. What is the pressure inside the tank at this time?

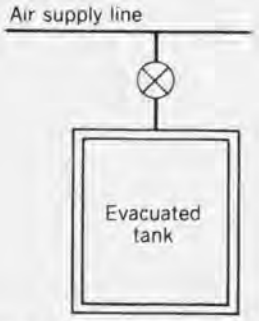


FIGURE 3.12 Sketch for Problem 3.2.

3.3 A hollow metal sphere of 150-mm inside diameter is weighed on a precision beam balance when evacuated and again when it is filled to 875 kPa with an unknown gas. The difference in reading is 0.0025 kg. The room temperature is 25°C. What is the gas, assuming it to be a pure substance?

3.3E A hollow metal sphere of 6-in. inside diameter is weighed on a precision beam balance when evacuated and again when filled to 110 lbf/in.^{2} with an unknown gas. The difference in reading is 0.005 lbm. The room temperature is 80 F. What is the gas, assuming it to be a pure substance?

3.4 A vertical cylinder fitted with a piston contains air initially at 120 kPa, 100°C. The piston is restrained by a set of stops, as shown in Fig. 3.13. The piston has a diameter of 0.1 m and a mass of 5 kg, and the ambient pressure and temperature are 100 kPa, 20°C. The cylinder now cools as heat is transferred to the ambient.

(a) At what temperature does the piston begin to fall away from the stops?

(b) How far has the piston dropped when the cylinder has cooled to ambient temperature?

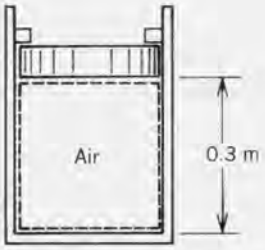


FIGURE 3.13 Sketch for Problem 3.4.

3.5 A vacuum pump is used to pump a vacuum over a bath of liquid helium. The volume rate of flow into the vacuum pump is 2.5 m^3/s. The pressure at the vacuum pump inlet is 20 Pa, and the temperature is −30°C. What is the mass flow rate of helium entering the pump?

3.5E A vacuum pump is used to pump a vacuum over a bath of liquid helium. The volume rate of flow into the vacuum pump is 4500 ft^3/min. The pressure at the vacuum pump inlet is 0.5 mm Hg and the temperature is −30 F. What is the mass rate of flow of helium entering the pump?

3.6 A vertical cylinder is fitted with a thick piston that is initially held in place by a pin, as shown in Fig. 3.14. The cylinder contains carbon dioxide gas at 150 kPa, and has an ambient temperature of 290 K. The metal piston has a density of 8000 kg/m^3, and the local ambient pressure is 101 kPa. The pin is released, which allows the piston to move. The gas eventually returns to ambient temperature. Is the piston against the stops?

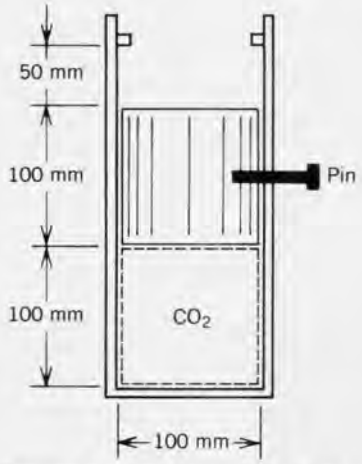


FIGURE 3.14 Sketch for Problem 3.6.

3.7 An initially deflated and flat balloon is connected by a valve to a storage tank containing helium gas at 1 MPa at an ambient temperature of 20°C. The valve is opened, and the balloon is inflated at constant pressure (equal to an ambient pressure of 100 kPa) until it becomes spherical at $D_1 = 1$ m. If the balloon becomes larger than this size, the combined effects of balloon curvature and elasticity of the balloon material will cause the pressure inside to be

$$P = P_0 + C(D^{*-1} - D^{*-2}), \qquad D^* = \frac{D}{D_1}$$

The balloon is to be inflated slowly to a final diameter of 4 m, at which point the pressure inside is 400 kPa. All temperatures remain at 20°C during the process. Determine the minimum volume of the helium tank to inflate this balloon.

3.8 Consider the process of inflating a helium balloon as described in Problem 3.7. What is the maximum pressure inside the balloon at any time during this inflation process? What is the pressure inside the helium storage tank at this time?

3.9 The helium balloon described in Problems 3.7 and 3.8 is released into the atmosphere and rises to an elevation of 5000 m, where the local ambient pressure is 50 kPa and the temperature is −20°C. What is the diameter of the balloon?

3.10 A cylinder is fitted with a 125-mm-diameter piston that is restrained by a linear spring (spring force proportional to distance), as shown in Fig. 3.15. The spring force constant is 20 N/mm. The piston is initially resting on the stops, at which point the cylinder volume is 1 L. The valve to the air line is opened, and the piston begins to rise when the cylinder pressure reaches 150 kPa. When the valve is closed, the cylinder volume is 1.5 L and the temperature is 60°C. What is the mass of air inside the cylinder?

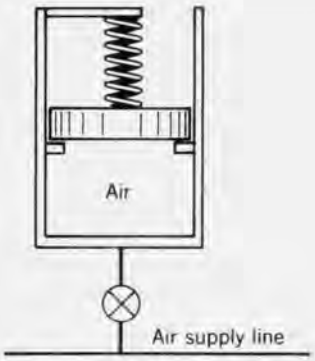


FIGURE 3.15 Sketch for Problems 3.10 and 3.10E.

3.10E A cylinder is fitted with a 5-in.-diameter piston that is restrained by a linear spring (spring force proportional to distance), as shown in Fig. 3.15. The spring force constant is 100 lbf/in. The piston is initially resting on the stops, at which point the cylinder volume is 60 in.^{3}. The valve to the air line is opened, and the piston begins to rise when the cylinder pressure reaches 22 lbf/in.^{2}. When the valve is closed, the cylinder volume is 90 in.^{3} and the temperature is 140 F. What is the mass of air inside the cylinder?

3.11 Is it reasonable to assume that at the given states the substance behaves as an ideal gas?

(a) Nitrogen at 30°C, 3 MPa.
(b) Carbon dioxide at 30°C, 3 MPa.
(c) Water at 1300°C, 3 MPa.
(d) Water at 50°C, 10 kPa.
(e) Water at 30°C, 10 kPa.

3.12 A 200-L tank contains carbon dioxide gas at 35°C, 2 MPa.

(a) Determine the mass inside the tank.
(b) Estimate the percent error in part a if the ideal-gas model is assumed.

3.12E A 5-ft^3 tank contains carbon dioxide gas at 95 F, 300 lbf/in.^{2}.

(a) Determine the mass inside the tank.
(b) Estimate the percent error in part a if the ideal-gas model is assumed.

3.13 Repeat Problem 3.12 for argon gas instead of carbon dioxide.

3.14 Determine whether water in each of the following states is a compressed liquid, a superheated vapor, or a mixture of saturated liquid and vapor.

(a) 120°C, 150 kPa.
(b) 0.35 MPa, 0.4 m^3/kg.
(c) 160°C, 0.4 m^3/kg.
(d) 200 kPa, 110°C.
(e) 300°C, 0.01 m^3/kg.
(f) 5 kPa, 10°C.

3.14E Determine whether water in each of the following states is a compressed liquid, a superheated vapor, or a mixture of saturated liquid and vapor.

(a) 250 F, 20 lbf/in.^{2}.
(b) 50 lbf/in.^{2}, 8 ft^3/lbm.
(c) 300 F, 8 ft^3/lbm.
(d) 30 lbf/in.^{2}, 230 F.
(e) 400 F, 0.02 ft^3/lbm.
(f) 0.5 lbf/in.^{2}, 60 F.

3.15 Determine whether the refrigerant R-22 in each of the following states is a compressed liquid, a superheated vapor, or a mixture of saturated liquid and vapor.

(a) 50°C, 0.05 m^3/kg.
(b) 1.0 MPa, 20°C.
(c) 0.1 MPa, 0.1 m^3/kg.
(d) 50°C, 0.3 m^3/kg.
(e) −20°C, 200 kPa.
(f) 2 MPa, 0.012 m^3/kg.

3.16 Determine the quality (if saturated) or temperature (if superheated) of the following substances in the given states.

(a) Ammonia: 20°C, 0.1 m^3/kg; 800 kPa, 0.2 m^3/kg.
(b) R-22: 130 kPa, 0.10 m^3/kg; 130 kPa, 0.17 m^3/kg.
(c) Water: 20°C, 1 m^3/kg; 8 MPa, 0.01 m^3/kg.
(d) Nitrogen: 0.5 MPa, 0.08 m^3/kg; 80 K, 0.14 m^3/kg.

3.17 Calculate the following specific volumes.

(a) Ammonia: 30°C, 15 percent quality.
(b) R-12: 50°C, 80 percent quality.
(c) Water: 8 MPa, 92 percent quality.
(d) Nitrogen: 90 K, 50 percent quality.

3.18 Plot a pressure–specific-volume diagram on log–log paper (3 × 5 cycles) for water. Show the following lines.

(a) Saturated liquid.
(b) Saturated vapor.
(c) The following constant-temperature lines, including the compressed liquid region: 150°C, 250°C, 350°C, 400°C, 500°C.
(d) The following constant-quality lines: 10 percent; 50 percent; 90 percent.

3.19 What is the percent error in specific volume if the ideal-gas model is used to represent the behavior of superheated vapor ammonia at 100°C, 2 MPa? What if the generalized compressibility chart, Fig. A.7, is used instead?

3.19E What is the percent error in specific volume if the ideal-gas model is used to represent the behavior of superheated vapor ammonia at 200 F, 280 lbf/in.^{2}? What if the generalized compressibility chart, Fig. A.7, is used instead?

3.20 What if the percent error in pressure if the ideal-gas model is used to represent the behavior of superheated vapor R-22 at 50°C, 0.03 m^3/kg? What if the generalized compressibility chart, Fig. A.7, is used instead?

3.21 A large hot-water storage tank in a solar heating system contains liquid and vapor in equilibrium at 80°C. The distance from the bottom of the tank to the liquid level is 10 m. What is the difference in pressure between the top of the tank and the bottom of the tank?

3.21E A large hot-water storage tank in a solar heating system contains liquid and vapor in equilibrium at 180 F. The distance from the bottom of the tank to the liquid level is 30 ft. What is the difference in pressure between the top of the tank and the bottom of the tank?

3.22 The mass of nitrogen gas in a 250-L tank at 6 MPa, 150 K, is to be calculated. Four different methods are suggested. Which is the most accurate, and what percent differences are the other three methods?

(a) Benedict–Webb–Rubin equation of state.
(b) Nitrogen tables, Table A.5.
(c) Ideal gas.
(d) Generalized compressibility chart, Fig. A.7.

3.23 A 200-m^3 storage tank is being constructed to hold liquified natural gas (LNG). The LNG is assumed to be essentially pure methane. If the tank is to contain 95 percent liquid and 5 percent vapor by volume at 100 kPa, what mass in kilograms of LNG will the tank hold? What is the quality in the tank?

3.24 It is estimated that the LNG storage tank in Problem 3.23 will warm up at the rate of 5°C per hour in the event its refrigeration system fails. The tank is designed to hold a pressure of up to 600 kPa. How much time is available to repair the system if there is no safety vent valve on the tank?

3.25 Consider compressed-liquid water at 40°C. What pressure is required to decrease the specific volume by 1 percent from its saturated-liquid value at the same temperature?

3.26 A boiler feed pump delivers 50 kg/s of water at 300°C, 20 MPa. What is the volume rate of flow in cubic meters per second? What will the percent error be if the properties of saturated-liquid water at 300°C are used in the calculation? What if the properties of saturated-liquid water at 20 MPa are used?

3.26E A boiler feed pump delivers 100 lbm/s of water at 300 F, 3000 lbf/in.^{2}. What is the volume rate of flow in cubic feet per minute? What will the percent error be if the properties of saturated liquid water at 300 F are used in the calculation? What if the properties of saturated liquid water at 3000 lbf/in.^{2} are used?

3.27 A 100-L rigid tank containing saturated vapor water at 200 kPa is cooled to −20°C. On a volume basis, what percentage of the water is solid at this temperature?

3.28 A cylinder fitted with a piston contains water at 105°C, 85 percent quality. The volume is 1 L. This system is heated, causing the piston to rise until it encounters a spring, as shown in Fig. 3.16. The cylinder volume at this point is 1.5 L, the piston diameter is 150 mm, and the spring constant is 100 N/mm. The heating continues,

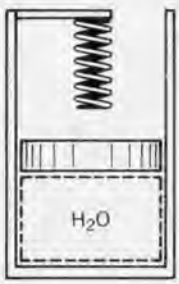


FIGURE 3.16 Sketch for Problem 3.28.

which causes the piston to rise further and compress the spring. What is the cylinder pressure when the temperature reaches 600°C?

3.29 A rigid vessel contains saturated (liquid + vapor) water at 100 kPa. On a volume basis, find the percentage of liquid in this state that will allow the water to pass through the critical point when this system is heated.

3.30 For a certain experiment, R-22 vapor is contained in a sealed glass tube at 20°C. We want to know the pressure at this condition, but there is no means for measuring it since the tube is sealed. If the tube is cooled to −20°C, however, small droplets of liquid are observed on the glass walls. What is the pressure inside the tube at 20°C?

3.31 A rigid vessel having a volume of 15 L contains 10 kg of water (liquid + vapor) at 30°C. The vessel is slowly heated. Will the liquid level inside eventually rise to the top or drop to the bottom of the vessel? What if the vessel contains 1 kg of water instead of 10 kg?

3.31E A rigid vessel having a volume of 0.25 ft^3 contains 10 lbm of water (liquid + vapor) at 100 F. The vessel is slowly heated. Will the liquid level inside eventually rise to the top or drop to the bottom of the vessel? What if the vessel contains 1 lbm of water instead of 10 lbm?

3.32 A cylinder containing ammonia is fitted with a piston restrained by an external force that is proportional to the cylinder volume squared. Initial conditions in the cylinder are 10°C, 90 percent quality, and the volume is 5 L. A valve on the cylinder is opened, and additional ammonia flows into the cylinder until the mass inside has doubled. At this point the pressure in the cylinder is 1.2 MPa. What is the final temperature?

3.33 A container of liquid methane at 500-kPa pressure has a cross-sectional area of 0.50 m^2 (Fig. 3.17). As heat is transferred to the liquid methane, some of the liquid evaporates, and the liquid level in the tank drops 30 mm in one hour. The vapor that leaves the container passes through a heater and then exits at 500 kPa, 275 K. Calculate the volume rate of flow of methane gas exiting the heater.

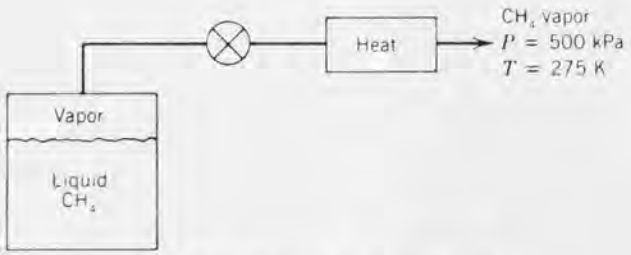


FIGURE 3.17 Sketch for Problem 3.33.

3.34 Consider two tanks, *A* and *B*, connected by a valve, as shown in Fig. 3.18. Each tank has a volume of 200 L. Tank *A* contains R-12 at 25°C, 10 percent liquid and 90 percent vapor by volume, but tank *B* is evacuated. The valve connecting the tanks is opened. Saturated vapor flows out of *A* until the pressure in *B* reaches that

in A, at which point the valve is closed. This process occurs slowly, so that all temperatures remain at 25°C throughout the process. How much has the quality changed in tank A through this process?

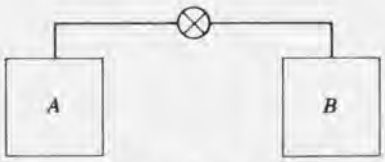


FIGURE 3.18 Sketch for Problem 3.34A.

COMPUTER PROBLEMS

3.1C For any specified substance, calculate the pressure according to the Benedict–Webb–Rubin equation of state for any given set (or sets) of temperature and specific volume. Compare the result with the ideal-gas equation of state.

3.2C For any specified substance, solve the Benedict–Webb–Rubin equation of state for specific volume at any given set (or sets) of pressure and temperature. Compare the result with the ideal-gas equation of state.

3.3C For any specified substance in Tables A.1 through A.6, fit a polynomial equation of degree n to tabular data for pressure as a function of density along any given isotherm in the superheated vapor region.

3.4C We wish to be able to calculate "standard" atmospheric pressure at any given elevation up to 10 km. The "standard" atmosphere assumes that gravitational acceleration drops by 0.0031 m/s^2 (from the sea level value of 9.8066 m/s^2) for each kilometer in elevation, and that the ambient temperature drops by 6.5°C (from the sea level standard value of 15°C) for each kilometer in elevation.

3.5C In Problem 3.28, we wish to follow the path of the process for the steam for any state between the initial and final states inside the cylinder.

3.6C In Problem 3.32, we wish to follow the path of the process for the ammonia for any state between the initial and final states inside the cylinder.

3.7C In Problem 3.34, we wish to follow the path of the process for the R-12 for any state between the initial and final states inside the two tanks.

4

WORK AND HEAT

In this chapter we consider work and heat. It is essential for the student of thermodynamics to understand clearly the definitions of both work and heat, because the correct analysis of many thermodynamic problems depends on distinguishing between them.

4.1 DEFINITION OF WORK

Work is usually defined as a force F acting through a displacement x, the displacement being in the direction of the force. That is,

$$W = \int_1^2 F\,dx \tag{4.1}$$

This is a very useful relationship because it enables us to find the work required to raise a weight, to stretch a wire, or to move a charged particle through a magnetic field.

However, when treating thermodynamics from a macroscopic point of view, it is advantageous to tie in the definition of work with the concepts of systems, properties, and processes. We therefore define work as follows: work is done by a system if the sole effect on the surroundings (everything external to the system) could be the raising of a weight. Notice that the raising of a weight is in effect a force acting through a distance. Notice also that our definition does not state that a weight was actually raised or that a force actually acted through a given distance, but that the sole effect external to the system could be the raising of a weight. Work done *by* a system is considered positive and work done *on* a system is considered negative. The symbol W designates the work done by a system.

In general, we will speak of work as a form of energy. No attempt will be made to give a rigorous definition of energy. Since the concept is familiar, the term energy will be used as appropriate, and various forms of energy will be identified. Work is the form of energy that fulfills the definition.

Let us illustrate this definition of work with a few examples. Consider as a system the battery and motor of Fig. 4.1*a* and let the motor drive a fan. Does work cross the boundary of the system? To answer this question using the definition of work given earlier, replace the fan with the pulley and weight arrangement shown in Fig. 4.1*b*. As the motor turns, the weight is raised, and the sole effect external to the system is the raising of a weight. Thus, for our original system of Fig. 4.1*a*, we conclude that work is crossing the boundary of the system since the sole effect external to the system could be the raising of a weight.

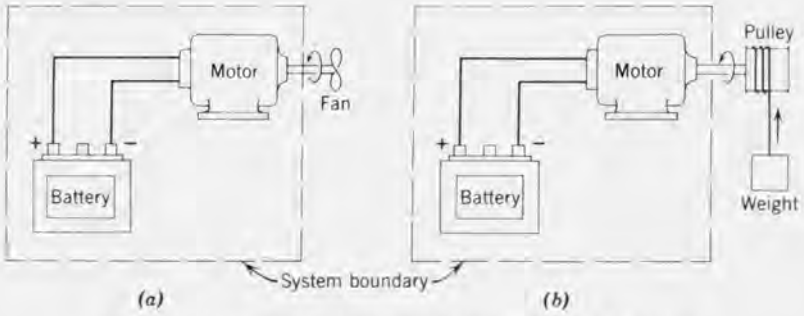


FIGURE 4.1 Example of work crossing the boundary of a system.

Let the boundaries of the system be changed now to include only the battery shown in Fig. 4.2. Again we ask the question, does work cross the boundary of the system? To answer this question, we need to ask a more general question. Does the flow of electrical energy across the boundary of a system constitute work?

The only limiting factor in having the sole external effect be the raising of a weight is the inefficiency of the motor. However, as we design a more efficient motor, with lower bearing and electrical losses, we recognize that we can approach a certain limit that meets the requirement of having the only external effect be the raising of a weight. Therefore, we can conclude that when there is a flow of electricity across the boundary of a system, as in Fig. 4.2, it is work.

4.2 UNITS FOR WORK

As already noted, work done *by* a system, such as that done by a gas expanding against a piston, is positive, and work done *on* a system, such as that done by a piston compressing a gas, is negative. Thus, positive work means that energy leaves the system, and negative work means that energy is added to the system.

Our definition of work involves the raising of a weight, that is, the product of a unit force (one newton) acting through a unit distance (one meter). This unit for

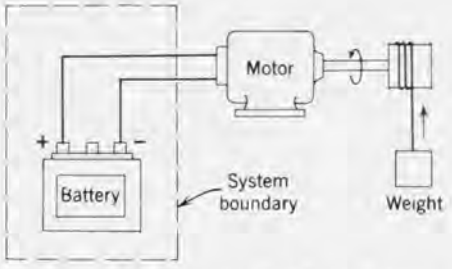


FIGURE 4.2 Example of work crossing the boundary of a system because of a flow of an electric current across the system boundary.

work in SI units is called the joule (J).

$$1 \text{ J} = 1 \text{ N m}$$

In the English system, the product of a unit force (one pound force) acting through a unit distance (one foot) gives us the basic work unit, the ft lbf.

Power is the time rate of doing work and is designated by the symbol $\dot{W}$:

$$\dot{W} \equiv \frac{\delta W}{dt}$$

The unit for power is a rate of work of one joule per second, which is a watt (W):

$$1 \text{ W} = 1 \text{ J/s}$$

A familiar unit for power in English units is the horsepower (hp), where

$$1 \text{ hp} = 550 \text{ ft lbf/s}$$

It is often convenient to speak of the work per unit mass of the system. This quantity is designated w and is defined

$$w \equiv \frac{W}{m}$$

4.3 WORK DONE AT THE MOVING BOUNDARY OF A SIMPLE COMPRESSIBLE SYSTEM IN A QUASI-EQUILIBRIUM PROCESS

We have already noted that there are a variety of ways in which work can be done on or by a system. These include work done by a rotating shaft, electrical work, and the work done by the movement of the system boundary, such as the work done in moving the piston in a cylinder. In this section we will consider in some detail the work done at the moving boundary of a simple compressible system during a quasi-equilibrium process.

Consider as a system the gas contained in a cylinder and piston, as in Fig. 4.3. Let one of the small weights be removed from the piston, which will cause the piston to move upward a distance dL. We can consider this quasi-equilibrium process and calculate the amount of work W done by the system during this process. The total force on the piston is PA, where P is the pressure of the gas

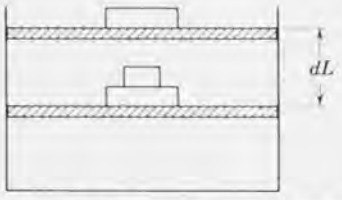


FIGURE 4.3 Example of work done at the moving boundary of a system in a quasi-equilibrium process.

and $\mathscr{A}$ is the area of the piston. Therefore, the work δW is

$$\delta W = P\mathscr{A}\, dL$$

But $\mathscr{A}\, dL = dV$, the change in volume of the gas. Therefore,

$$\delta W = P\, dV \tag{4.2}$$

The work done at the moving boundary during a given quasi-equilibrium process can be found by integrating Eq. 4.2. However, this integration can be performed only if we know the relationship between P and V during this process. This relationship may be expressed in the form of an equation, or it may be shown in the form of a graph.

Let us consider a graphical solution first. We use as an example a compression process such as occurs during the compression of air in a cylinder, Fig. 4.4. At the beginning of the process the piston is at position 1, and the pressure is relatively low. This state is represented on a pressure–volume diagram (usually referred to as a P–V diagram). At the conclusion of the process the piston is in position 2, and the corresponding state of the gas is shown at point 2 on the P–V diagram. Let us assume that this compression was a quasi-equilibrium process, and that during the process the system passed through the states shown by the line connecting states 1 and 2 on the P–V diagram. The assumption of a quasi-equilibrium process is essential here because each point on line 1–2 represents a definite state, and these states will correspond to the actual state of the system only if the deviation from equilibrium is infinitesimal. The work done on the air during this compression process can be found by integrating Eq. 4.2:

$$_1W_2 = \int_1^2 \delta W = \int_1^2 P\, dV \tag{4.3}$$

The symbol $_1W_2$ is to be interpreted as the work done during the process form state 1 to state 2. It is clear from examining the P–V diagram that the work done

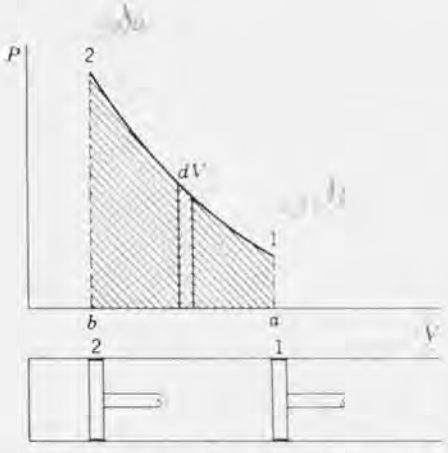


FIGURE 4.4 Use of pressure–volume diagram to show work done at the moving boundary of a system in a quasi-equilibrium process.

during this process,

$$\int_1^2 P\,dV$$

is represented by the area under the curve 1–2, area a–1–2–b–a. In this example the volume decreased, and the area a–1–2–b–a represents work done on the system. If the process had proceeded from state 2 to state 1 along the same path, the same area would represent work done by the system.

Further consideration of a P–V diagram, such as Fig. 4.5, leads to another important conclusion. It is possible to go from state 1 to state 2 along many different quasi-equilibrium paths, such as A, B, or C. Since the area underneath each curve represents the work for each process, it is evident that the amount of work done during each process not only is a function of the end states of the process, but depends on the path that is followed in going from one state to another. For this reason work is called a path function or, in mathematical parlance, δW is an inexact differential.

This concept leads to a brief consideration of point and path functions or, to use another term, exact and inexact differentials. Thermodynamic properties are point functions, a name that comes from the fact that for a given point on a diagram (such as Fig. 4.5) or surface (such as Fig. 3.9), the state is fixed, and thus there is a definite value of each property corresponding to this point. The differentials of point functions are exact differentials, and the integration is simply

$$\int_1^2 dV = V_2 - V_1$$

Thus, we can speak of the volume in state 2 and the volume in state 1, and the change in volume depends only on the initial and final states.

Work, on the other hand, is a path function, for, as has been indicated, the work done in a quasi-equilibrium process between two given states depends on the path followed. The differentials of path functions are inexact differentials, and the symbol δ will be used in this text to designate inexact differentials (in contrast to d for exact differentials). Thus, for work we write

$$\int_1^2 \delta W = {}_1W_2$$

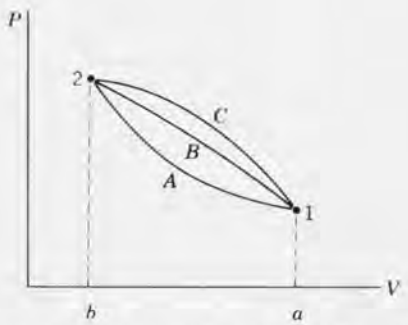


FIGURE 4.5 Various quasi-equilibrium processes between two given states, indicating that work is a path function.

It would be more precise to use the notation, ${}_1W_{2,A}$, which would indicate the work done during the change from state 1 to state 2 along path A. However, it is implied in the notation ${}_1W_2$ that the process between states 1 and 2 has been specified. It should be noted that we never speak about the work in the system in state 1 or state 2, and thus we would never write $W_2 - W_1$.

In evaluating the integral of Eq. 4.3, we should always keep in mind that we wish to determine the area under the curve on Fig. 4.5. In connection with this point, we identify the following two classes of problems:

1. The relationship between P and V is given in terms of experimental data or in graphical form (as, for example, the trace on an oscilloscope). Therefore, we may evaluate the integral, Eq. 4.3, by graphical or numerical integration.
2. The relationship between P and V makes it possible to fit an analytical relationship between them. We may then integrate directly.

One common example of this second type of functional relationship is a process called a polytropic process, one in which

$$PV^n = \text{constant}$$

throughout the process. The exponent n may possibly be any value from $-\infty$ to $+\infty$, depending on the particular process. For this type of process, we can integrate Eq. 4.3 as follows:

$$PV^n = \text{constant} = P_1V_1^n = P_2V_2^n$$

$$P = \frac{\text{constant}}{V^n} = \frac{P_1V_1^n}{V^n} = \frac{P_2V_2^n}{V^n}$$

$$\int_1^2 P\,dV = \text{constant}\int_1^2 \frac{dV}{V^n} = \text{constant}\left(\frac{V^{-n+1}}{-n+1}\right)\Bigg|_1^2$$

$$= \frac{\text{constant}}{1-n}(V_2^{1-n} - V_1^{1-n}) = \frac{P_2V_2^nV_2^{1-n} - P_1V_1^nV_1^{1-n}}{1-n}$$

$$\int_1^2 P\,dV = \frac{P_2V_2 - P_1V_1}{1-n} \tag{4.4}$$

Note that the resulting Eq. 4.4 is valid for any exponent n, except $n = 1$. Where $n = 1$, then

$$PV = \text{constant} = P_1V_1 = P_2V_2$$

and

$$\int_1^2 P\,dV = P_1V_1\int_1^2 \frac{dV}{V} = P_1V_1 \ln\frac{V_2}{V_1} \tag{4.5}$$

Note that in Eqs. 4.4 and 4.5 we did not say that the work is equal to the expressions given in these equations. These expressions give us the value of a certain integral, that is, a mathematical result. Whether or not that integral equals the work in a particular process depends on the result of a thermodynamic analysis of that process. It is important to keep the mathematical result separate from the thermodynamic analysis, for there are many situations in which work is not given by Eq. 4.3.

The polytropic process as described demonstrates one special functional relationship between P and V during a process. There are many other possible relations, some of which will be examined in the problems at the end of this chapter.

EXAMPLE 4.1

Consider as a system the gas in the cylinder shown in Fig. 4.6; the cylinder is fitted with a piston on which a number of small weights are placed. The initial pressure is 200 kPa and the initial volume of the gas is 0.04 m^3.

1. Let a Bunsen burner be placed under the cylinder, and let the volume of the gas increase to 0.1 m^3 while the pressure remains constant. Calculate the work done by the system during this process.

$$_1W_2 = \int_1^2 P\,dV$$

Since the pressure is constant, we conclude from Eq. 4.3 that

$$_1W_2 = P\int_1^2 dV = P(V_2 - V_1)$$

$$_1W_2 = 200\ \text{kPa} \times (0.1 - 0.04)\ \text{m}^3 = 12.0\ \text{kJ}$$

2. Consider the same system and initial conditions, but at the same time the Bunsen burner is under the cylinder and the piston is rising, let weights be removed from the piston at such a rate that, during the process, the temperature of the gas remains constant.

If we assume that the ideal-gas model is valid, then, from Eq. 3.4,

$$PV = mRT$$

We note that this is a polytropic process with exponent $n = 1$. From our analysis, we conclude that the work is given by Eq. 4.3 and that the integral in this equation is given by Eq. 4.5. Therefore,

$$_1W_2 = \int_1^2 P\,dV = P_1V_1 \ln\frac{V_2}{V_1}$$

$$= 200\ \text{kPa} \times 0.04\ \text{m}^3 \times \ln\frac{0.10}{0.04} = 7.33\ \text{kJ}$$

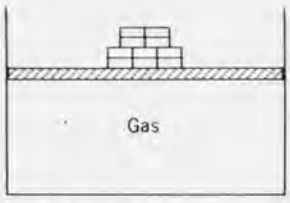


FIGURE 4.6 Sketch for Example 4.1.

3. Consider the same system, but during the heat transfer let the weights be removed at such a rate that the expression $PV^{1.3} = \text{constant}$ describes the relation between pressure and volume during the process. Again the final volume is 0.1 m^3. Calculate the work.

This is a polytropic process in which $n = 1.3$. Analyzing the process, we conclude again that the work is given by Eq. 4.3, and that the integral is given by Eq. 4.4. Therefore,

$$P_2 = 200\left(\frac{0.04}{0.10}\right)^{1.3} = 60.77 \text{ kPa}$$

$$_1W_2 = \int_1^2 P\,dV = \frac{P_2V_2 - P_1V_1}{1 - 1.3} = \frac{60.77 \times 0.1 - 200 \times 0.04}{1 - 1.3}$$

$$= 6.41 \text{ kJ}$$

4. Consider the system and initial state given in the first three examples, but let the piston be held by a pin so that the volume remains constant. In addition, let heat be transferred from the system until the pressure drops to 100 kPa. Calculate the work.

Since $\delta W = P\,dV$ for a quasi-equilibrium process, the work is zero, because there is no change in volume.

The process for each of the four examples is shown on the P–V diagram of Fig. 4.7. Process 1–2a is a constant-pressure process, and area 1–2a–f–e–1 represents the work. Similarly, line 1–2b represents the process in which $PV = \text{constant}$, line 1–2c the process in which $PV^{1.3} = \text{constant}$, and line 1–2$d$ the constant-volume process. The student should compare the relative areas under each curve with the numerical results obtained for the amounts of work done.

In this section we have discussed boundary movement work in a quasi-equilibrium process. We should also realize that there may very well be boundary movement work in a nonequilibrium process. Then the total force exerted on the piston

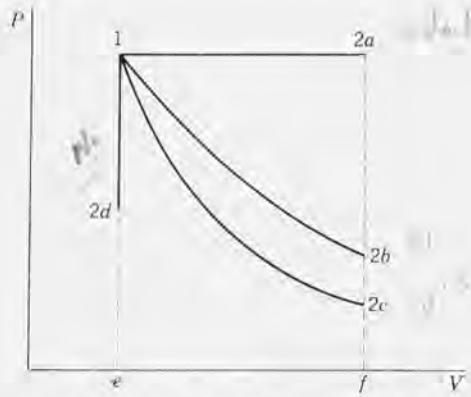


FIGURE 4.7 Pressure–volume diagram showing work done in the various processes of Example 4.1.

by the gas inside the cylinder, $P\mathscr{A}$, does not equal the external force, F_{ext}, and the work is not given by Eq. 4.2. The work can, however, be evaluated in terms of F_{ext} or, dividing by area, an equivalent external pressure, P_{ext}. The work done at the moving boundary in this case is

$$\delta W = F_{ext}\, dL = P_{ext}\, dV \tag{4.6}$$

Evaluation of Eq. 4.6 in any particular instance requires a knowledge of how the external force or pressure changes during the process.

4.4 SOME OTHER SYSTEMS IN WHICH WORK IS DONE AT A MOVING BOUNDARY

In the preceding section we considered the work done at the moving boundary of a simple compressible system during a quasi-equilibrium process and also during a nonequilibrium process. There are other types of systems in which work is done at a moving boundary. In this section we briefly consider two such systems, a stretched wire and a surface film.

Consider as a system a stretched wire that is under a given tension $\mathscr{T}$. When the length of the wire changes by the amount dL, the work done by the system is

$$\delta W = -\mathscr{T}\, dL \tag{4.7}$$

The minus sign is necessary because work is done by the system when dL is negative. This equation can be integrated to give

$${}_1W_2 = -\int_1^2 \mathscr{T}\, dL \tag{4.8}$$

The integration can be performed either graphically or analytically if the relation between $\mathscr{T}$ and L is known. The stretched wire is a simple example of the type of problem in solid-body mechanics that involves the calculation of work.

EXAMPLE 4.2

A metallic wire of initial length L_0 is stretched. Assuming elastic behavior, determine the work done in terms of the modulus of elasticity and the strain.

Let σ = stress, e = strain, and E = the modulus of elasticity.

$$e = \frac{\Delta L}{L_0} \qquad \sigma = \frac{\mathscr{T}}{\mathscr{A}} = Ee \qquad \sigma = \frac{F}{A}$$

Therefore,

$$\mathscr{T} = \mathscr{A}Ee \qquad E = \frac{\text{Stress}}{\text{Strain}} = \frac{\sigma}{e}$$

From the definition of strain,

$$de = \frac{dL}{L_0}$$

Therefore,

$$\delta W = -\mathcal{F}\, dL = -\mathcal{A}Ee L_0\, de$$

$$W = -\mathcal{A}EL_0 \int_{e=0}^{e} e\, de = -\frac{\mathcal{A}EL_0}{2}(e)^2$$

Now consider a system that consists of a liquid film having a surface tension $\mathcal{S}$. A schematic arrangement of such a film, maintained on a wire frame, one side of which can be moved, is shown in Fig. 4.8. When the area of the film is changed, for example, by sliding the movable wire along the frame, work is done on or by the film. When the area changes by an amount $d\mathcal{A}$, the work done by the system is

$$\delta W = -\mathcal{S}\, d\mathcal{A} \tag{4.9}$$

For finite changes,

$${}_1W_2 = -\int_1^2 \mathcal{S}\, d\mathcal{A} \tag{4.10}$$

4.5 SYSTEMS THAT HAVE OTHER MODES OF WORK

There are systems that have other modes of work. In this section we will consider two of these systems—those for which the mode of work is magnetic and those for which the mode of work is electric. We will consider a quasi-equilibrium process for these systems and present expressions for the work done during such a process.

To visualize how work can be accomplished by magnetic effects, let us briefly describe magnetic cooling, or adiabatic demagnetization, which is a process used to produce temperatures well below 1 K. A temperature of 1.0 K can be produced by pumping a vacuum over a bath of liquid helium (helium has the lowest normal boiling point of any substance, namely 4.2 K at one atmosphere pressure). An apparatus in which the magnetic cooling is accomplished is shown schematically in Fig. 4.9. The paramagnetic salt is the magnetic substance in which temperatures well below 1 K are achieved. When the magnetic field is slowly increased, work is done on the paramagnetic salt. From a microscopic point of view, this work is associated with the fact that in the presence of the magnetic field the ions in the salt tend to align themselves with their magnetic axes in the direction of the field.

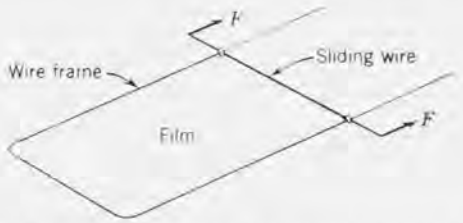


FIGURE 4.8 Schematic arrangement showing work done on a surface film.

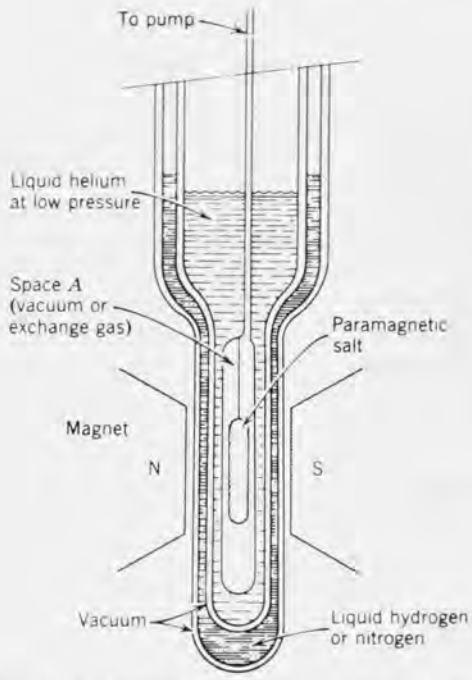


FIGURE 4.9 Schematic arrangement for magnetic cooling.

Through this work done on the salt, the temperature of the salt tends to increase. However, at this point in the experiment, space A is filled with low-pressure helium gas, and heat is transferred from the paramagnetic salt to the liquid helium, which is maintained at about 1 K. When the magnetic field is at full strength and the paramagnetic salt is at the temperature of the liquid helium, space A is evacuated, thus insulating the paramagnetic salt. The magnetic field is now reduced to zero. In this process work is done by the paramagnetic salt, and its temperature drops sharply. This entire process may be compared to the compression of a gas that is initially at ambient pressure and temperature. As a result of the compression, the temperature of the gas tends to increase. However, the high-pressure gas can be cooled to the ambient temperature. If this gas is then isolated form the surroundings and allowed to expand and do work (against a piston, for example), the temperature of the gas will decrease below the ambient temperature during the expansion process.

The basic parameters in this process are the intensity of the magnetic field and the magnetization. It may be shown that in a reversible quasi-equilibrium process, the work done on a simple magnetic substance is

$$\delta W = -\mu_0 \mathscr{H}\, d(V\mathscr{M}) \tag{4.11}$$

where

μ_0 = permeability of free space
V = volume

$\mathscr{H}$ = intensity of the magnetic field

$\mathscr{M}$ = magnetization

The minus sign indicates that as the magnetization increases, work is done on the simple magnetic substance.

We have already noted that electrical energy flowing across the boundary of a system is work. We can gain further insight into such a process by considering a system in which the only work mode is electrical. As examples of such a system, we can think of a charged condenser, an electrolytic cell, and the type of fuel cell described in Chapter 1. Consider a quasi-equilibrium process for such a system, and during this process let the potential difference be $\mathscr{E}$ and the amount of electrical charge that flows into the system be dZ. For this quasi-equilibrium process the work is given by the relation

$$\delta W = -\mathscr{E}\, dZ \tag{4.12}$$

Since the current, i, equals dZ/dt (where t = time), we can also write

$$\delta W = -\mathscr{E} i\, dt$$

$$_1W_2 = -\int_1^2 \mathscr{E} i\, dt \tag{4.13}$$

Equation 4.13 may also be written as a rate equation for work (the power).

$$\frac{\delta W}{dt} = -\mathscr{E} i \tag{4.14}$$

Since the ampere (electric current) is one of the fundamental units in the International System, and the watt has been defined previously, this relation serves as the definition of the unit for electric potential, the volt (V), which is one watt divided by one ampere.

4.6 SOME CONCLUDING REMARKS REGARDING WORK

The similarity of the expressions for work in the two processes discussed in Section 4.5 and in the three processes in which work is done at a moving boundary should be noted. In each of these quasi-equilibrium processes, the work is given by the integral of the product of an intensive property and the change of an extensive property. The following is a summary list of these processes and their work expressions.

Simple compressible system	$_1W_2 = \int_1^2 P\, dV$
Stretched wire	$_1W_2 = -\int_1^2 \mathscr{T}\, dL$
Surface film	$_1W_2 = -\int_1^2 \mathscr{S}\, d\mathscr{A}$
System in which the work is completely magnetic	$_1W_2 = -\int_1^2 \mu_0 \mathscr{H}\, d(V\mathscr{M})$
System in which the work is completely electrical	$_1W_2 = -\int_1^2 \mathscr{E}\, dZ$

(4.15)

Although we will deal primarily with systems in which there is only one mode of work, it is quite possible to have more than one work mode in a given process. Thus, we could write

$$\delta W = P\,dV - \mathcal{T}\,dL - \mathcal{S}\,d\mathcal{A} - \mu_0 \mathcal{H}\,d(V\mathcal{M}) - \mathcal{E}\,dZ + \cdots \tag{4.16}$$

where the dots represent other products of an intensive property and the derivative of a related extensive property. In each term the intensive property can viewed as the driving force that causes a change to occur in the related extensive property, which is often termed the displacement.

It should also be noted that many other forms of work can be identified in processes that are not quasi-equilibrium processes. For example, there is the work done by shearing forces in the friction in a viscous fluid or the work done by a rotating shaft that crosses the system boundary.

The identification of work is an important aspect of many thermodynamic problems. We have already noted that work can be identified only at the boundaries of the system. For example, consider Fig. 4.10, which shows a gas separated from the vacuum by a membrane. Let the membrane rupture and the gas fill the entire volume. Neglecting any work associated with the rupturing of the membrane, we can ask whether work is done in the process. If we take as our system the gas and the vacuum space, we readily conclude that no work is done because no work can be identified at the system boundary. If we take the gas as a system, we do have a change of volume, and we might be tempted to calculate the work from the integral

$$\int_1^2 P\,dV$$

However, this is not a quasi-equilibrium process, and therefore the work cannot be calculated from this relation. Because there is no resistance at the system boundary as the volume increases, we conclude that for this system no work is done in this process of filling the vacuum.

Another example can be cited with the aid of Fig. 4.11. In Fig. 4.11*a* the system consists of the container plus the gas. Work crosses the boundary of the system at the point where the system boundary intersects the shaft, and can be associated with the shearing forces in the rotating shaft. In Fig. 4.11*b* the system includes shaft and weight as well as the gas and the container. Therefore, no work crosses the system boundary as the weight moves downward. As we will see in the next chapter, we can identify a change of potential energy within the system, but this should not be confused with work crossing the system boundary.

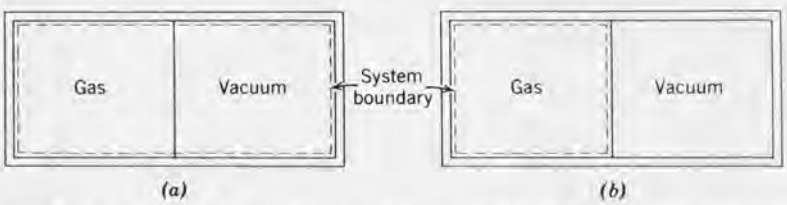


FIGURE 4.10 Example of process involving a change of volume for which the work is zero.

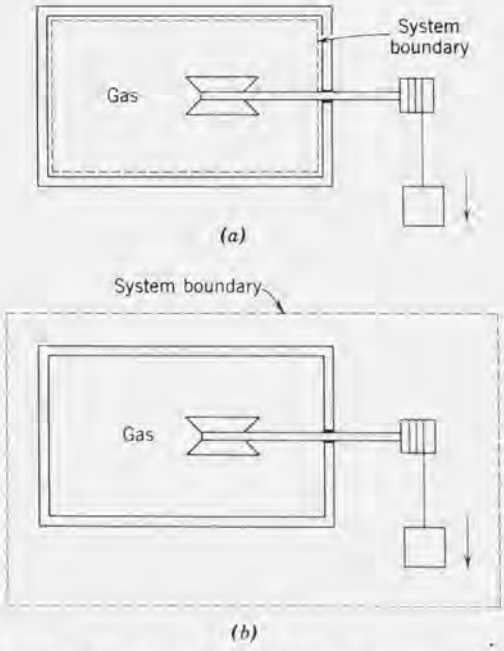


FIGURE 4.11 Example showing how selection of the system determines whether work is involved in a process.

4.7 DEFINITION OF HEAT

The thermodynamic definition of heat is somewhat different from the everyday understanding of the word. It is essential to understand clearly the definition of heat given here, because it plays a part in so many thermodynamic problems.

If a block of hot copper is placed in a beaker of cold water, we know from experience that the block of copper cools down and the water warms up until the copper and water reach the same temperature. What causes this decrease in the temperature of the copper and the increase in the temperature of the water? We say that it is the result of the transfer of energy from the copper block to the water. It is out of such a transfer of energy that we arrive at a definition of heat.

Heat is defined as the form of energy that is transferred across the boundary of a system at a given temperature to another system (or the surroundings) at a lower temperature by virtue of the temperature difference between the two systems. That is, heat is transferred from the system at the higher temperature to the system at the lower temperature, and the heat transfer occurs solely because of the temperature difference between the two systems. Another aspect of this definition of heat is that a body never contains heat. Rather, heat can be identified only as it crosses the boundary. Thus, heat is a transient phenomenon. If we consider the hot block of copper as one system and the cold water in the beaker as another system, we recognize that originally neither system contains any heat (they do contain energy, of course). When the copper block is placed in the water and the two are in thermal communication, heat is transferred from the copper to the water until equilibrium of temperature is established. At this point we no longer

have heat transfer, because there is no temperature difference. Neither of the systems contains heat at the conclusion of the process. It also follows that heat is identified at the boundary of the system, for heat is defined as energy being transferred across the system boundary.

4.8 UNITS OF HEAT

Heat, like work, is a form of energy transfer to or from a system. Therefore, the units for heat, and to be more general, for any other form of energy as well, are the same as the units for work, or are at least directly proportional to them. In the International System the unit for heat (energy) is the joule. Similarly, in the English System, the foot pound force is an appropriate unit for heat. However, another unit came to be used naturally over the years, the result of an association with the process of heating water, such as that used in connection with defining heat in the previous section. Consider as a system 1 lbm of water at 59.5 F. Let a block of hot copper of appropriate mass and temperature be placed in the water, so that when thermal equilibrium is established the temperature of the water is 60.5 F. This unit amount of heat transferred from the copper to the water in this process is called the British thermal unit (Btu). More specifically, it is called the 60-degree Btu, defined as the amount of heat required to raise 1 lbm of water from 59.5 F to 60.5 F. (The Btu as used today is actually defined in terms of the standard SI units.) It is worth noting here that a unit of heat in metric units, the calorie, originated naturally in a manner similar to the origin of the Btu in the English system. The calorie is defined as the amount of heat required to raise 1 gram of water from 14.5°C to 15.5°C.

Heat transferred *to* a system is considered positive, and heat transferred *from* a system is negative. Thus, positive heat represents energy transferred to a system, and negative heat represents energy transferred from a system. The symbol Q represents heat. A process in which there is no heat transfer ($Q = 0$) is called an adiabatic process.

From a mathematical perspective, heat, like work, is a path function and is recognized as an inexact differential. That is, the amount of heat transferred when a system undergoes a change from state 1 to state 2 depends on the path that the system follows during the change of state. Since heat is an inexact differential, the differential is written δQ. On integrating, we write

$$\int_1^2 \delta Q = {}_1Q_2$$

In words, ${}_1Q_2$ is the heat transferred during the given process between state 1 and state 2.

The rate at which heat is transferred to a system is designated by symbol $\dot{Q}$.

$$\dot{Q} \equiv \frac{\delta Q}{dt}$$

It is also convenient to speak of the heat transfer per unit mass of the system, q, which is defined as

$$q \equiv \frac{Q}{m}$$

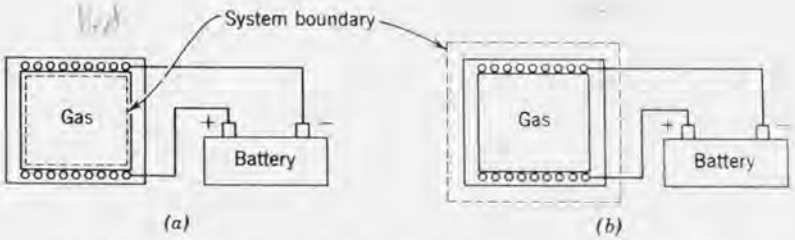


FIGURE 4.12 An example showing the difference between heat and work.

4.9 COMPARISON OF HEAT AND WORK

At this point it is evident that there are many similarities between heat and work.

1. Heat and work are both transient phenomena. Systems never possess heat or work, but either or both cross the system boundary when a system undergoes a change of state.
2. Both heat and work are boundary phenomena. Both are observed only at the boundaries of the system, and both represent energy crossing the boundary of the system.
3. Both heat and work are path functions and inexact differentials.

It should also be noted that in our sign convention, $+Q$ represents heat transferred *to* the system and thus is energy added to the system, and $+W$ represents work done *by* the system and thus represents energy leaving the system.

A final illustration may help explain the difference between heat and work. Figure 4.12 shows a gas contained in a rigid vessel. Resistance coils are wound around the outside of the vessel. When current flows through the resistance coils, the temperature of the gas increases. Which crosses the boundary of the system, heat or work?

In Fig. 4.12*a* we consider only the gas as the system. The energy crosses the boundary of the system because the temperature of the walls is higher than the temperature of the gas. Therefore, we recognize that heat crosses the boundary of the system.

In Fig. 4.12*b* the system includes the vessel and the resistance heater. Electricity crosses the boundary of the system, and as indicated earlier, this is work.

PROBLEMS

4.1 A cylinder fitted with a frictionless piston contains 5 kg of superheated water vapor at 1 MPa, 250°C. This system is cooled at constant pressure until the water reaches a quality of 50 percent. Calculate the work done during this process.

4.1E A cylinder fitted with a frictionless piston contains 10 lbm of superheated water vapor at 100 lbf/in.^{2}, 500 F. This system is cooled at constant pressure until the water reaches a quality of 50 percent. Calculate the work done during this process.

4.2 A vertical cylinder fitted with a frictionless piston, as shown in Fig. 4.13, initially contains air at 150 kPa, 400°C. This system is allowed to cool to an ambient temperature of 20°C.

(a) Is the piston resting on the stops at the final state? What is the final pressure in the cylinder?

(b) Considering the air in the cylinder as the system, determine the work done during this process.

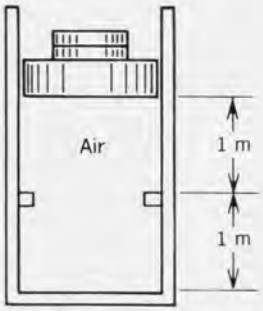


FIGURE 4.13 Sketch for Problem 4.2.

4.3 Consider the process described in Problem 2.12. For a control volume that consists of the space inside the cylinder, determine the boundary movement work done from the point at which the valve is first opened (piston resting at the bottom of the cylinder) to the final state given in Problem 2.12.

4.4 The refrigerant R-22 is contained in a vertical cylinder fitted with a frictionless piston, as shown in Fig. 4.14. The initial state is −30°C, 150 kPa, and the cylinder volume is 10 L. This system is brought indoors and allowed to warm to room temperature, that is, 15°C. At the piston stops shown in Fig. 4.14, the cylinder volume is 11 L.

(a) Is the piston at the stops at the final state?

(b) Calculate the work done by the R-22 during this process.

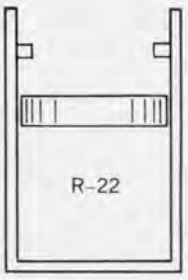


FIGURE 4.14 Sketch for Problem 4.4.

4.5 Methane gas is contained in a cylinder fitted with a piston at 10°C, 200 kPa, and the volume is 200 L. The gas is compressed slowly in an isothermal process to 600 kPa.

(a) Show it is reasonable to assume that the methane behaves as an ideal gas during this process.

(b) Determine the work done during the process.

4.6 The cylinder–piston arrangement shown in Fig. 4.15 contains carbon dioxide at 300 kPa, 200°C, and the volume is 0.2 m^3. Weights are removed so that the gas expands according to the relation

$$PV^{1.2} = \text{constant}$$

until the final temperature is 100°C. Determine the work done during this process.

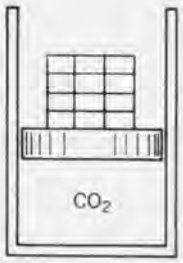


FIGURE 4.15 Sketch for Problems 4.6 and 4.6E

4.6E The cylinder–piston arrangement shown in Fig. 4.15 contains carbon dioxide at 50 lbf/$in.^2$, 350 F, and the volume is 5 ft^3. Weights are removed so that the gas expands according to the relation

$$PV^{1.2} = \text{constant}$$

until the final temperature is 200 F. Determine the work done during this process.

4.7 Determine the work done by the air inside the cylinder for the process described in Problem 3.10.

4.8 Water initially at 50 kPa, 100°C, is contained in a piston and cylinder arrangement with an initial volume of 3 m^3. The water is slowly compressed according to the relation, PV = constant, until a final pressure of 1 MPa is reached. Determine the work for this process.

4.9 Consider the two-part process described in Problem 3.28. Determine the work done by the water inside the cylinder.

4.10 A cylinder fitted with a piston contains propane gas at 100 kPa, 300 K, and the volume is 200 L. The gas is slowly compressed according to the relation

$$PV^{1.1} = \text{constant}$$

until the final temperature reaches 340 K.

(a) What is the final pressure?

(b) Justify the reasonableness of the ideal-gas model.

(c) How much work is done during the process?

4.11 Consider the process described in Problem 3.32. For a control volume that consists of the space inside the cylinder, what is the boundary movement work done against the piston during the process?

4.12 The gas space above the water in a closed storage tank contains nitrogen at 25°C, 100 kPa. The tank has a total volume of 4 m^3 and contains 500 kg of water at 25°C. An additional 500 kg of water is slowly forced into the tank. Assuming the temperature remains constant, calculate the final pressure of the nitrogen and the work done on the nitrogen during the process.

4.12E The gas space above the water in a closed storage tank contains nitrogen at 75 F, 15 lbf/in.^{2}. The tank has a total volume of 150 ft^3 and contains 1000 lbm of water at 75 F. An additional 1000 lbm of water is slowly forced into the tank. Assuming the temperature remains constant, calculate the final pressure of the nitrogen and the work done on the nitrogen during the process.

4.13 Consider the process of inflating a helium balloon, as described in Problem 3.7. For a control volume that consists of the space inside the balloon, determine the work done during the overall process.

4.14 Ammonia vapor is compressed inside a cylinder by an external force acting on the piston. The ammonia is initially at 30°C, 500 kPa, and the final pressure is 1400 kPa. The following data have been measured experimentally for this process:

Pressure, kPa	*Volume, L*
500	1.25
653	1.08
802	0.96
945	0.84
1100	0.72
1248	0.60
1400	0.50

(a) Determine the work for the process, considering the ammonia as the system.
(b) What is the final temperature of the ammonia?

4.15 A certain balloon is constructed of a material that allows the pressure inside to be proportional to the balloon diameter squared (in the range of variables covered in this process). This balloon contains 2 kg of ammonia initially at 0°C, 60 percent quality. The balloon is heated until the final pressure inside reaches 600 kPa. Considering the ammonia as a system, how much work is done during the process?

4.16 Saturated vapor water at 200°C is contained in a cylinder fitted with a piston. The initial volume of the cylinder is 25 L. The steam then expands in a quasi-equilibrium isothermal process until the final pressure in the cylinder is 200 kPa. In so doing, the steam does work against the piston.

(a) Determine the work done during the process.
(b) If we assume that the steam behaves as an ideal gas, what is the amount of error?

4.16E Saturated vapor water at 400 F is contained in a cylinder fitted with a piston. The initial volume of the cylinder is 0.3 ft^3. The steam then expands in a quasi-equilibrium isothermal process until the final pressure in the cylinder is 20 lbf/in.^{2}. In so doing, the steam does work against the piston.

(a) Determine the work done during the process.
(b) If we assume that the steam behaves as an ideal gas, what is the amount of error?

4.17 A spherical elastic balloon initially containing 5 kg of saturated-vapor ammonia at 20°C is connected by a valve to a rigid 3-m^3 evacuated tank. The balloon material allows the pressure inside to be proportional to the balloon diameter (within the range of variables of this process). The valve is opened, which allows ammonia to flow from the balloon to the tank until the pressure inside the balloon has dropped to 600 kPa, at which point the valve is closed. The final temperature in both the balloon and tank is 20°C. Determine

(a) The final pressure in the tank.
(b) The work done by the ammonia during the process.

4.18 A cylinder having an initial volume of 2 m^3 contains 0.1 kg of water at 40°C. The water is compressed in an isothermal quasi-equilibrium process until it has a quality of 50 percent. Calculate the work done during this process.

4.19 Consider the nonequilibrium process described in Problem 3.6. Determine the work done by the carbon dioxide in the cylinder during the process.

4.20 Air at 200 kPa, 30°C, is contained in a cylinder fitted with a piston. The cylinder volume is 100 L, and the pressure balances the outside ambient pressure of 100 kPa plus an externally imposed mechanical force that is proportional to $V^{0.5}$. Heat is transferred to the system until the temperature reaches 200°C. Find the final pressure in the cylinder and the work done during the process.

4.20E Air at 30 lbf/$in.^2$, 85 F, is contained in cylinder fitted with a piston. The cylinder volume is 3.5 ft^3, and the pressure balances the outside ambient pressure of 14.7 lbf/$in.^2$ plus an externally imposed mechanical force that is proportional to $V^{0.5}$. Heat is transferred to the system until the temperature reaches 400 F. Find the final pressure in the cylinder and the work done during the process.

4.21 Tank *A* shown in Fig. 4.16 has a volume of 400 L and contains argon gas at 250 kPa, 30°C. Cylinder *B* contains a frictionless piston of a mass that requires a pressure of 150 kPa inside the cylinder to raise the piston. The valve connecting the two tanks is opened, allowing gas to flow into the cylinder. The argon eventually reaches a uniform state of 150 kPa, 30°C, throughout. Calculate the work done by the argon during this process.

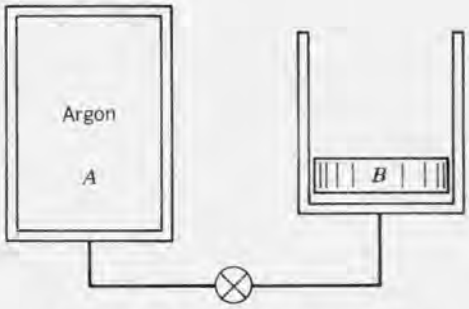


FIGURE 4.16 Sketch for Problem 4.21.

4.22 A cylinder fitted with a piston contains R-12 at 10°C, 50 percent quality, and the volume is 50 L. The system is heated, and the R-12 expands and slowly moves the

piston against an external resisting force. When the last remaining amount of liquid evaporates, the temperature in the cylinder is 25°C. The process continues until the temperature reaches 150°C, at which point the system pressure is 800 kPa. How much work is done during this process?

4.23 A cylinder containing 1 kg of ammonia is fitted with a piston restrained by a variable external force. The initial state of the ammonia is 2 MPa, 180°C. The cylinder is allowed to cool, and the external force varies in such a manner that when the ammonia reaches the two-phase region, its temperature is 40°C. The process continues until the ammonia has cooled to 20°C, at which point the quality is 50 percent. Calculate the work for the overall process.

4.23E A cylinder containing 2 lbm of ammonia is fitted with a piston restrained by a variable external force. The initial state of the ammonia is 280 lbf/in.^{2}, 360 F. The cylinder is allowed to cool, and the external force varies in such a manner that when the ammonia reaches the two-phase region, its temperature is 105 F. The process continues until the ammonia has cooled to 65 F, at which point the quality is 50 percent. Calculate the work for the overall process.

4.24 A vertical cylinder fitted with a piston contains 10 L of R-22 at 10°C, 90 percent quality. The piston has a mass of 90 kg and a cross-sectional area of 0.006 m^2; it is held in place by a pin, as shown in Fig. 4.17. The local ambient pressure is 100 kPa. The pin is removed, allowing the piston to move. After a period of time, the system comes to equilibrium, with the final temperature being 10°C.

(a) Determine the final pressure and volume of the system.
(b) Calculate the work done by the R-22 during this process.

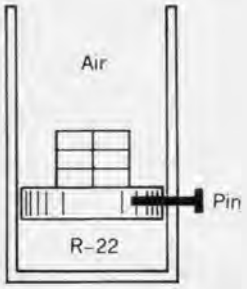


FIGURE 4.17 Sketch for Problem 4.24.

4.25 A steel bar 10 mm in diameter and 500 mm long is pulled in tension in a tensile testing machine. How much work is required to produce a strain of 0.1 percent? The modulus of elasticity of steel is 200 GN/m^2.

4.25E A steel bar 0.5 in. in diameter and 1 ft long is pulled in tension in a tensile testing machine. How much work is required to produce a strain of 0.1 percent? The modulus of elasticity of steel is 30×10^6 lbf/in.^{2}.

4.26 At 20°C ethanol has a surface tension of 22.3 mN/m. Suppose that a film of ethanol is maintained on the wire frame shown in Fig. 4.18. One side of the frame is movable. The initial dimensions of the wire frame are as shown. Considering the film as the system, determine the work done when the wire is moved 10 mm in the indicated direction.

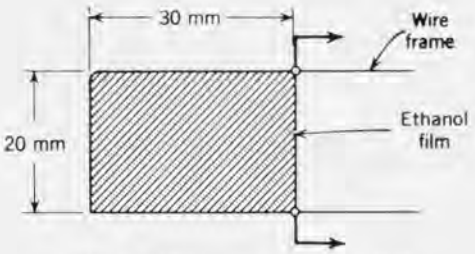


FIGURE 4.18 Sketch for Problem 4.26.

4.27 Consider a paramagnetic salt such as that described in Section 4.5. Assume that the magnetization of this substance is proportional to the magnetic field intensity divided by the temperature. Derive an expression for the work done in changing the magnetization in an isothermal process.

4.28 Repeat Problem 4.27 for a process taking place at constant magnetic field intensity.

4.29 An electric storage battery is well insulated thermally while it is being recharged. The charging voltage is 12.3 V and the current is 25 A. Considering the battery as the system, what are the heat transfer and the work in a 30-minute period?

4.30 Consider as a thermodynamic system the operating portion of a window-mounted room air conditioner used to cool incoming air. Examine the system boundaries for rates of work and heat transfer, including sign.

4.31 Consider a hot-air heating system for a home. Examine the following systems for heat transfer.

(a) The combustion chamber and combustion gas side of the heat transfer area.
(b) The furnace as a whole, including the hot- and cold-air ducts and chimney.

4.32 Consider a household refrigerator that is loaded with room temperature food. Define a thermodynamic system, and examine its boundaries for rates of work and heat transfer, including sign,

(a) Immediately after the food is loaded into the refrigerator.
(b) After a long period of time has elapsed.

4.33 A room is heated with steam radiators on a winter day. Examine the following systems regarding heat transfer, including sign.

(a) The radiator.
(b) The room.
(c) The radiator and the room together.

COMPUTER PROBLEMS

4.1C Write a computer program to determine the boundary movement work for a specified substance undergoing a process for a given set of data (values of pressure and corresponding volume during the process).

4.2C Write a computer program to determine the boundary movement work for a specified gas undergoing an isothermal process at temperature T from v_1 to v_2. Use the Benedict–Webb–Rubin equation of state. Compare the result with that found assuming ideal-gas behavior.

4.3C In Problem 4.9, determine the work done by the water at any point during the process.

4.4C In Problem 4.11, determine the work done by the ammonia at any point during the process.

4.5C Consider the process described in Problem 4.17, in which ammonia is transferred from a balloon to a rigid tank. Follow the process from the initial state, point-by-point, until the pressures in the balloon and tank eventually equalize.

4.6C Reconsider the process of Problem 4.23, in which three states were specified. Solve the problem by fitting a single smooth curve (P versus v) through the three points. Map out the path followed (including temperature or quality) during the process.

4.7C The elastic balloon described in Problem 3.7 is to be filled with one of the real working fluids listed in Tables A.1 through A.6. Determine the state inside the balloon at any intermediate point and the boundary movement work done to this point during the inflation process to a given final pressure.

5

THE FIRST LAW OF THERMODYNAMICS

Having completed our consideration of basic definitions and concepts, we are ready to proceed to a discussion of the first law of thermodynamics. Often this law is called the law of the conservation of energy and, as we will see later, this is essentially true. Our procedure will be to state this law for a system undergoing a cycle, and then for a change of state of a system. The law of the conservation of matter will also be considered in this chapter.

5.1 THE FIRST LAW OF THERMODYNAMICS FOR A SYSTEM UNDERGOING A CYCLE

The first law of thermodynamics states that during any cycle a system undergoes, the cyclic integral of the heat is proportional to the cyclic integral of the work.

To illustrate this law, consider as a system the gas in the container shown in Fig. 5.1. Let this system go through a cycle that is made up of two processes. In the first process work is done on the system by the paddle that turns as the weight is lowered. Let the system then return to its initial state by transferring heat from the system until the cycle has been completed.

Historically, work was measured in mechanical units of force times distance, such as, foot pounds force or joules, and heat was measured in thermal units, such as the British thermal unit or the calorie. Measurements of work and heat were made during a cycle for a wide variety of systems and for various amounts of work and heat. When the amounts of work and heat were compared, it was found that they were always proportional. Such observations led to the formulation of the first law of thermodynamics, which in equation form is written

$$J \oint \delta Q = \oint \delta W \tag{5.1}$$

The symbol $\oint \delta Q$, which is called the cyclic integral of the heat transfer, represents the net heat transfer during the cycle, and $\oint \delta W$, the cyclic integral of the work, represents the net work during the cycle. Here J is a proportionality factor that depends on the units used for work and heat.

The basis of every law of nature is experimental evidence, and this is true also of the first law of thermodynamics. Many different experiments have been conducted

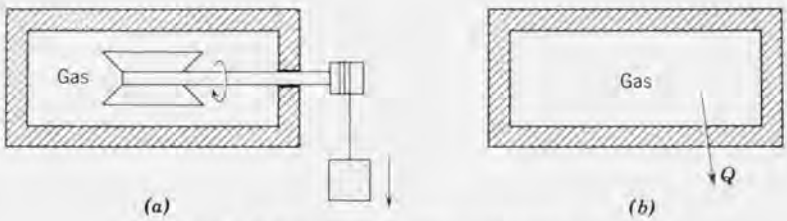


FIGURE 5.1 Example of a system undergoing a cycle.

on the first law, and every one thus far has verified it either directly or indirectly. The first law has never been disproved.

As was discussed in Chapter 4, the units for work and heat or for any other form of energy either are the same or are directly proportional. In SI units, the joule is used as the unit for both work and heat and for any other energy unit. In English units, the basic unit for work is the foot pound force, and the basic unit for heat is the British thermal unit (Btu). James P. Joule (1818–1889) did the first accurate work in the 1840s on measurement of the proportionality factor J, which relates these units. Today, the Btu is defined in terms of the basic SI metric units,

$$1 \text{ Btu} = 778.17 \text{ ft lbf}$$

This unit is termed the International British thermal unit. For much engineering work, the accuracy of other data does not warrant more accuracy than the relation 1 Btu = 778 ft lbf, which is the value used with English units in the problems in this text. Because these units are equivalent, it is not necessary to include the factor J explicitly in Eq. 5.1, but simply to recognize that for any system of units, each equation must have consistent units throughout. Therefore, we may write Eq. 5.1 as

$$\oint \delta Q = \oint \delta W \tag{5.2}$$

which can be considered the basic statement of the first law of thermodynamics.

5.2 THE FIRST LAW OF THERMODYNAMICS FOR A CHANGE IN STATE OF A SYSTEM

Equation 5.2 states the first law of thermodynamics for a system during a cycle. Many times, however, we are concerned with a process rather than a cycle. We now consider the first law of thermodynamics for a system that undergoes a change of state. We begin by introducing a new property, the energy, which is given the symbol E. Consider a system that undergoes a cycle, in which it changes from state 1 to state 2 by process A, and returns from state 2 to state 1 by process B. This cycle is shown in Fig. 5.2 on a pressure (or other intensive property)–volume (or other extensive property) diagram. From the first law of thermodynamics, Eq. 5.2,

$$\oint \delta Q = \oint \delta W$$

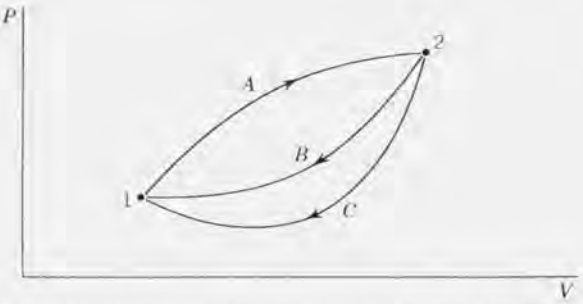


FIGURE 5.2 Demonstration of the existence of thermodynamic property E.

Considering the two separate processes, we have

$$\int_1^2 \delta Q_A + \int_2^1 \delta Q_B = \int_1^2 \delta W_A + \int_2^1 \delta W_B$$

Now consider another cycle in which the system changes from state 1 to state 2 by process A, as before, and returns to state 1 by process C. For this cycle we can write

$$\int_1^2 \delta Q_A + \int_2^1 \delta Q_C = \int_1^2 \delta W_A + \int_2^1 \delta W_C$$

Subtracting the second of these equations from the first, we have

$$\int_2^1 \delta Q_B - \int_2^1 \delta Q_C = \int_2^1 \delta W_B - \int_2^1 \delta W_C$$

or, by rearranging,

$$\int_2^1 (\delta Q - \delta W)_B = \int_2^1 (\delta Q - \delta W)_C \tag{5.3}$$

Since B and C represent arbitrary processes between states 1 and 2, the quantity $\delta Q - \delta W$ is the same for all processes between state 1 and state 2. Therefore, $\delta Q - \delta W$ depends only on the initial and final states and not on the path followed between the two states. We conclude that this is a point function, and therefore it is the differential of a property of the system. This property is the energy of the system and is given the symbol E. Thus, we can write

$$\delta Q - \delta W = dE$$

$$\delta Q = dE + \delta W \tag{5.4}$$

Because E is a property, its derivative is written dE. When Eq. 5.4 is integrated from an initial state 1 to final state 2, we have

$${}_1Q_2 = E_2 - E_1 + {}_1W_2 \tag{5.5}$$

where ${}_1Q_2$ is the heat transferred to the system during the process from state 1 to state 2, E_1 and E_2 are the initial and final values of the energy E of the system, and ${}_1W_2$ is the work done by the system during the process.

The physical significance of the property E is that it represents all the energy of the system in the given state. This energy might be present in a variety of forms, such as the kinetic or potential energy of the system as a whole with respect to the chosen coordinate frame, energy associated with the motion and position of the molecules, energy associated with the structure of the atom, chemical energy present in a storage battery, energy present in a charged condenser, or in any of a number of other forms.

In the study of thermodynamics, it is convenient to consider the bulk kinetic and potential energy separately and then to consider all the other energy of the system in a single property that we call the internal energy, and to which we give the symbol U. Thus, we would write

$$E = \text{Internal energy} + \text{Kinetic energy} + \text{Potential energy}$$

or

$$E = U + \text{KE} + \text{PE}$$

The kinetic and potential energy of the system are associated with the coordinate frame that we select and can be specified by the macroscopic parameters of mass, velocity, and elevation. The internal energy U includes all other forms of energy of the system and is associated with the thermodynamic state of the system.

Since the terms comprising E are point functions, we can write

$$dE = dU + d(\text{KE}) + d(\text{PE}) \tag{5.6}$$

The first law of thermodynamics for a change of state may therefore be written

$$\delta Q = dU + d(\text{KE}) + d(\text{PE}) + \delta W \tag{5.7}$$

In words this equation states that as a system undergoes a change of state, energy may cross the boundary as either heat or work, and each may be positive or negative. The net change in the energy of the system will be exactly equal to the net energy that crosses the boundary of the system. The energy of the system may change in any of three ways—by a change in internal energy, in kinetic energy, or in potential energy. Because the mass of a system is fixed, we can also say that a quantity of matter may have energy in three forms, internal energy, kinetic energy, or potential energy.

This section concludes by deriving an expression for the kinetic and potential energy of a system. Consider a system that is initially at rest relative to the earth, which is taken as the coordinate frame. Let this system be acted on by an external horizontal force F that moves the system a distance dx in the direction of the force. Thus, there is no change in potential energy. Let there be no heat transfer and no change in internal energy. Then from the first law, Eq. 5.7,

$$\delta W = -F\,dx = -d\text{KE}$$

But

$$F = ma = m\frac{d\mathbf{V}}{dt} = m\frac{dx}{dt}\frac{d\mathbf{V}}{dx} = m\mathbf{V}\frac{d\mathbf{V}}{dx}$$

Then

$$d\mathrm{KE} = F\,dx = m\mathbf{V}\,d\mathbf{V}$$

Integrating, we obtain

$$\int_{\mathrm{KE}=0}^{\mathrm{KE}} d\mathrm{KE} = \int_{\mathbf{V}=0}^{\mathbf{V}} m\mathbf{V}\,d\mathbf{V}$$

$$\mathrm{KE} = \tfrac{1}{2}m\mathbf{V}^2 \tag{5.8}$$

A similar expression for potential energy can be found. Consider a system that is initially at rest and at the elevation of some reference level. Let this system be acted on by a vertical force F of such magnitude that it raises (in elevation) the system with constant velocity an amount dZ. Let the acceleration due to gravity at this point be g. From the first law, Eq. 5.7,

$$\delta W = -F\,dZ = -d\mathrm{PE}$$
$$F = ma = mg$$

Then

$$d\mathrm{PE} = F\,dZ = mg\,dZ$$

Integrating gives

$$\int_{\mathrm{PE}_1}^{\mathrm{PE}_2} d\mathrm{PE} = m\int_{Z_1}^{Z_2} g\,dZ$$

Assuming that g does not vary with Z (which is a very reasonable assumption for moderate changes in elevation),

$$\mathrm{PE}_2 - \mathrm{PE}_1 = mg(Z_2 - Z_1) \tag{5.9}$$

Substituting the expressions for kinetic and potential energy into Eq. 5.6, we have

$$dE = dU + m\mathbf{V}\,d\mathbf{V} + mg\,dZ$$

Integrating for a change of state from state 1 to state 2 with constant g, we have

$$E_2 - E_1 = U_2 - U_1 + \frac{m\mathbf{V}_2^2}{2} - \frac{m\mathbf{V}_1^2}{2} + mgZ_2 - mgZ_1$$

Similarly, substituting these expressions for kinetic and potential energy into Eq. 5.7, we have

$$\delta Q = dU + \frac{d(m\mathbf{V}^2)}{2} + d(mgZ) + \delta W \tag{5.10}$$

Assuming g is a constant, in the integrated form of this equation,

$${}_1Q_2 = U_2 - U_1 + \frac{m(\mathbf{V}_2^2 - \mathbf{V}_1^2)}{2} + mg(Z_2 - Z_1) + {}_1W_2 \tag{5.11}$$

Three observations should be made regarding this equation. The first observation is that the property E, the energy of the system, was found to exist, and we were able to write the first law for a change of state using Eq. 5.5. However, rather than deal with this property E, we find it more convenient to consider the internal energy and the kinetic and potential energies of the system. In general, this procedure will be followed in the rest of this book.

The second observation is that Eqs. 5.10 and 5.11 are in effect a statement of the conservation of energy. The net change of the energy of the system is always equal to the net transfer of energy across the system boundary as heat and work. This is somewhat analogous to a joint checking account shared by a husband and wife. There are two ways in which deposits and withdrawals can be made—either by the husband or by the wife—and the balance will always reflect the net amount of the transaction. Similarly, there are two ways in which energy can cross the boundary of a system—either as heat or as work—and the energy of the system will change by the exact amount of the net energy crossing the system boundary. The concept of energy and the law of the conservation of energy are basic to thermodynamics.

The third observation is that Eqs. 5.10 and 5.11 can give only changes in internal energy, kinetic energy, and potential energy. We can learn nothing about absolute values of these quantities from these equations. If we wish to assign values to internal energy, kinetic energy, and potential energy, we must assume reference states and assign a value to the quantity in this reference state. The kinetic energy of a body with zero velocity relative to the earth is assumed to be zero. Similarly, the value of the potential energy is assumed to be zero when the body is at some reference elevation. With internal energy, therefore, we must also have a reference state if we wish to assign values of this property. This matter is considered in the following section.

5.3 INTERNAL ENERGY—A THERMODYNAMIC PROPERTY

Internal energy is an extensive property, because it depends on the mass of the system. Similarly, the kinetic and potential energies are extensive properties.

The symbol U designates the internal energy of a given mass of a substance. Following the convention used with other extensive properties, the symbol u designates the internal energy per unit mass. We could speak of u as the specific internal energy, as we do with specific volume. However, because the context will usually make it clear whether u or U is referred to, we will simply use the term internal energy to refer to both internal energy per unit mass and the total internal energy.

In Chapter 3 it was noted that in the absence of the effects of motion, gravity, surface effects, electricity, and magnetism, the state of a pure substance is specified by two independent properties. It is very significant that with these restrictions, the internal energy may be one of the independent properties of a pure substance. This means, for example, that if we specify the pressure and internal energy (with reference to an arbitrary base) of superheated steam, the temperature is also specified.

Thus, in a table of thermodynamic properties such as the steam tables, the value of internal energy can be tabulated along with other thermodynamic properties. Tables 1 and 2 of the steam tables by Keenan and his colleagues (Tables A.1.1 and A.1.2) list the internal energy for saturated states. Included are the internal energy of saturated liquid u_f, the internal energy of saturated vapor u_g, and the difference between the internal energy of saturated liquid and saturated vapor u_{fg}. The values are given in relation to an arbitrarily assumed reference state, which will be discussed later. The internal energy of saturated steam of a given quality is calculated in the same way as specific volume. The relations are

$$U = U_{\text{liq}} + U_{\text{vap}}$$

or

$$mu = m_{\text{liq}}u_f + m_{\text{vap}}u_g$$

Dividing by m and introducing the quality x, gives

$$u = (1 - x)u_f + xu_g$$
$$u = u_f + xu_{fg}$$

As an example, the specific internal energy of saturated steam having a pressure of 0.6 MPa and a quality of 95 percent can be calculated as

$$u = u_f + xu_{fg} = 669.9 + 0.95(1897.5) = 2472.5 \text{ kJ/kg}$$

EXAMPLE 5.1

A tank containing a fluid is stirred by a paddle wheel. The work input to the paddle wheel is 5090 kJ. The heat transfer from the tank is 1500 kJ. Considering the tank and the fluid as the system, determine the change in the internal energy of the system.

The first law of thermodynamics is (Eq. 5.11)

$${}_1Q_2 = U_2 - U_1 + m\frac{\mathbf{V}_2^2 - \mathbf{V}_1^2}{2} + mg(Z_2 - Z_1) + {}_1W_2$$

Since there is no change in kinetic and potential energy, this reduces to

$${}_1Q_2 = U_2 - U_1 + {}_1W_2$$
$$-1500 = U_2 - U_1 - 5090$$
$$U_2 - U_1 = 3590 \text{ kJ}$$

EXAMPLE 5.2

Consider a system composed of a stone having a mass of 10 kg and a bucket containing 100 kg of water. Initially the stone is 10.2 m above the water, and the stone and water are at the same temperature. The stone then falls into the water.

Determine ΔU, ΔKE, ΔPE, Q, and W for the following changes of state, assuming standard gravitational acceleration, 9.806 65 m/s^2.

1. The stone is about to enter the water.
2. The stone has just come to rest in the bucket.

3. Heat has been transferred to the surroundings in such an amount that the stone and water are at the same temperature as they were initially.

Analysis and Solution

The first law of thermodynamics is

$$ {}_1Q_2 = U_2 - U_1 + m\frac{\mathbf{V}_2^2 - \mathbf{V}_1^2}{2} + mg(Z_2 - Z_1) + {}_1W_2 $$

1. The stone is about to enter the water. Assuming no heat transfer to or from the stone as it falls, we conclude that, during the change from the initial state to the state that exists at the moment the stone enters the water,

$$ {}_1Q_2 = 0, \qquad {}_1W_2 = 0, \qquad \Delta U = 0 $$

Therefore, the first law reduces to

$$ \begin{aligned} -\Delta\text{KE} = \Delta\text{PE} &= mg(Z_2 - Z_1) \\ &= 10\text{ kg} \times 9.806\,65\text{ m/s}^2 \times (-10.2\text{ m}) \\ &= -1000\text{ J} = -1\text{ kJ} \end{aligned} $$

That is,

$$ \Delta\text{KE} = 1\text{ kJ} \qquad \text{and} \qquad \Delta\text{PE} = -1\text{ kJ} $$

2. Just after the stone comes to rest in the bucket,

$$ {}_1Q_2 = 0, \qquad {}_1W_2 = 0, \qquad \Delta\text{KE} = 0 $$

Then

$$ \Delta\text{PE} = -\Delta U = mg(Z_2 - Z_1) = -1\text{ kJ} $$

$$ \Delta U = 1\text{ kJ}, \qquad \Delta\text{PE} = -1\text{ kJ} $$

3. After enough heat has been transferred so that the stone and water are at the same temperature that they were initially, we conclude that $\Delta U = 0$. Therefore,

$$ \Delta U = 0, \qquad \Delta\text{KE} = 0, \qquad {}_1W_2 = 0 $$

$$ {}_1Q_2 = \Delta\text{PE} = mg(Z_2 - Z_1) = -1\text{ kJ} $$

5.4 PROBLEM ANALYSIS AND SOLUTION TECHNIQUE

At this point in our study of thermodynamics, we have progressed sufficiently far (that is, we have accumulated sufficient tools to work with) that it is worthwhile to develop a somewhat formal technique or procedure for analyzing and solving thermodynamic problems. For the time being it may not seem entirely necessary to use such a rigorous procedure for many of our problems, but we should keep in mind that as we acquire more analytical tools the problems that we are capable of dealing with will become much more complicated. Thus, it is appropriate that we begin to practice this technique now in anticipation of these future problems.

Our problem analysis and solution technique is contained within the framework of the following set of questions that must be answered in the process of an orderly solution of a thermodynamic problem.

1. What is the system or control volume? It may be helpful to draw a sketch of the system at this point.
2. What do we know about the initial state (which properties)?
3. What do we know about the final state?
4. What do we know about the process that takes place? Is anything constant or zero? Is there some known functional relation between two properties?
5. Is it helpful to draw a diagram of the information in steps 2 to 4 (for example, a T–v or P–v diagram)?
6. What is our model for the behavior of the substance (for example, steam tables, ideal gas, and so on)?
7. What is our analysis of the problem (examine boundaries for various work modes, first law, and so on)?
8. What is our solution technique (in other words, from what we have done so far in steps 1 to 7, how do we proceed to find whatever it is that is desired)? Is a trial-and-error solution necessary?

It is not always necessary to write out all these steps, and in the majority of the examples throughout this text we will not do so. However, when faced with a new and unfamiliar problem, the student should always at least think through this set of questions to develop the ability to solve increasingly more challenging problems. In solving the following example, we will use this technique in detail.

EXAMPLE 5.3

A vessel having a volume of 5 m^3 contains 0.05 m^3 of saturated liquid water and 4.95 m^3 of saturated water vapor at 0.1 MPa. Heat is transferred until the vessel is filled with saturated vapor. Determine the heat transfer for this process.

System: All the water inside the vessel.

Sketch: Fig. 5.3.

Initial state: Pressure, volume of liquid, volume of vapor; therefore, state 1 is fixed.

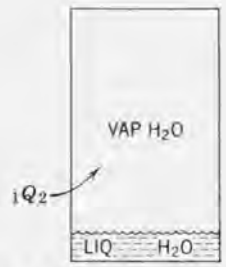


FIGURE 5.3 Sketch for Example 5.3.

Final state: Somewhere along the saturated-vapor curve; the water was heated, so $P_2 > P_1$.

Process: Constant volume and mass; therefore, constant specific volume.

Diagram: Fig. 5.4.

Model: Steam tables.

Analysis:

First law: $$ {}_1Q_2 = U_2 - U_1 + m\frac{\mathbf{V}_2^2 - \mathbf{V}_1^2}{2} + mg(Z_2 - Z_1) + {}_1W_2$$

From examining the boundaries for various work modes, we conclude that the work for this process is zero. Furthermore, the system is not moving, so there is no change in kinetic energy. There is a small change in the center of mass of the system but we will assume that the corresponding change in potential energy is negligible (in kilojoules). Therefore,

$$ {}_1Q_2 = U_2 - U_1 $$

Solution

The heat transfer will be found from the first law. State 1 is known, so U_1 can be calculated. The specific volume at state 2 is also known (from state 1 and the process). Since state 2 is saturated vapor, state 2 is fixed, as is seen from Fig. 5.4. Therefore, U_2 can also be found.

The solution proceeds as follows:

$$m_{1\ \text{liq}} = \frac{V_{\text{liq}}}{v_f} = \frac{0.05}{0.001\ 043} = 47.94\ \text{kg}$$

$$m_{1\ \text{vap}} = \frac{V_{\text{vap}}}{v_g} = \frac{4.95}{1.6940} = 2.92\ \text{kg}$$

Then

$$\begin{aligned} U_1 &= m_{1\ \text{liq}}u_{1\ \text{liq}} + m_{1\ \text{vap}}u_{1\ \text{vap}} \\ &= 47.94(417.36) + 2.92(2506.1) = 27\ 326\ \text{kJ} \end{aligned}$$

To determine u_2 we need to know two thermodynamic properties, since this determines the final state. The properties we know are the quality, $x = 100$ percent,

State 2: $x = 100\%$

$V_2 = V_g$

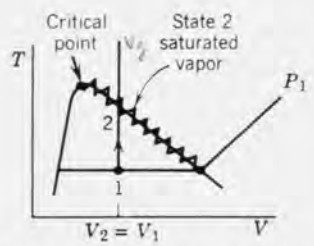


FIGURE 5.4 Diagram for Example 5.3.

and v_2, the final specific volume, which can readily be determined.

$$m = m_{1\,\text{liq}} + m_{1\,\text{vap}} = 47.94 + 2.92 = 50.86 \text{ kg}$$

$$v_2 = \frac{V}{m} = \frac{5.0}{50.86} = 0.098\,31 \text{ m}^3/\text{kg}$$

In Table 2 of the steam tables we find, by interpolation, that at a pressure of 2.03 MPa, $v_g = 0.098\ 31\ \text{m}^3/\text{kg}$. The final pressure of the steam is therefore 2.03 MPa. Then

$$u_2 = 2600.5 \text{ kJ/kg}$$

$$U_2 = mu_2 = 50.86(2600.5) = 132\,261 \text{ kJ}$$

$${}_1Q_2 = U_2 - U_1 = 132\,261 - 27\,326 = 104\,935 \text{ kJ}$$

Up to this point, we have discussed how internal energies are listed in the saturation tables of the steam tables. The internal energy of superheated vapor steam is listed as a function of temperature and pressure in Table A.1.3. Similarly, Tables A.1.4 and A.1.5 list values in the compressed-liquid region and in the saturated-solid–saturated-vapor region, respectively. In summary, all the values of internal energy are listed in the tables in the same manner as are values of specific volume.

5.5 THE THERMODYNAMIC PROPERTY ENTHALPY

In analyzing specific types of processes, we frequently encounter certain combinations of thermodynamic properties, which are therefore also properties of the substance undergoing the change of state. To demonstrate one such situation, let us consider a system undergoing a quasi-equilibrium constant-pressure process, as shown in Fig. 5.5. Assume that there are no changes in kinetic or potential energy and that the only work done during the process is that associated with the boundary movement. Taking the gas as our system and applying the first law, Eq. 5.11, we have

$${}_1Q_2 = U_2 - U_1 + {}_1W_2$$

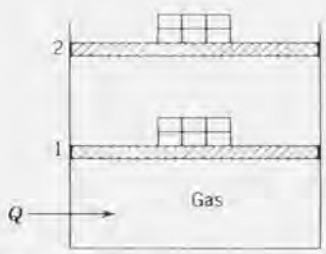


FIGURE 5.5 The constant-pressure quasi-equilibrium process.

The work can be calculated from the relation

$$_1W_2 = \int_1^2 P\,dV$$

Since the pressure is constant,

$$_1W_2 = P\int_1^2 dV = P(V_2 - V_1)$$

Therefore,

$$\begin{aligned} _1Q_2 &= U_2 - U_1 + P_2V_2 - P_1V_1 \\ &= (U_2 + P_2V_2) - (U_1 + P_1V_1) \end{aligned}$$

We find that in this very restricted case, the heat transfer during the process is given in terms of the change in the quantity $U + PV$ between the initial and final states. Because all these quantities are thermodynamic properties, that is, functions only of the state of the system, their combination must also have these same characteristics. Therefore, we find it convenient to define a new extensive property, the enthalpy,

$$H = U + PV \tag{5.12}$$

or, per unit mass,

$$h = u + Pv \tag{5.13}$$

As for internal energy, we could speak of specific enthalpy, h, and total enthalpy, H. However, we will refer to both as enthalpy, since the context will make it clear which is being discussed.

The heat transfer in a constant-pressure quasi-equilibrium process is equal to the change in enthalpy, which includes both the change in internal energy and the work for this particular process. This is by no means a general result. It is valid for this special case only because the work done during the process is equal to the difference in the PV product for the final and initial states. This would not be true if the pressure had not remained constant during the process.

The significance and use of enthalpy is not restricted to the special process just described. Other cases in which this same combination of properties $u + Pv$ appear will be developed later, notably in Section 6.2, in which we discuss control volume analyses. Our reason for introducing enthalpy at this time is that although the steam tables list values for internal energy, many other tables and charts of thermodynamic properties give values for enthalpy but not for the internal energy. Therefore, it is necessary to calculate the internal energy at a state using the tabulated values and Eq. 5.13:

$$u = h - Pv$$

Students often become confused about the validity of this calculation when analyzing system processes that do not occur at constant pressure, for which enthalpy has no physical significance. We must keep in mind that enthalpy, being a property, is a state or point function, and its use in calculating internal energy at the same state is not related to, or dependent on, any process that may be taking place.

Tabular values of enthalpy, such as those included in Tables A.1 through A.6, are all relative to some arbitrarily selected base. In the steam tables, the internal energy of saturated liquid at 0.01°C is the reference state and is given a value of zero. For refrigerants, such as ammonia and chlorofluorocarbons R-12 and R-22, the reference state is arbitrarily taken as saturated liquid at −40°C. The enthalpy in this reference state is assigned the value of zero. Cryogenic fluids, such as nitrogen or methane, have other arbitrary reference states chosen for enthalpy values listed in their tables. Because each of these reference states is arbitrarily selected, it is always possible to have negative values for enthalpy, as for saturated-solid water in Table A.1.5. When enthalpy and internal energy are given values relative to the same reference state, as they are in essentially all thermodynamic tables, the difference between internal energy and enthalpy at the reference state is equal to Pv. Since the specific volume of the liquid is very small, this product is negligible as far as the significant figures of the tables are concerned, but the principle should be kept in mind, for in certain cases it is significant.

In the superheat region of many thermodynamic tables, values of the specific internal energy u are not given. As mentioned earlier, these values can be readily calculated from the relation $u = h - Pv$, though it is important to keep the units in mind. As an example, let us calculate the internal energy u of superheated R-12 at 0.4 MPa, 70°C.

$$\begin{aligned} u &= h - Pv \\ &= 232.400 - 400 \times 0.056\,014 \\ &= 209.994 \text{ kJ/kg} \end{aligned}$$

The enthalpy of a substance in a saturation state and with a given quality is found in the same way as the specific volume and internal energy. The enthalpy of saturated liquid has the symbol h_f, saturated vapor h_g, and the increase in enthalpy during vaporization h_{fg}. For a saturation state, the enthalpy can be calculated by one of the following relations:

$$h = (1 - x)h_f + xh_g$$
$$h = h_f + xh_{fg}$$

The enthalpy of compressed water may be found from Table A.1.4. For substances for which compressed-liquid tables are not available, the enthalpy is taken as that of saturated liquid at the same temperature.

EXAMPLE 5.4

A cylinder fitted with a piston has a volume of 0.1 m^3 and contains 0.5 kg of steam at 0.4 MPa. Heat is transferred to the steam until the temperature is 300°C, while the pressure remains constant.

Determine the heat transfer and the work for this process.

System: Water inside cylinder.

Initial state: P_1, V_1, m; therefore v_1 is known, state 1 is fixed (at P_1, v_1, check steam tables—two-phase region).

Final state: P_2, T_2; therefore state 2 is fixed (superheated).

Process: Constant pressure.

Diagram: Fig. 5.6.

Model: Steam tables.

Analysis: No change in kinetic energy, no change in potential energy. Work is done by movement at the boundary. Assume the process to be quasi-equilibrium. Since the pressure is constant,

$$ {}_1W_2 = \int_1^2 P\,dV = P\int_1^2 dV = P(V_2 - V_1) = m(P_2v_2 - P_1v_1) $$

Therefore, the first law is

$$ \begin{aligned} {}_1Q_2 &= m(u_2 - u_1) + {}_1W_2 \\ &= m(u_2 - u_1) + m(P_2v_2 - P_1v_1) = m(h_2 - h_1) \end{aligned} $$

Solution

There is a choice of procedures to follow. State 1 is known, so v_1 and h_1 (or u_1) can be found. State 2 is also known, so v_2 and h_2 (or u_2) can be found. Using the first law and the work equation, we can calculate the heat transfer and work. Using the enthalpies, we have

$$ v_1 = \frac{V_1}{m} = \frac{0.1}{0.5} = 0.2 = 0.001\,084 + x_1 0.4614 $$

$$ x_1 = \frac{0.1989}{0.4614} = 0.4311 $$

$$ \begin{aligned} h_1 &= h_f + x_1 h_{fg} \\ &= 604.74 + 0.4311 \times 2133.8 = 1524.7 \end{aligned} $$

$$ h_2 = 3066.8 $$

$$ {}_1Q_2 = 0.5(3066.8 - 1524.7) = 771.1 \text{ kJ} $$

$$ {}_1W_2 = mP(v_2 - v_1) = 0.5 \times 400(0.6548 - 0.2) = 91.0 \text{ kJ} $$

Therefore,

$$ U_2 - U_1 = {}_1Q_2 - {}_1W_2 = 771.1 - 91.0 = 680.1 \text{ kJ} $$

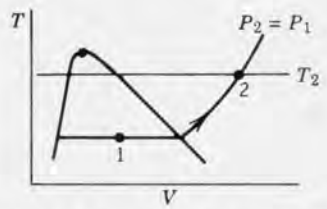


FIGURE 5.6 Diagram for Example 5.4.

The heat transfer could also have been found from u_1 and u_2,

$$u_1 = u_f + x_1 u_{fg}$$
$$= 604.31 + 0.4311 \times 1949.3 = 1444.7$$
$$u_2 = 2804.8$$

and

$${}_1Q_2 = U_2 - U_1 + {}_1W_2$$
$$= 0.5(2804.8 - 1444.7) + 91.0 = 771.1 \text{ kJ}$$

5.6 THE CONSTANT-VOLUME AND CONSTANT-PRESSURE SPECIFIC HEATS

In this section we will consider a homogeneous phase of a substance of constant composition. This phase may be a solid, a liquid, or a gas, but no change of phase will occur. We will then define a variable termed the specific heat, the amount of heat required per unit mass to raise the temperature by one degree. Since it would be of interest to examine the relation between the specific heat and other thermodynamic variables, we note first that the heat transfer is given by Eq. 5.10. Neglecting changes in kinetic and potential energies, and assuming a simple compressible substance and quasi-equilibrium process, for which the work in Eq. 5.10 is given by Eq. 4.2, we have

$$\delta Q = dU + \delta W = dU + P\,dV$$

We find that this expression can be evaluated for two separate special cases.

1. Constant volume, for which the work term ($P\,dV$) is zero, so that the specific heat (at constant volume) is

$$C_v = \frac{1}{m}\left(\frac{\delta Q}{\delta T}\right)_v = \frac{1}{m}\left(\frac{\partial U}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v \tag{5.14}$$

2. Constant pressure, for which the work term can be integrated and the resulting PV terms at the initial and final states be associated with the internal energy terms, as in Section 5.5, thereby leading to the conclusion that the heat transfer can be expressed in terms of the enthalpy change. The corresponding specific heat (at constant pressure) is

$$C_p = \frac{1}{m}\left(\frac{\delta Q}{\delta T}\right)_p = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial h}{\partial T}\right)_p \tag{5.15}$$

Note that in each of these special cases, the resulting expression, Eq. 5.14 or 5.15, contains only thermodynamic properties, from which we conclude that the constant-volume and constant-pressure specific heats must themselves be thermodynamic properties. This means that, although we began this discussion by considering the amount of heat transfer required to cause a unit temperature change and then proceeded through a very specific development leading to Eq. 5.14 (or 5.15), the result ultimately expresses a relation among a set of thermodynamic

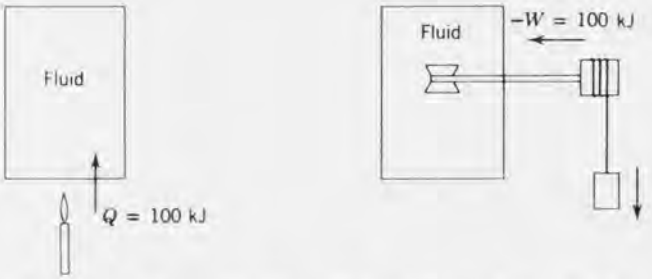


FIGURE 5.7 Sketch showing two ways in which a given ΔU may be achieved.

properties and therefore constitutes a definition that is independent of the particular process leading to it (in the same sense that the definition of enthalpy in the previous section is independent of the process used to illustrate one situation in which the property is useful in a thermodynamic analysis). As an example, consider the two identical systems shown in Fig. 5.7. In the first system 100 kJ of heat is transferred to it, and in the second system 100 kJ of work is done on it. Thus, the change of internal energy is the same in each system, and therefore the final state and the final temperature are the same in each. In accordance with Eq. 5.14, therefore, exactly the same value for the average constant-volume specific heat would be found for this substance for the two processes, even though the two processes are very different as far as heat transfer is concerned.

It should also be noted that this development was carried out for a simple compressible substance, for which the work was given by Eq. 4.2. Where there are different work modes, such as those described in Sections 4.4 through 4.6, different specific heats become appropriate. For any particular quasi-equilibrium work mode, there is one specific heat at constant displacement and one at constant driving force, as these terms were discussed in connection with Eq. 4.16. For example, in a system involving magnetic effects, it is convenient to utilize a specific heat at constant magnetization and one at constant magnetic field intensity.

EXAMPLE 5.5

Estimate the constant-pressure specific heat of steam at 0.5 MPa, 375°C.

Solution

If we consider a change of state at constant pressure, Eq. 5.15 may be written

$$C_p \approx \left(\frac{\Delta h}{\Delta T}\right)_p$$

From the steam tables,

at 0.5 MPa, 350°C, $h = 3167.7$
at 0.5 MPa, 400°C, $h = 3271.8$

Since we are interested in C_p at 0.5 MPa, 375°C,

$$C_p \simeq \frac{104.1}{50} = 2.082 \text{ kJ/kg K}$$

As a special case, consider either a solid or a liquid. For both of these phases the specific volume is very small. Consequently, for any process

$$dh = du + d(Pv) \simeq du \tag{5.16}$$

and we can say further that

$$dh \simeq du \simeq C\,dT \tag{5.17}$$

where C is either the constant-volume or the constant-pressure specific heat, as the two would be nearly the same. In many processes involving a solid or a liquid, we might further assume that the specific heat in Eq. 5.17 is constant (unless the process is at low temperature or over a wide range of temperature). Equation 5.17 can then be integrated to

$$h_2 - h_1 \simeq u_2 - u_1 \simeq C(T_2 - T_1) \tag{5.18}$$

Specific heats for various solids and liquids are listed in Table A.8.

In other processes for which it is not possible to assume constant specific heat, there may be a known relation for C as a function of temperature. Equation 5.17 could then also be integrated.

5.7 THE INTERNAL ENERGY, ENTHALPY, AND SPECIFIC HEAT OF IDEAL GASES

At this point certain comments about the internal energy, enthalpy, and the constant-pressure and constant-volume specific heats of an ideal gas should be made. An ideal gas has been defined in Chapter 3 as a gas at sufficiently low density so that intermolecular forces and the associated energy are negligibly small. Therefore, an ideal gas has the equation of state

$$Pv = RT$$

It can be shown that for an ideal gas, the internal energy is a function of the temperature only. That is, for an ideal gas,

$$u = f(T) \tag{5.19}$$

This means that an ideal gas at a given temperature has a certain definite specific internal energy u, regardless of the pressure. This will be demonstrated mathematically using the methods of classical thermodynamics in Chapter 12.

In 1843, Joule demonstrated this fact when he conducted the following classical experiment in thermodynamics. Two pressure vessels (Fig. 5.8), connected by a pipe and valve, were immersed in a bath of water. Initially vessel A contained air at 22-atm pressure and vessel B was highly evacuated. When thermal equilibrium

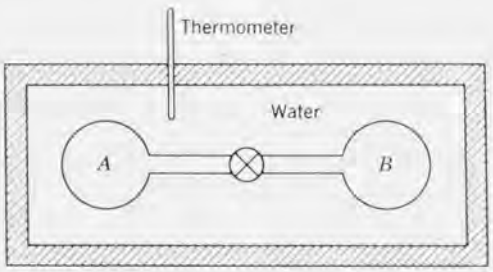


FIGURE 5.8 Apparatus for conducting Joule's experiment.

was attained, the valve was opened, allowing the pressures in A and B to equalize. No change in the temperature of the bath was detected during or after this process. Because there was no change in the temperature of the bath, Joule concluded that no heat had been transferred to the air. Because the work was also zero, he concluded from the first law of thermodynamics that there was no change in the internal energy of the gas. Because the pressure and volume changed during this process, one concludes that internal energy is not a function of pressure and volume. Because air does not conform exactly to the definition of an ideal gas, a small change in temperature will be detected when very accurate measurements are made in Joule's experiment.

The relation between the internal energy u and the temperature can be established by using the definition of constant-volume specific heat given by Eq. 5.14.

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v$$

Since the internal energy of an ideal gas is not a function of volume, for an ideal gas we can write

$$C_{v0} = \frac{du}{dT}$$

$$du = C_{v0}\, dT \tag{5.20}$$

where the subscript 0 denotes the specific heat of an ideal gas. For a given mass m,

$$dU = mC_{v0}\, dT \tag{5.21}$$

From the definition of enthalpy and the equation of state of an ideal gas, it follows that

$$h = u + Pv = u + RT \tag{5.22}$$

Since R is a constant and u is a function of temperature only, it follows that the enthalpy, h, of an ideal gas is also a function of temperature only. That is,

$$h = f(T) \tag{5.23}$$

The relation between enthalpy and temperature is found from the constant-pressure

specific heat as defined by Eq. 5.15.

$$C_p = \left(\frac{\partial h}{\partial T}\right)_p$$

Since the enthalpy of an ideal gas is a function of the temperature only and is independent of the pressure, it follows that

$$C_{p0} = \frac{dh}{dT}$$

$$dh = C_{p0}\, dT \tag{5.24}$$

For a given mass m,

$$dH = mC_{p0}\, dT \tag{5.25}$$

The consequences of Eqs. 5.20 and 5.24 are demonstrated in Fig. 5.9, which shows two lines of constant temperature. Since internal energy and enthalpy are functions of temperature only, these lines of constant temperature are also lines of constant internal energy and constant enthalpy. From state 1 the high temperature can be reached by a variety of paths, and in each case the final state is different. However, regardless of the path, the change in internal energy is the same, as is the change in enthalpy, for lines of constant temperature are also lines of constant u and constant h.

Because the internal energy and enthalpy of an ideal gas are functions of temperature only, it also follows that the constant-volume and constant-pressure specific heats are also functions of temperature only. That is,

$$C_{v0} = f(T) \qquad C_{p0} = f(T) \tag{5.26}$$

Because all gases approach ideal-gas behavior as the pressure approaches zero, the ideal-gas specific heat for a given substance is often called the zero-pressure specific heat, and the zero-pressure, constant-pressure specific heat is given the symbol C_{p0}. The zero-pressure, constant-volume specific heat is given the symbol C_{v0}. Figure 5.10 shows $\overline{C}_{p0}$ as a function of temperature for a number of different substances. These values are determined by the techniques of statistical thermodynamics, which will be discussed later in this text. However, a brief qualitative

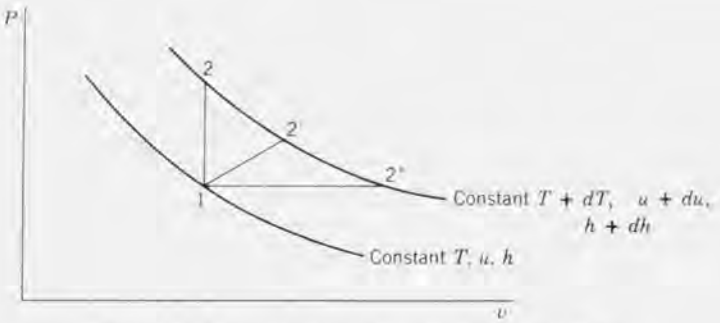


FIGURE 5.9 Pressure–volume diagram for an ideal gas.

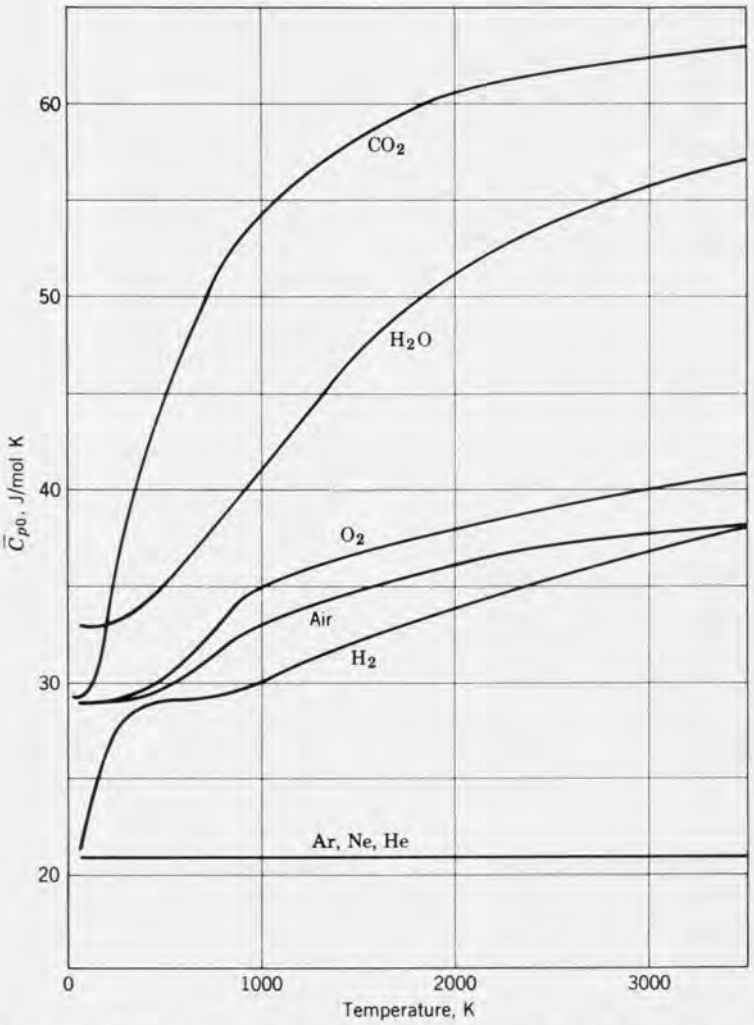


FIGURE 5.10 Constant-pressure specific heats for a number of gases at zero pressure.

discussion at this point should provide some insight into this behavior and will be beneficial in determining under what conditions an assumption of constant specific heat is justified.

As was discussed in Section 2.6, the energy possessed by molecules may be stored in several forms. The translational and rotational energies increase linearly with temperature, which means that these contributions to the specific heat are not temperature-dependent. Contributions from vibrational and electronic modes, on the other hand, are temperature-dependent (the electronic usually being very small). From Fig. 5.10, it is evident that the specific heat of a diatomic gas (such as hydrogen or oxygen) increases with an increase in temperature, primarily because of the vibration. A polyatomic gas (such as carbon dioxide or water) shows a much greater increase in specific heat as the temperature increases, and this is due to the additional

vibrational modes of a polyatomic molecule. A monatomic gas (such as helium, argon, or neon), possessing only translational and electronic energies, shows little or no variation of specific heat over a wide range of temperatures.

A very important relation between the constant-pressure and constant-volume specific heats of an ideal gas may be developed from the definition of enthalpy.

$$h = u + Pv = u + RT$$

Differentiating and substituting Eqs. 5.20 and 5.24, we have

$$dh = du + R\,dT$$
$$C_{p0}\,dT = C_{v0}\,dT + R\,dT$$

Therefore,

$$C_{p0} - C_{v0} = R \tag{5.27}$$

On a mole basis this equation is written

$$\overline{C}_{p0} - \overline{C}_{v0} = \overline{R} \tag{5.28}$$

This tells us that the difference between the constant-pressure and constant-volume specific heats of an ideal gas is always constant, though both are functions of temperature. Thus, we need examine only the temperature dependency of one, and the other is given by Eq. 5.27.

Let us consider the specific heat C_{p0}. There are three possibilities to examine. The situation is simplest if we assume constant specific heat, that is, no temperature dependence. Then it is possible to integrate Eq. 5.24 directly to

$$h_2 - h_1 = C_{p0}(T_2 - T_1) \tag{5.29}$$

We note from Fig. 5.10 the circumstances under which this will be an accurate model. It should be added, however, that it may be a reasonable approximation under other conditions, especially if an average specific heat in the particular temperature range is used in Eq. 5.29. Values of specific heat at room temperature and gas constants for various gases are given in Table A.9.

The second possibility for the specific heat is to use an analytical equation for C_{p0} as a function of temperature. Because the results of specific-heat calculations from statistical thermodynamics do not lend themselves to convenient mathematical forms, these results have been approximated empirically. The equations for C_{p0} as a function of temperature are listed in Table A.10 for a number of gases.

The third possibility is to integrate the results of the calculations of statistical thermodynamics from an arbitrary reference temperature to any other temperature T, and to define a function

$$h_T = \int_{T_0}^{T} C_{p0}\,dT$$

This function can then be tabulated in a single-entry (temperature) table. Then, between any two states 1 and 2,

$$h_2 - h_1 = \int_{T_0}^{T_2} C_{p0}\,dT - \int_{T_0}^{T_1} C_{p0}\,dT = h_{T_2} - h_{T_1} \tag{5.30}$$

and it is seen that the reference temperature cancels out. This function h_T (and a similar function $u_T = h_T - RT$) is listed for air in Table A.11. The enthalpy function (with respect to a reference temperature of 25°C) is listed for other gases in Table A.12.

To summarize the three possibilities, we note that using the ideal-gas tables, Tables A.11 and A.12, gives us the most accurate answer, but that the equations in Table A.10 would give a close empirical approximation. Constant specific heat would be less accurate, except for monatomic gases and gases below room temperature. It should be remembered that all these results are a part of the ideal-gas model, which in many of our problems is not a valid assumption for the behavior of the substance.

EXAMPLE 5.6

Calculate the change of enthalpy as 1 kg of oxygen is heated from 300 to 1500 K. Assume ideal-gas behavior.

Solution

For an ideal gas, the enthalpy change is given by Eq. 5.24. However, we also need to make an assumption about the dependence of specific heat on temperature. Let us solve this problem in several ways and compare the answers.

Our most accurate answer for the ideal-gas enthalpy change for oxygen between 300 and 1500 K would be from the ideal-gas tables, Table A.12. This result is, using Eq. 5.30,

$$h_2 - h_1 = \frac{\bar{h}_{1500} - \bar{h}_{300}}{M} = \frac{40\,600 - 54}{32} = 1267.0 \text{ kJ/kg}$$

The empirical equation from Table A.10 should give a good approximation to this result. Integrating Eq. 5.24, we have

$$\bar{h}_2 - \bar{h}_1 = \int_{T_1}^{T_2} \bar{C}_{p0}\, dT = \int_{\theta_1}^{\theta_2} \bar{C}_{p0}(\theta) \times 100\, d\theta$$

$$\bar{h}_{1500} - \bar{h}_{300} = 100\left(37.432\theta + \frac{0.020\,102}{2.5}\theta^{2.5} + \frac{178.57}{0.5}\theta^{-0.5} - 236.88\theta^{-1} \right)\Bigg|_{\theta_1 = 3}^{\theta_2 = 15}$$

$$= 40\,525 \text{ kJ/kmol}$$

$$h_2 - h_1 = \frac{\bar{h}_{1500} - \bar{h}_{300}}{M} = \frac{40\,525}{32}$$

$$= 1266.4 \text{ kJ/kg}$$

which is different than the first result by less than 0.1 percent.

If we assume constant specific heat, we must be concerned about what value we are going to use. If we use the value at 300 K from Table A.9, we find, from Eq. 5.29, that

$$h_2 - h_1 = C_{p0}(T_2 - T_1) = 0.9216 \times 1200 = 1105.9 \text{ kJ/kg}$$

which is low by 12.7 percent. On the other hand, suppose we assume that the specific heat is constant at its value at 900 K, the average temperature. Substituting 900 K into the equation for specific heat from Table A.10, we have

$$\begin{aligned}\overline{C}_{p0} &= 37.432 + 0.020\,102(9)^{1.5} - 178.57(9)^{-1.5} + 236.88(9)^{-2} \\ &= 34.2855 \text{ kJ/kmol K}\end{aligned}$$

or

$$C_{p0} = \frac{34.2855}{32} = 1.0714 \text{ kJ/kg K}$$

Substituting this value into Eq. 5.29 gives the result

$$h_2 - h_1 = 1.0714 \times 1200 = 1285.7 \text{ kJ/kg}$$

which is high by about 1.5 percent, a much closer result than the one using the room temperature specific heat. It should be kept in mind that part of the model involving ideal gas with constant specific heat is the choice of what value is to be used.

EXAMPLE 5.7

A cylinder fitted with a piston has an initial volume of 0.1 m^3 and contains nitrogen at 150 kPa, 25°C. The piston is moved, compressing the nitrogen until the pressure is 1 MPa and the temperature is 150°C. During this compression process heat is transferred from the nitrogen, and the work done on the nitrogen is 20 kJ. Determine the amount of this heat transfer.

System: Nitrogen.

Initial state: P_1, T_1, V_1; state 1 fixed.

Final state: P_2, T_2; state 2 fixed.

Process: Work input known.

Model: Ideal gas, constant specific heat with value at 300 K, Table A.9.

Analysis:

First law: $${}_1Q_2 = m(u_2 - u_1) + {}_1W_2$$

Solution

The mass of nitrogen is found from the equation of state with the value of R from Table A.9.

$$m = \frac{PV}{RT} = \frac{150 \times 0.1}{0.2968 \times 298.15} = 0.1695 \text{ kg}$$

Assuming constant specific heat as given in Table A.9, we have

$$\begin{aligned}{}_1Q_2 &= mC_{v0}(T_2 - T_1) + {}_1W_2 \\ &= 0.1695(0.7448)(150 - 25) - 20.0 \\ &= 15.8 - 20.0 = -4.2 \text{ kJ}\end{aligned}$$

It would of course be somewhat more accurate to use Table A.12 than to assume constant specific heat (room temperature value), but often the slight increase in accuracy does not warrant the added difficulties of manually interpolating the tables.

5.8 THE FIRST LAW AS A RATE EQUATION

We frequently find it desirable to use the first law as a rate equation that expresses either the instantaneous or average rate at which energy crosses the system boundary as heat and work and the rate at which the energy of the system changes. In so doing we are departing from a strictly classical point of view, because basically classical thermodynamics deals with systems that are in equilibrium, and time is not a relevant parameter for systems that are in equilibrium. However, since these rate equations are developed from the concepts of classical thermodynamics and are used in many applications of thermodynamics, they are included in this book. This rate form of the first law will be used in the development of the first law for the control volume in Chapter 6, and in this form the first law finds extensive applications in thermodynamics, fluid mechanics, and heat transfer.

Consider a time interval δt during which an amount of heat δQ crosses the system boundary, an amount of work δW is done by the system, the internal energy change is ΔU, the kinetic energy change is ΔKE, and the potential energy change is ΔPE. From the first law we can write

$$\delta Q = \Delta U + \Delta \text{KE} + \Delta \text{PE} + \delta W$$

Dividing by δt we have the average rate of energy transfer as heat and work and increase of the energy of the system.

$$\frac{\delta Q}{\delta t} = \frac{\Delta U}{\delta t} + \frac{\Delta \text{KE}}{\delta t} + \frac{\Delta \text{PE}}{\delta t} + \frac{\delta W}{\delta t}$$

Taking the limit for each of these quantities as δt approaches zero, we have

$$\lim_{\delta t \to 0} \frac{\delta Q}{\delta t} = \dot{Q}, \quad \text{the heat transfer rate}$$

$$\lim_{\delta t \to 0} \frac{\delta W}{\delta t} = \dot{W}, \quad \text{the power}$$

$$\lim_{\delta t \to 0} \frac{\Delta U}{\delta t} = \frac{dU}{dt}, \qquad \lim_{\delta t \to 0} \frac{\Delta(\text{KE})}{\delta t} = \frac{d(\text{KE})}{dt}, \qquad \lim_{\delta t \to 0} \frac{\Delta(\text{PE})}{\delta t} = \frac{d(\text{PE})}{dt}$$

Therefore, the rate equation form of the first law is

$$\dot{Q} = \frac{dU}{dt} + \frac{d(\text{KE})}{dt} + \frac{d(\text{PE})}{dt} + \dot{W} \tag{5.31}$$

We could also write this in the form

$$\dot{Q} = \frac{dE}{dt} + \dot{W} \tag{5.32}$$

EXAMPLE 5.8

During the charging of a storage battery, the current is 20 A and the voltage is 12.8 V. The rate of heat transfer from the battery is 10 W. At what rate is the internal energy increasing?

Solution

Since changes in kinetic and potential energy are insignificant, the first law can be written as a rate equation in the form, Eq. 5.31,

$$\dot{Q} = \frac{dU}{dt} + \dot{W}$$

$$\dot{W} = -\mathscr{E} i = -20 \times 12.8 = -256 \text{ W}$$

Therefore,

$$\frac{dU}{dt} = \dot{Q} - \dot{W} = -10 \text{ W} - (-256) = 246 \text{ J/s}$$

5.9 CONSERVATION OF MASS

In the previous sections we considered the first law of thermodynamics for a system undergoing a change of state. A system is defined as a fixed quantity of mass. The question now is whether the mass of the system changes when the energy of a system changes? If it does, our definition of a system as a fixed quantity of mass is no longer valid when the energy of the system changes.

We know from relativistic considerations that mass and energy are related by the well-known equation

$$E = mc^2 \tag{5.33}$$

where c = velocity of light and E = energy. We conclude from this equation that the mass of a system does change when its energy changes. Let us calculate the magnitude of this change of mass for a typical problem and determine whether this change in mass is significant.

Consider as a system a rigid vessel that contains a 1-kg stoichiometric mixture of a hydrocarbon fuel (such as gasoline) and air. From our knowledge of combustion, we know that after combustion takes place it will be necessary to transfer about 2900 kJ from the system to restore it to its initial temperature. From the first law

$${}_1Q_2 = U_2 - U_1 + {}_1W_2$$

we conclude that since ${}_1W_2 = 0$ and ${}_1Q_2 = -2900$ kJ, the internal energy of the system decreases by 2900 kJ during the heat transfer process. Let us now calculate the decrease in mass during this process using Eq. 5.33.

The velocity of light, c, is 2.9979×10^8 m/s. Therefore,

$$2900 \text{ kJ} = 2\,900\,000 \text{ J} = m \text{ (kg)} \times (2.9979 \times 10^8 \text{ m/s})^2$$

$$m = 3.23 \times 10^{-11} \text{ kg}$$

Thus, when the energy of the system decreases by 2900 kJ, the decrease in mass is 3.23×10^{-11} kg.

A change in mass of this magnitude cannot be detected by even our most accurate chemical balance. Certainly, a fractional change in mass of this magnitude is beyond the accuracy required in essentially all engineering calculations. Therefore, if we use the laws of conservation of mass and conservation of energy as separate laws, we will not introduce significant error into most thermodynamic problems, and our definition of a system as having a fixed mass can be used even though the energy of the system changes.

PROBLEMS

5.1 A small elevator is being designed for a construction site. It is expected to carry four 75-kg workers to the top of a 100-m-tall building in less than two minutes. The elevator cage will have a counterweight to balance its mass. What is the smallest-size (power) electric motor that can drive this unit?

5.1E A small elevator is being designed for a construction site. It is expected to carry four 150-lbm workers to the top of a 300-ft-tall building in less than two minutes. The elevator cage itself will have a counterweight to balance its mass. What is the smallest-size (power) electric motor that can drive this unit?

5.2 The rate of heat transfer to the surroundings from a person at rest is about 400 kJ/h. Suppose that the ventilation system fails in an auditorium containing 100 people.

(a) How much will the internal energy of the air in the auditorium increase during the first ten minutes after the ventilation system fails?

(b) Considering the auditorium and all the people in it as a system, how much does the internal energy of this system change? How do you explain the fact that the temperature of the air increases?

5.3 A "bomb calorimeter," a closed, rigid vessel, will be used to measure the energy released by a certain chemical reaction. This calorimeter initially contains the appropriate chemicals and is located in a large tank of water. When the chemicals react, heat is transferred from the bomb to the water, causing its temperature to rise. The electric power input to a stirrer used to circulate the water is 0.05 kW. During a 25-minute period, the heat transfer from the bomb to the water is 1400 kJ and the heat transfer from the water tank to the surrounding air is 70 kJ. Assuming that no water evaporates, what is the increase in the internal energy of the water during this period of time?

5.4 A 50-L closed, rigid tank contains water at 120°C, 60 percent quality. The tank is then cooled to −10°C. Calculate the heat transfer during the process.

5.4E A 2-ft^3 closed, rigid tank contains water at 250 F, 60 percent quality. The tank is then cooled to 10 F. Calculate the heat transfer during the process.

5.5 Calculate the heat transfer for the process described in Problem 4.8.

5.6 A closed tube has a volume of 100 mL and contains the appropriate fraction of liquid and vapor water in equilibrium at 100 kPa so that when the tube is heated

the water will pass through the critical point. Calculate the heat transfer to the tube needed to change the water from 100 kPa to the critical-point state.

5.6E A closed tube has a volume of 5 $in.^3$ and contains the appropriate fraction of liquid and vapor water in equilibrium at 14.7 $lbf/in.^2$ so that when the tube is heated the water will pass through the critical point. Calculate the heat transfer to the tube needed to change the water from 14.7 $lbf/in.^2$ to the critical point state.

5.7 A 10-L rigid tank contains R-22 at $-10°C$, 80 percent quality. A 10-A electric current (from a 6-V battery) is passed through a resistor inside the tank for ten minutes, after which the R-22 temperature is 40°C. What was the heat transfer to or from the tank during this process?

5.8 A 500-L rigid tank contains ammonia at 1 MPa, 100°C. The tank is cooled to 0°C. Determine the heat transfer for this process.

5.9 Consider the 100-L Dewar (a rigid, double-walled vessel for storing cryogenic liquids) shown in Fig. 5.11. The Dewar contains liquid nitrogen at 77.35 K, 95 percent liquid and 5 percent vapor by volume. The insulation holds heat transfer into the Dewar from the ambient to a very low rate, 5 J/s. The vent valve is accidentally closed, so that the pressure inside slowly rises. It is estimated that the Dewar will rupture when the pressure reaches 500 kPa. How long will it take to reach this pressure?



FIGURE 5.11 Sketch for Problem 5.9.

5.10 A vertical cylinder fitted with a piston contains 5 kg of R-22 at 10°C. Heat is transferred to the system, causing the piston to rise until it reaches a set of stops, at which point the volume has doubled. Additional heat is transferred until the temperature inside reaches 50°C, at which point the pressure inside the cylinder is 1.3 MPa.

(a) What is the quality at the initial state?
(b) Calculate the heat transfer for the overall process.

5.10E A vertical cylinder fitted with a piston contains 10 lbm of R-22 at 50 F. Heat is transferred to the system, causing the piston to rise until it reaches a set of stops,

at which point the volume has doubled. Additional heat is transferred until the temperature inside reaches 120 F, at which point the pressure inside the cylinder is 200 lbf/in.^{2}.

(a) What is the quality at the initial state?
(b) Calculate the heat transfer for the overall process.

5.11 A cylinder fitted with a piston restrained by a linear spring (force proportional to distance) has a diameter of 0.25 m and initial volume of 20 L. The cylinder contains ammonia at 1 MPa, 60°C. The spring constant is 150 kN/m. Heat is rejected from the system, and the piston moves until 5.0 kJ of work has been done on the ammonia.

(a) Find the final temperature of the ammonia.
(b) Calculate the heat transfer for the process.

5.12 An insulated cylinder fitted with a piston contains R-12 at 25°C with a quality of 90 percent. The volume at this state is 30 L. The piston is allowed to move, and the R-12 expands until it exists as saturated vapor. During this process the R-12 does 4.0 kJ of work against the piston. Determine the final temperature, assuming the process to be adiabatic.

5.13 A spherical balloon contains 2 kg of R-22 at 0°C, 30 percent quality. This system is heated until the pressure in the balloon reaches 600 kPa. In the range of variables of this process, it can be assumed that the pressure in the balloon is directly proportional to the balloon diameter. What is the heat transfer for the process?

5.14 Consider the system shown in Fig. 5.12. Tank *A* has a volume of 100 L and contains saturated vapor R-22 at 15°C. When the valve is cracked open, R-22 flows slowly into cylinder *B*. The piston mass requires a pressure of 200 kPa in cylinder *B* to raise the piston. The process ends when the pressure in tank *A* has fallen to 200 kPa. During this process heat is transferred with the surroundings so that the temperature of all the R-22 always remains at 15°C. Calculate the heat transfer for this process.

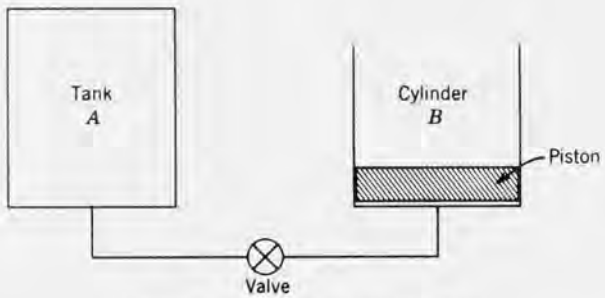


FIGURE 5.12 Sketch for Problem 5.14.

5.15 An insulated cylinder containing water has a piston held by a pin, as shown in Fig. 5.13. The water is initially saturated vapor at 65°C, and the volume is 5 L. The piston and weights have a total mass of 10 kg, the piston cross-sectional area is 3000 mm^2, and the ambient pressure is 100 kPa. The pin is released, which allows the piston to move. Determine the final state of the water, assuming the process to be adiabatic.

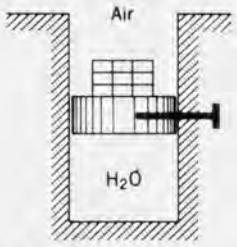


FIGURE 5.13 Sketch for Problem 5.15.

5.16 Two heavily insulated tanks are connected by a valve. Tank *A* has a volume of 600 L and contains water at 200 kPa, 200°C. Tank *B* has a volume of 300 L and contains water at 500 kPa, 90 percent quality. The valve is opened, and the two tanks eventually come to a uniform state. Assuming the process to be adiabatic, what is the final pressure?

5.16E Two heavily insulated tanks are connected by a valve. Tank *A* has a volume of 25 ft^3 and contains water at 20 $lbf/in.^2$, 400 F. Tank *B* has a volume of 15 ft^3 and contains water at 80 $lbf/in.^2$, 90 percent quality. The valve is opened, and the two tanks eventually come to a uniform state. Assuming the process to be adiabatic, what is the final pressure?

5.17 A cylinder having a piston restrained by a linear spring contains 0.5 kg of saturated vapor water at 120°C, as shown in Fig. 5.14. Heat is transferred to the water, causing the piston to rise, and during this process the spring resisting force is proportional to the distance moved. The spring constant is 15 kN/m. The piston cross-sectional area is 0.05 m^2.

(a) What is the pressure in the cylinder when the temperature inside reaches 600°C?

(b) Calculate the heat transfer for this process.

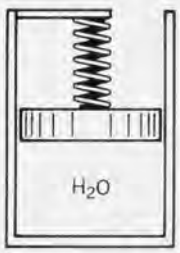


FIGURE 5.14 Sketch for Problem 5.17.

5.18 A cylinder fitted with a piston contains 2 kg of R-12 at 10 C, 90 percent quality. The system undergoes a quasi-equilibrium, polytropic expansion to 100 kPa, during which the system receives a heat transfer of 52.5 kJ. What is the final temperature of the R-12?

5.18E A cylinder fitted with a piston contains 4 lbm of R-12 at 50 F, 90 percent quality. The system undergoes a quasi-equilibrium, polytropic expansion to 15 $lbf/in.^2$, during which the system receives a heat transfer of 50 Btu. What is the final temperature of the R-12?

5.19 Calculate the heat transfer for the process described in Problem 4.22.

5.20 Consider the cylinder–piston arrangement shown in Fig. 5.15, in which a frictionless piston is free to move between two sets of stops. When the piston rests on the lower stops, the enclosed volume is 400 L. When the piston reaches the upper stops, the volume is 600 L. The cylinder initially contains water at 100 kPa, 20 percent quality. This system is heated until the water eventually exists as a saturated vapor. If the mass of the piston requires 300-kPa pressure to move it against the outside ambient pressure, determine

(a) The final pressure in the cylinder.
(b) The heat transfer and work for the overall process.

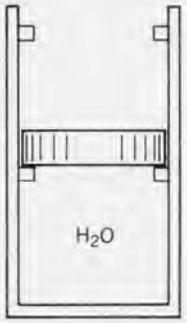


FIGURE 5.15 Sketch for Problem 5.20.

5.21 Calculate the heat transfer for the process described in Problem 4.23.

5.22 An insulated and otherwise evacuated 20-L vessel contains a 1-L capsule of water at 700 kPa, 150°C. The capsule breaks and its contents fill the entire volume. What is the final pressure?

5.23 A spherical balloon initially 150 mm in diameter and containing R-12 at 100 kPa is connected to a 30-L uninsulated, rigid tank containing R-12 at 500 kPa. Both tanks are at an ambient temperature of 20°C. The valve connecting the two tanks is opened slightly and remains open until the pressures equalize. During this process heat is transferred so that the temperature of all the R-12 remains at 20°C. It can also be assumed that in this range of variables the pressure inside the balloon is proportional to its diameter at any time. Calculate

(a) The final pressure.
(b) Work done by the R-12 during the process.
(c) Heat transferred to the R-12 during the process.

5.23E A spherical balloon initially 6 in. in diameter and containing R-12 at 15 lbf/in.^{2} is connected to a 1-ft^3 uninsulated, rigid tank containing R-12 at 80 lbf/in.^{2}. Both tanks are at an ambient temperature of 80 F. The valve connecting the two tanks is opened slightly and remains open until the pressures equalize. During this process heat is transferred so that the temperature of all the R-12 remains at 80 F. It can also be assumed that in this range of variables the pressure inside the balloon is proportional to its diameter at any time. Calculate

(a) The final pressure.
(b) Work done by the R-12 during the process.
(c) Heat transferred to the R-12 during the process.

5.24 A house is being designed to use a thick concrete floor mass as thermal storage material for solar-energy heating. The concrete is 0.3-m thick, and the area exposed to the sun during the daytime is 4 m × 6 m. It is expected that this mass will undergo an average temperature rise of about 3°C during the day. How much energy will be available for heating during the nighttime hours?

5.25 A 10-kg bar of a certain alloy having essentially the same specific heat and density as iron is quenched from 700°C in a 100-L oil bath initially at 20°C. Assuming no heat transfer with the surroundings, what is the final temperature?

5.25E A 20-lbm bar of a certain alloy having essentially the same specific heat and density as iron is quenched from 1300 F in a 3.5 ft^3 oil bath initially at 70 F. Assuming no heat transfer with the surroundings, what is the final temperature?

5.26 A hollow spherical aluminum vessel has an inside diameter of 0.5 m and a 10-mm-thick wall. The vessel contains water at 25°C, 1 percent quality. The vessel is heated until the water inside is saturated vapor. Considering the vessel and water together as a system, calculate the heat transfer for the process.

5.27 An ideal gas is heated from 500 to 1000 K. The enthalpy change per kilogram is to be calculated assuming constant specific heat (room temperature value) from Table A.9. Calculate this value, and discuss the accuracy of the result, if the gas is

(a) Argon.
(b) Oxygen.
(c) Carbon dioxide.

5.28 A mass of 1 kg of water at 50 kPa, 50 percent quality, is heated to 200 kPa, 2000°C. Calculate the change in internal energy for this process, using the Appendix tables and an appropriate model (or combination of models).

5.29 One kilogram of nitrogen gas is heated from 30° to 1500°C. Calculate the change in enthalpy by the following methods.

(a) Constant specific heat, value from Table A.9.
(b) Constant specific heat, value at the average temperature from the equation, Table A.10.
(c) Variable specific heat, integrating the equation, Table A.10.
(d) Variable specific heat, values from the ideal-gas tables, Table A.12.

5.30 A 250-L rigid tank contains methane gas at 500°C, 600 kPa. The tank is cooled to −80°C.

(a) Calculate the final pressure and the heat transfer for the process.
(b) What is the percent error in the heat transfer if the specific heat is assumed constant at the room temperature value?

5.30E A 2-ft^3 rigid tank contains methane gas at 1000 F, 100 $lbf/in.^2$. The tank is cooled to −100 F.

(a) Calculate the final pressure and the heat transfer for the process.
(b) What is the percent error in the heat transfer if the specific heat is assumed constant at the room temperature value?

5.31 Calculate the heat transfer for the process described in Problem 4.10.

5.32 A cylinder with a piston restrained by a linear spring contains 2 kg of carbon dioxide at 500 kPa, 400°C. This system is cooled to 40°C, at which point the pressure is 300 kPa. Calculate the heat transfer for the process.

5.33 A cylinder fitted with a piston contains 0.2 kg of air initially at 110 kPa, 20°C. The air is compressed in a quasi-equilibrium, polytropic process with a polytropic exponent n of 1.25 until the final temperature reaches 300°C. Determine the final pressure and the heat transfer for this process.

5.34 A certain elastic balloon will support an internal pressure equal to $P_0 = 100$ kPa until the balloon becomes spherical at a diameter of $D_0 = 1$ m, beyond which

$$P = P_0 + C(D^{*-1} - D^{*-7}), \qquad D^* = \frac{D}{D_0}$$

because of the offsetting effects of balloon curvature and elasticity. This balloon contains helium gas at 250 K, 100 kPa, with a 0.4-m^3 volume. The balloon is heated until the volume reaches 2.0 m^3. During the process the maximum pressure inside the balloon is 200 kPa.

(a) What is the temperature inside the balloon when the pressure is at its maximum value?
(b) What are the final temperature and pressure inside the balloon?
(c) Determine the work and heat transfer for the overall process.

5.34E A certain elastic balloon will support an internal pressure equal to $P_0 = 14.7$ lbf/in.^{2} until the balloon becomes spherical at a diameter of $D_0 = 3$ ft, beyond which

$$P = P_0 + C(D^{*-1} - D^{*-7}), \qquad D^* = \frac{D}{D_0}$$

because of the offsetting effects of balloon curvature and elasticity. This balloon contains helium gas at 450 R, 14.7 lbf/in.^{2}, with a 10-ft^3 volume. The balloon is heated until the volume reaches 50 ft^3. During the process the maximum pressure inside the balloon is 30 lbf/in.^{2}.

(a) What is the temperature inside the balloon when the pressure is at its maximum value?
(b) What are the final temperature and pressure inside the balloon?
(c) Determine the work and heat transfer for the overall process.

5.35 A cylinder fitted with a piston contains argon gas at 140 kPa, 10°C, and the volume is 200 L. The gas is compressed in a polytropic process to 700 kPa, 180°C. Calculate the heat transfer during the process.

5.36 A cylinder fitted with a piston contains 1 kg of methane gas at 700 kPa, 40°C. The piston cross-sectional area is 0.5 m^2, and the total external force restraining the piston is directly proportional to the cylinder volume squared. Heat is transferred to the methane until its temperature reaches 1100°C. Determine the final pressure inside the cylinder, the work done by the methane, and the heat transfer during the process.

5.37 A closed cylinder is divided into two parts by a frictionless piston held in place by a pin. Side A is 10 L and contains air at 100 kPa, 30°C, and side B is 300 L and contains saturated vapor water at 30°C. The pin is pulled, releasing the piston. Both sides eventually come to equilibrium at 30°C. Considering the air and water together as a system, determine

(a) The work done by the system.
(b) The heat transfer to the system.

5.37E A closed cylinder is divided into two parts by a frictionless piston held in place by a pin. Side A is 0.3 ft^3 and contains air at 14.7 $lbf/in.^2$, 90 F, and side B is 10 ft^3 and contains saturated vapor water at 90 F. The pin is pulled, releasing the piston. Both sides eventually come to equilibrium at 90 F. Considering the air and water together as a system, determine

(a) The work done by the system.
(b) The heat transfer to the system.

5.38 Heat is transferred at a given rate to a mixture of liquid and vapor in equilibrium in a closed container. Determine the rate of change of temperature as a function of the thermodynamic properties of the liquid and vapor and the masses of liquid and vapor.

5.39 A frictionless, thermally conducting piston separates the air and water in the cylinder shown in Fig. 5.16. The initial volumes of A and B are each 500 L, and the initial pressure on each side is 700 kPa. The volume of the liquid in B is 2 percent of the volume of B at this state. Heat is transferred to both A and B until all the liquid in B evaporates. Determine

(a) The total heat transfer during the process.
(b) The work done by the piston on the air and the heat transferred to the air during the process.

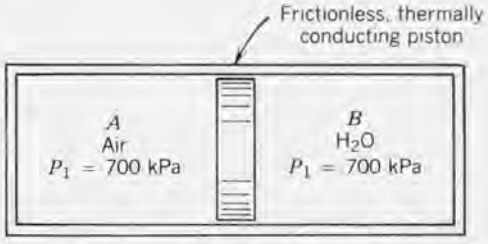


FIGURE 5.16 Sketch for Problem 5.39.

COMPUTER PROBLEMS

5.1C For one of the substances listed in Table A.10, compare the enthalpy change between any two temperatures, T_1 and T_2, as calculated by integrating the specific heat equation; by assuming constant specific heat at the average temperature; and by assuming constant specific heat at temperature T_1.

5.2C Fit a polynomial expression of degree n in the temperature for ideal-gas specific heat. Use the ideal-gas enthalpy values for one of the substances listed in Table

A.12 as data. The accuracy of the correlation should be studied as a function of the temperature range of the fit, as well as of the polynomial degree.

5.3C Write a program to solve Problem 5.15, in which the initial state of the water and the piston mass and area are input variables.

5.4C Consider a general version of Problem 5.17. Write a program in which the initial state and the final temperature of the water and, in addition, the spring constant are input variables.

5.5C Write a program to solve Problem 5.22 for the general case in which the two volumes and the initial state of the water are all variables.

5.6C Write a program to solve Problem 5.26 for the case in which the vessel wall thickness, the initial temperature, and the water quality are all variables.

5.7C Consider a general version of Problem 5.30, in which a substance listed in Table A.10, the initial temperature and pressure, and the final temperature are program inputs.

5.8C Write a program to solve the general case of Problem 5.33, in which all the state properties and the polytropic exponent are input parameters.

5.9C Write a program to follow the state path of the helium gas in the process of Problem 5.34. The initial state, the initial and final volumes, and the maximum pressure should all be input variables in the program.

5.10C Consider the general case of Problem 5.39. Write a program in which the initial volumes, pressures, and volume percent of liquid water are all input variables.

6

FIRST-LAW ANALYSIS FOR A CONTROL VOLUME

In the preceding chapter we developed the first-law analysis for a system undergoing a process. Many applications in thermodynamics do not readily lend themselves to a system approach, but are conveniently handled by the more general control volume techniques, as discussed in Chapter 2. The present chapter is concerned with development of the control volume forms for the conservation of mass and the first law of thermodynamics, and includes a number of special forms of these expressions.

6.1 CONSERVATION OF MASS AND THE CONTROL VOLUME

A control volume is a volume in space that has interest for a particular study or analysis. The surface of this control volume is referred to as a control surface and always consists of a closed surface. The size and shape of the control volume are completely arbitrary, and are defined to best suit the analysis. The surface may be fixed, or it may move or expand. However, the surface must be defined relative to some coordinate system. In some analyses it may be desirable to consider a rotating or moving coordinate system, and to describe the position of the control surface relative to such a coordinate system.

Mass, heat, and work can cross the control surface. The mass in the control volume, as well as the properties of this mass, can change with time. Figure 6.1 is a schematic diagram of a control volume, showing its heat transfer and shaft work, the accumulation of mass within the control volume, and its moving boundary.

Let us consider the law of the conservation of mass as it relates to the control volume. We first consider the mass flow into and out of the control volume and the net increase of mass within the control volume. During a time interval δt, let the mass δm_i, as shown in Fig. 6.2, enter the control volume, and the mass δm_e leave the control volume. Let us then designate the mass within the control volume at the beginning of this time interval as m_t, and the mass within the control volume after this interval as $m_{t+\delta t}$. From the law of the conservation of mass, we can write

$$m_t + \delta m_i = m_{t+\delta t} + \delta m_e$$

We can also look at this mass from the view of the net flow across the control surface and the change of mass within the control volume.

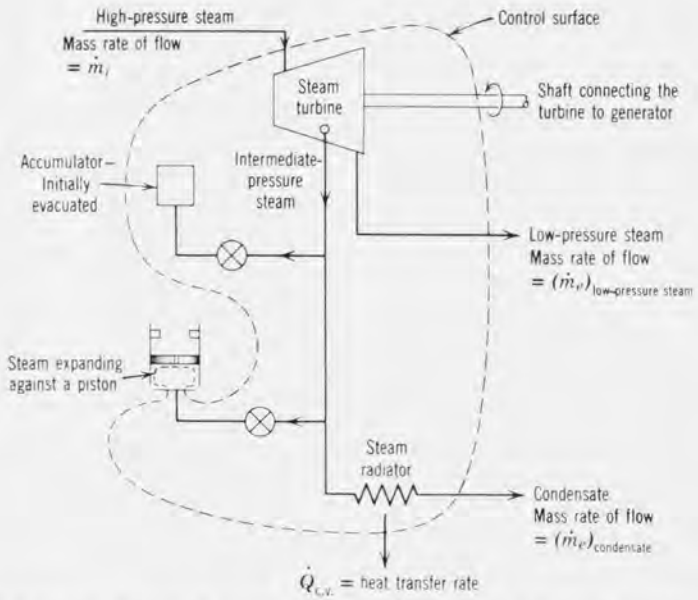


FIGURE 6.1 Schematic diagram of a control volume showing mass and energy transfers and accumulation.

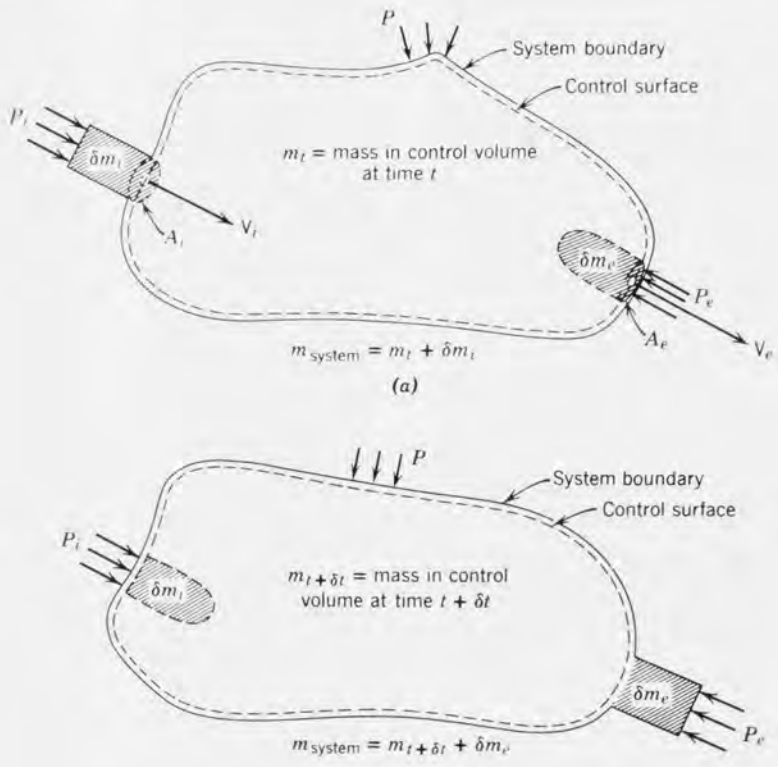


FIGURE 6.2 Schematic diagram of a control volume for analysis of the continuity equation as applied to a control volume. (a) System and control volume at time t. (b) System and control volume at time $t + \delta t$.

Net flow into the control volume during δt equals the increase of mass within the control volume during δt,

$$\delta m_i - \delta m_e = m_{t+\delta t} - m_t$$

or

$$(m_{t+\delta t} - m_t) + (\delta m_e - \delta m_i) = 0 \tag{6.1}$$

As written, this equation simply states that the change of mass within the control volume during δt—$m_{t+\delta t} - m_t$—and the net mass flow into the control volume during δt—$\delta m_i - \delta m_e$—are equal. However, in many problems requiring a thermodynamic analysis, we find it very convenient to have the law of the conservation of mass (as well as the first and second laws of thermodynamics and the momentum equation) expressed as a rate equation for the control volume. This equation must account for the instantaneous rate of mass flow across the control surface and the instantaneous rate of change of mass within the control volume. Let us therefore write an expression for the average rate of change of mass within the control volume during δt and the average mass rates of flow across the control surface during δt by dividing Eq. 6.1 by δt:

$$\frac{m_{t+\delta t} - m_t}{\delta t} + \frac{\delta m_e}{\delta t} - \frac{\delta m_i}{\delta t} = 0 \tag{6.2}$$

To obtain the rate equation for the control volume, we find the limit of each term as δt approaches zero. The system and control volume coincide at this point.

$$\lim_{\delta t \to 0} \left(\frac{m_{t+\delta t} - m_t}{\delta t} \right) = \frac{dm_{\text{c.v.}}}{dt}$$

$$\lim_{\delta t \to 0} \left(\frac{\delta m_e}{\delta t} \right) = \dot{m}_e$$

$$\lim_{\delta t \to 0} \left(\frac{\delta m_i}{\delta t} \right) = \dot{m}_i$$

The symbol $m_{\text{c.v.}}$ denotes the instantaneous mass inside the control volume; $\dot{m}_i$ is the instantaneous rate of flow entering the control volume across area $\mathscr{A}_i$; and $\dot{m}_e$ is the instantaneous rate of flow leaving across area $\mathscr{A}_e$. We recognize that, in practice, there may well be several areas on the control surface across which flow occurs (in mixing processes or processes involving chemical reactions, for example). We account for this possibility by including summation signs, implying a summation of flows over the various discrete flow areas. Thus, the instantaneous rate form becomes

$$\frac{dm_{\text{c.v.}}}{dt} + \sum \dot{m}_e - \sum \dot{m}_i = 0 \tag{6.3}$$

Equation 6.3 for the conservation of mass is commonly termed the continuity equation. Although this form of the equation is sufficient for the majority of applications in thermodynamics, for the study of fluid mechanics and heat transfer,

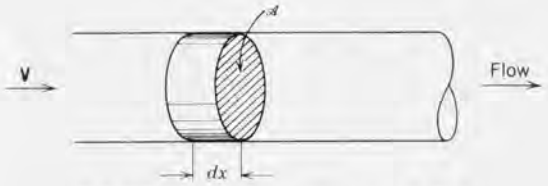


FIGURE 6.3 Flow across a control surface.

it is frequently rewritten in terms of local fluid properties. In this text we consider Eq. 6.3 the general expression of the continuity equation.

Let us consider one further aspect of mass flow across a control surface. For simplicity, we assume that a fluid is flowing uniformly inside a pipe or duct, as shown in Fig. 6.3.

We wish to examine the flow in terms of the amount of mass crossing the surface $\mathscr{A}$ during the time interval δt. As seen from Fig. 6.3, the fluid moves a distance dx during this time; and therefore, the volume of fluid crossing surface $\mathscr{A}$ is $\mathscr{A}\,dx$. Consequently, the mass crossing surface $\mathscr{A}$ is given by

$$\delta m = \frac{\mathscr{A}\,dx}{v}$$

Now, if we divide both sides of this expression by δt and take the limit as $\delta t \to 0$, the result is

$$\dot{m} = \frac{\mathscr{A}\vec{\mathbf{V}}}{v} \tag{6.4}$$

It should be noted that Eq. 6.4 has been developed for a stationary control surface $\mathscr{A}$, and that we tacitly assumed that the flow was normal to this surface and was uniform across the surface. It should also be pointed out that Eq. 6.4 applies to any of the various flow streams entering or leaving the control volume, subject to the assumptions mentioned.

EXAMPLE 6.1

Air is flowing in a 0.2-m-diameter pipe at a uniform velocity of 0.1 m/s. The temperature is 25°C and the pressure 150 kPa. Determine the mass flow rate.

Solution

From Eq. 6.4,

$$\dot{m} = \frac{\mathscr{A}\mathbf{V}}{v}$$

For air, using R from Table A.9, we have

$$v = \frac{RT}{P} = \frac{0.287 \times 298.2}{150} = 0.5705 \text{ m}^3/\text{kg}$$

The cross-sectional area is

$$\mathscr{A} = \frac{\pi}{4}(0.2)^2 = 0.0314 \text{ m}^2$$

Therefore,

$$\dot{m} = \frac{0.0314 \times 0.1}{0.5705} = 0.0055 \text{ kg/s}$$

6.2 THE FIRST LAW OF THERMODYNAMICS FOR A CONTROL VOLUME

We have already considered the first law of thermodynamics for a system, which consists of a fixed quantity of mass, and have noted, Eq. 5.5, that it may be written

$${}_1Q_2 = E_2 - E_1 + {}_1W_2$$

We have also noted that this may be written as an average rate equation over the time interval δt by dividing by δt:

$$\frac{\delta Q}{\delta t} = \frac{E_2 - E_1}{\delta t} + \frac{\delta W}{\delta t} \tag{6.5}$$

To write the first law as a rate equation for a control volume, we proceed in a manner analogous to that used in developing a rate equation for the law of the conservation of mass. A system and control volume are shown in Fig. 6.4. The system consists of all the mass initially in the control volume plus the mass δm_i.

Consider the changes that take place in the system and control volume during the time interval δt. During this time δt, the mass δm_i enters the control volume through the discrete area $\mathscr{A}_i$, and the mass δm_e leaves the control volume through the area $\mathscr{A}_e$.

In our analysis we assume that the increment of mass, δm_i, has uniform properties, and similarly that δm_e has uniform properties. The total work done by the system during this process, δW, is that associated with the masses δm_i and δm_e crossing the control surface, usually referred to as flow work, and the work $\delta W_{\text{c.v.}}$, which includes all other forms of work, such as work associated with a rotating shaft that crosses the system boundary, shear forces, electrical, magnetic, and surface effects, and expansion or contraction of the control volume. An amount of heat δQ crosses the boundary during δt.

Let us now consider each of the terms of the first law as it is written for the system and transform each term into an equivalent form that applies to the control volume. Consider first the term $E_2 - E_1$. Let

E_t = the energy in the control volume at time t.

$E_{t+\delta t}$ = the energy in the control volume at time $t + \delta t$.

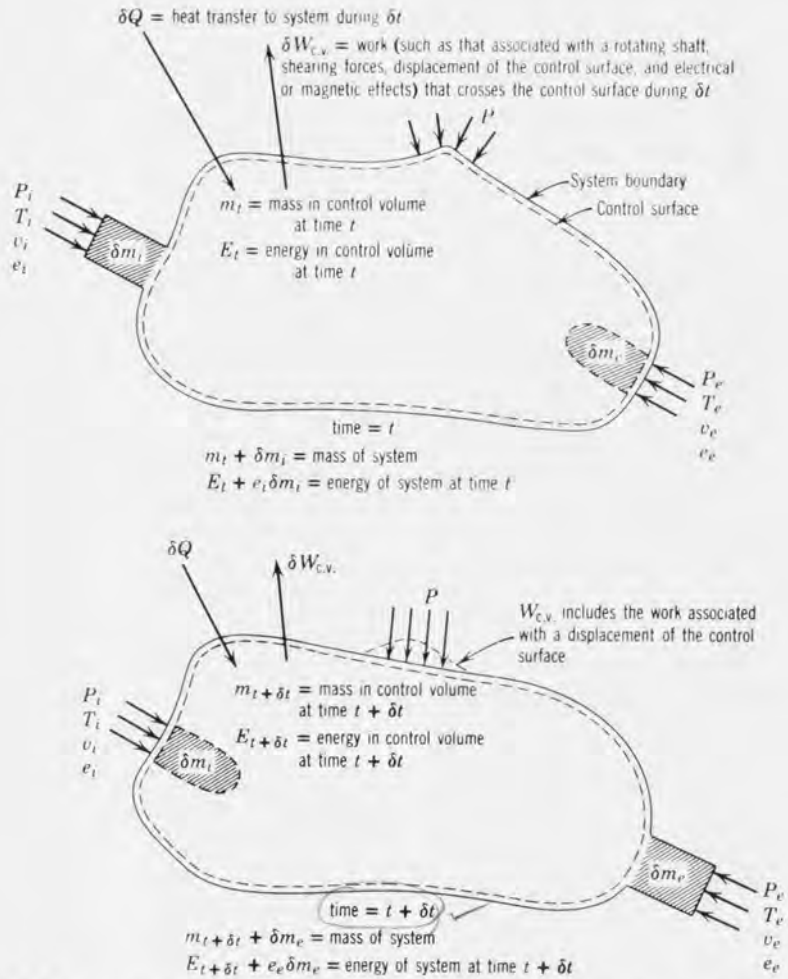


FIGURE 6.4 Schematic diagram for a first law analysis of a control volume, showing heat and work as well as mass crossing the control surface.

Then

$$E_1 = E_t + e_i\,\delta m_i = \text{energy of the system at time } t.$$

$$E_2 = E_{t+\delta t} + e_e\,\delta m_e = \text{energy of the system at time } t + \delta t.$$

Therefore,

$$\begin{aligned} E_2 - E_1 &= E_{t+\delta t} + e_e\,\delta m_e - E_t - e_i\,\delta m_i \\ &= (E_{t+\delta t} - E_t) + (e_e\,\delta m_e - e_i\,\delta m_i) \end{aligned} \tag{6.6}$$

The term $e_e\,\delta m_e - e_i\,\delta m_i$ represents the net flow of energy that crosses the control surface during δt as the result of the masses δm_e and δm_i crossing the control surface.

Let us consider in more detail the work associated with the masses δm_i and δm_e crossing the control surface. Work is done by the normal force (normal to area $\mathscr{A}$) acting on δm_i and δm_e as these masses cross the control surface. This normal force is equal to the product of the normal tensile stress, $-\sigma_n$, and the area, $\mathscr{A}$. The work done is

$$-\sigma_n \mathscr{A}\, dl = -\sigma_n\, \delta V = -\sigma_n v\, \delta m \tag{6.7}$$

A complete analysis of the nature of the normal stress, σ_n, for an actual fluid examines both static pressure and viscous effects and is beyond the scope of this book. We will assume in this book that the normal stress, σ_n, at a point is equal to the static pressure at this point, P, and simply note that in many applications this is a very reasonable assumption and yields results of good accuracy.

With this assumption the work done on mass δm_i as it enters the control volume is $P_i v_i\, \delta m_i$, and the work done by mass δm_e as it leaves the control volume is $P_e v_e\, \delta m_e$. We refer to these terms as the flow work. Various other terms are encountered in the literature, such as flow energy, work of introduction, and work of expulsion.

Thus, the total work done by the system during time δt is

$$\delta W = \delta W_{\text{c.v.}} + (P_e v_e\, \delta m_e - P_i v_i\, \delta m_i) \tag{6.8}$$

Let us now divide Eqs. 6.6 and 6.8 by δt and substitute into the first law, Eq. 6.5. Combining terms and rearranging, we have

$$\frac{\delta Q}{\delta t} + \frac{\delta m_i}{\delta t}(e_i + P_i v_i) = \left(\frac{E_{t+\delta t} - E_t}{\delta t}\right) + \frac{\delta m_e}{\delta t}(e_e + P_e v_e) + \frac{\delta W_{\text{c.v.}}}{\delta t} \tag{6.9}$$

We recognize that each of the flow terms in this expression can be rewritten in the form

$$e + Pv = u + Pv + \frac{\mathbf{V}^2}{2} + gZ = h + \frac{\mathbf{V}^2}{2} + gZ \tag{6.10}$$

using the definition of the thermodynamic property enthalpy, Eq. 5.13. The appearance of the combination $u + Pv$ whenever mass flows across a control surface is the principal reason for defining the property enthalpy. Its introduction in Chapter 5 in conjunction with the constant-pressure process was to facilitate use of the tables of thermodynamic properties.

Using Eq. 6.10 for the masses entering and leaving the control volume, Eq. 6.9 becomes

$$\frac{\delta Q}{\delta t} + \frac{\delta m_i}{\delta t}\left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) = \left(\frac{E_{t+\delta t} - E_t}{\delta t}\right) + \frac{\delta m_e}{\delta t}\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right) + \frac{\delta W_{\text{c.v.}}}{\delta t} \tag{6.11}$$

To reduce this expression to a rate equation, we consider what happens to each of the terms in Eq. 6.11 as δt approaches zero. The heat transfer and work terms become rate transfer quantities, as in Section 5.8. Similarly, the two mass quantities

become mass flow rates, as in Section 6.1, and the energy term becomes the time rate of change of energy in the control volume, in a manner analogous to the mass term in the conservation of mass. In addition, we originally assumed uniform properties for the incremental mass δm_i entering the control volume across area $\mathscr{A}_i$, and made a similar assumption for δm_e leaving across area $\mathscr{A}_e$. Consequently, in taking the limits, this reduces to the restriction of uniform properties across area $\mathscr{A}_i$ and also across $\mathscr{A}_e$ at an instant of time. These properties may of course be time-dependent.

In using the limiting values to express the rate equation of the first law for a control volume, we again include summation signs on the flow terms to account for the possibility of additional flow streams entering or leaving the control volume. Therefore, the result is

$$\dot{Q}_{\text{c.v.}} + \sum \dot{m}_i \left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i \right) = \frac{dE_{\text{c.v.}}}{dt} + \sum \dot{m}_e \left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e \right) + \dot{W}_{\text{c.v.}} \quad (6.12)$$

which is, for our purposes, the general expression of the first law of thermodynamics. In words, this equation says that the rate of heat transfer into the control volume plus the rate of energy flowing in as a result of mass transfer is equal to the rate of change of energy inside the control volume, plus the rate of energy flowing out as a result of mass transfer, plus the power output associated with shaft, shear, and electrical effects and other factors that have already been mentioned.

Equation 6.12 can be integrated over the total time of a process to give the total energy changes that occur during this period. However, to do so requires knowledge of the time dependency of the various mass flow rates and the states at which mass enters and leaves the control volume. An example of this type of process will be considered in Section 6.5.

Another point to be noted is that if there is no mass flow into or out of the control volume, these terms simply drop out of Eq. 6.12, which then reduces to the rate equation form of the first law for a system,

$$\dot{Q} = \frac{dE}{dt} + \dot{W}$$

which was discussed in Section 5.8.

Because the control volume approach is more general and reduces to the usual statement of the first law for a system when there is no mass flow across the control surface, we will, when making a general statement of the first law, use Eq. 6.12, which is the rate form of the first law for a control volume.

The term flux should also be introduced at this point. Flux is defined as a rate of flow of any quantity per unit area across a control surface. Thus, the mass flux is the rate of mass flow per unit area, and heat flux is the heat flow rate per unit area across the control surface.

Finally, it should be pointed out that in fluid mechanics and heat transfer, the control volume expression for the first law is commonly written in terms of local properties, as it was for the conservation of mass. This form will not be introduced in this text. For our purposes, we will consider Eq. 6.12 the general expression of the first law for a control volume analysis.

6.3 THE STEADY-STATE, STEADY-FLOW PROCESS

Our first application of the control volume equations will be to develop a suitable analytical model for the long-term steady operation of devices such as turbines, compressors, nozzles, boilers, condensers—which makes up a very large class of problems in thermodynamic analysis. This model will not include the short-term transient start-up or shutdown of such devices, but only the steady operating period of time.

Let us consider a certain set of assumptions (beyond those leading to Eqs. 6.3 and 6.12) that will help us form a reasonable model for this type of process, which we call the steady-state, steady-flow process. For convenience, we often refer to this process as the SSSF process.

1. The control volume does not move relative to the coordinate frame.
2. The state of the mass at each point in the control volume does not vary with time.
3. The mass flux and the state of the mass that flows across the control surface do not vary with time at each discrete area of flow. The rates at which heat and work cross the control surface remain constant.

As an example of a steady-state, steady-flow process, consider a centrifugal air compressor that operates with a constant mass rate of flow into and out of the compressor, constant properties at each point across the inlet and exit ducts, a constant rate of heat transfer to the surroundings, and a constant power input. At each point in the compressor the properties are constant with time, even though the properties of a given elemental mass of air vary as it flows through the compressor. Usually such a process is referred to simply as a steady-flow process, since we are concerned primarily with the properties of the fluid entering and leaving the control volume. On the other hand, in the analysis of certain heat-transfer problems in which the same assumptions apply, we are primarily interested in the spatial distribution of properties, particularly temperature. Such a process is often referred to as a steady-state process. Since this is an introductory book, we use the term steady-state, steady-flow process to emphasize the basic assumptions. The student should realize that the terms steady-state process and steady-flow process are both used extensively in the literature.

Let us now consider the significance of each of these assumptions for the SSSF process.

1. The assumption that the control volume does not move relative to the coordinate frame means that all velocities measured relative to the coordinate frame are also velocities relative to the control surface, and that there is no work associated with the acceleration of the control volume.
2. The assumption that the state of the mass at each point in the control volume does not vary with time requires that

$$\frac{dm_{\text{c.v.}}}{dt} = 0$$

and

$$\frac{dE_{\text{c.v.}}}{dt} = 0$$

Therefore, we conclude that for the SSSF process we can write, from Eqs. 6.3 and 6.12,

Continuity equation:

$$\sum \dot{m}_i = \sum \dot{m}_e \tag{6.13}$$

First law:

$$\dot{Q}_{\text{c.v.}} + \sum \dot{m}_i\left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) = \sum \dot{m}_e\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right) + \dot{W}_{\text{c.v.}} \tag{6.14}$$

3. The assumption that the various mass flows, states, and rates at which heat and work cross the control surface remain constant requires that every quantity in Eqs. 6.13 and 6.14 be steady with time. This means that the application of Eqs. 6.13 and 6.14 to the operation of some device is independent of time.

Many of the applications of the SSSF model have only one flow stream entering and only one leaving the control volume. For this type of process, we can write

Continuity equation:

$$\dot{m}_i = \dot{m}_e = \dot{m} \tag{6.15}$$

First law:

$$\dot{Q}_{\text{c.v.}} + \dot{m}\left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) = \dot{m}\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right) + \dot{W}_{\text{c.v.}} \tag{6.16}$$

Rearranging this equation, we have

$$q + h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i = h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e + w \tag{6.17}$$

where, by definition,

$$q = \frac{\dot{Q}_{\text{c.v.}}}{\dot{m}} \quad \text{and} \quad w = \frac{\dot{W}_{\text{c.v.}}}{\dot{m}} \tag{6.18}$$

Note that the units for q and w are kJ/kg. From their definition, q and w can be thought of as the heat transfer and work (other than flow work) per unit mass flowing into and out of the control volume for this particular SSSF process.

The symbols q and w are also used for the heat transfer and work per unit mass of a system. However, because it is always evident from the context whether a process is for a system (fixed mass) or for a control volume (involving a flow of mass), the significance of the symbols q and w will also be readily evident in each situation.

The SSSF process is often used in the analysis of reciprocating machines, such as reciprocating compressors or engines. In these machines the rate of flow, which may actually be pulsating, is considered the average rate of flow for an integral

number of cycles. A similar assumption is made about the properties of the fluid flowing across the control surface, and the heat transfer and work crossing the control surface. It is also assumed that for an integral number of cycles the reciprocating device undergoes, the energy and mass within the control volume do not change.

A number of examples are now given to illustrate the analysis of SSSF processes.

EXAMPLE 6.2

The mass rate of flow into a steam turbine is 1.5 kg/s, and the heat transfer from the turbine is 8.5 kW. The following data are known for the steam entering and leaving the turbine.

	Inlet Conditions	Exit Conditions
Pressure	2.0 MPa	0.1 MPa
Temperature	350°C	
Quality		100 percent
Velocity	50 m/s	200 m/s
Elevation above reference plane	6 m	3 m
$g = 9.8066$ m/s^2		

Determine the power output of the turbine.

Control volume: Turbine (Fig. 6.5).

Inlet state: Fixed (given in table).

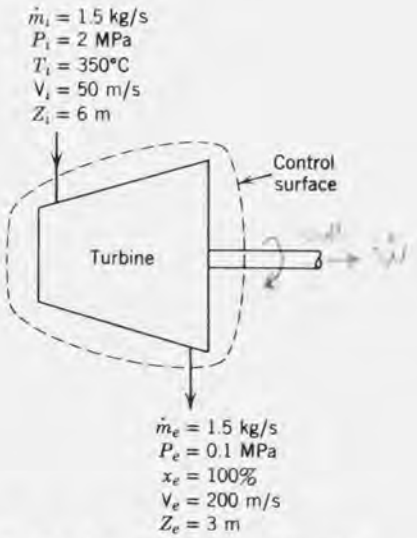


FIGURE 6.5 Illustration for Example 6.2.

Exit state: Fixed (given in table).
Process: SSSF.
Model: Steam tables.
Analysis:

First law (Eq. 6.16):

$$\dot{Q}_{c.v.} + \dot{m}\left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) = \dot{m}\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZe\right) + \dot{W}_{c.v.}$$

with

$$\dot{Q}_{c.v.} = -8.5 \text{ kW}$$

Solution

Here $h_i = 3137.0$ kJ/kg (from the steam tables) and

$$\frac{\mathbf{V}_i^2}{2} = \frac{50 \times 50}{2 \times 1000} = 1.25 \text{ kJ/kg}$$

$$gZ_i = \frac{6 \times 9.8066}{1000} = 0.059 \text{ kJ/kg}$$

Similarly, $h_e = 2675.5$ kJ/kg and

$$\frac{\mathbf{V}_e^2}{2} = \frac{200 \times 200}{2 \times 1000} = 20.0 \text{ kJ/kg}$$

$$gZ_e = \frac{3 \times 9.8066}{1000} = 0.029 \text{ kJ/kg}$$

Therefore, substituting into Eq. 6.16, gives

$$-8.5 + 1.5(3137 + 1.25 + 0.059) = 1.5(2675.5 + 20.0 + 0.029) + \dot{W}_{c.v.}$$

$$\dot{W}_{c.v.} = -8.5 + 4707.5 - 4043.3 = 655.7 \text{ kW}$$

If Eq. 6.17 is used, the work per kilogram of fluid flowing is found first.

$$q + h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i = h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e + w$$

$$q = \frac{-8.5}{1.5} = -5.667 \text{ kJ/kg}$$

Therefore, substituting into Eq. 6.17 gives

$$-5.667 + 3137 + 1.25 + 0.059 = 2675.5 + 20.0 + 0.029 + w$$

$$w = 437.11 \text{ kJ/kg}$$

$$\dot{W}_{c.v.} = 1.5 \text{ kg/s} \times 437.11 \text{ kJ/kg} = 655.7 \text{ kW}$$

Two further observations can be made by referring to this example. First, in many engineering problems potential energy changes are insignificant compared with

changes in the other energy quantities. In this example the potential energy change did not affect any of the significant figures. In most problems in which the change in elevation is small, the potential energy terms may be neglected.

Second, if velocities are small, say, under 20 m/s, the kinetic energy is often insignificant compared with other energy quantities. Furthermore, when the velocities entering and leaving the system are essentially the same, the change in kinetic energy is small. Because it is the change in kinetic energy that is important in the SSSF energy equation, the kinetic energy terms can usually be neglected when there is no significant difference between the velocity of the fluid entering and leaving the control volume. Thus, in many thermodynamic problems, one must make judgments about which quantities may be negligible for a given analysis.

EXAMPLE 6.3

Steam at 0.6 MPa, 200°C, enters an insulated nozzle at a velocity of 50 m/s. It leaves at a pressure of 0.15 MPa and a velocity of 600 m/s. Determine the final temperature if the steam is superheated in the final state, and the quality if it is saturated.

Control volume: Nozzle.

Inlet state: Fixed (see Fig. 6.6).

Exit state: P_e known.

Process: SSSF.

Model: Steam tables.

Analysis: $\dot{Q}_{c.v.} \approx 0$ (nozzle insulated)

$\dot{W}_{c.v.} = 0, \qquad \mathrm{PE}_i \approx \mathrm{PE}_e$

First law (Eq. 6.17):

$$h_i + \frac{\mathbf{V}_i^2}{2} = h_e + \frac{\mathbf{V}_e^2}{2}$$

Solution

$$h_e = 2850.1 + \frac{(50)^2}{2 \times 1000} - \frac{(600)^2}{2 \times 1000} = 2671.4 \text{ kJ/kg}$$

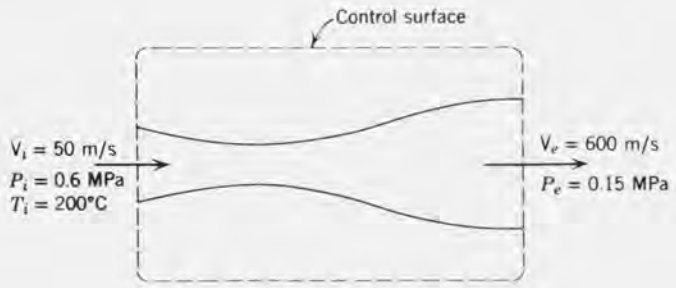


FIGURE 6.6 Illustration for Example 6.3.

The two known properties of the fluid leaving are pressure and enthalpy; therefore, the state of this fluid is determined. Since h_e is less than h_g at 0.15 MPa, the quality is calculated.

$$h = h_f + xh_{fg}$$
$$2671.4 = 467.1 + x_e 2226.5$$
$$x_e = 0.99$$

EXAMPLE 6.4

In a refrigeration system having refrigerant-12 as the working fluid, the R-12 enters the compressor at 150 kPa, $-10°C$, and leaves at 1.0 MPa, 90°C. The mass rate of flow is 0.016 kg/s, and the power input to the compressor is 1 kW.

On leaving the compressor, the R-12 enters a water-cooled condenser at 1.0 MPa, 80°C, and leaves as a liquid at 0.95 MPa, 35°C. Water enters the condenser at 10°C and leaves at 20°C. Determine

1. The heat transfer rate from the compressor.
2. The rate at which cooling water flows through the condenser.

First control volume: Compressor.

Inlet state: P_i, T_i; state fixed.

Exit state: P_e, T_e; state fixed.

Process: SSSF.

Model: R-12 tables.

Analysis: Because the velocity of the vapor entering a refrigeration compressor is low and not greatly different from the velocity leaving, kinetic energy and potential energy changes can be neglected. Therefore, the first law, Eq. 6.17, is

$$q + h_i = h_e + w$$

Solution

$$w = \frac{-1}{0.016} = -62.5 \text{ kJ/kg}$$

From the R-12 tables,

$$h_i = 184.75 \text{ kJ/kg}, \qquad h_e = 240.28 \text{ kJ/kg}$$

Therefore,

$$q = 240.28 - 62.5 - 184.75 = -6.97 \text{ kJ/kg}$$
$$\dot{Q}_{c.v.} = 0.016 \text{ kg/s} \times (-6.97 \text{ kJ/kg}) = -0.1115 \text{ kW}$$

Second control volume: Condenser.

Sketch: Fig. 6.7.

Inlet states: R-12, fixed; water, fixed.

Exit states: R-12, fixed; water, fixed.

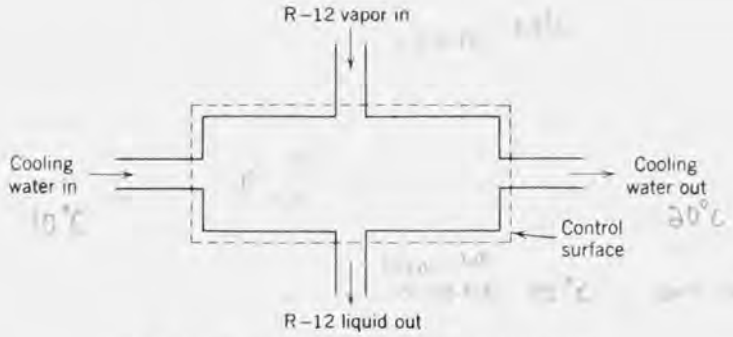


FIGURE 6.7 Schematic diagram of R-12 condenser.

Process: SSSF.

Model: R-12 tables, steam tables.

Analysis: We have two fluid streams, the R-12 and the water, entering and leaving the control volume. It is reasonable to assume that the kinetic and potential energy changes are negligible. We note that the work is zero, and we make the other reasonable assumption that there is no heat transfer across the control surface. Therefore, the first law, Eq. 6.14, reduces to

$$\sum \dot{m}_i h_i = \sum \dot{m}_e h_e$$

Using the subscript r for refrigerant and w for water, we have

$$\dot{m}_r(h_i)_r + \dot{m}_w(h_i)_w = \dot{m}_r(h_e)_r + \dot{m}_w(h_e)_w$$

Solution

From the R-12 and steam tables,

$$(h_i)_r = 232.91 \text{ kJ/kg}, \qquad (h_i)_w = 42.00 \text{ kJ/kg}$$
$$(h_e)_r = 69.55 \text{ kJ/kg}, \qquad (h_e)_w = 83.95 \text{ kJ/kg}$$

Solving this equation for $\dot{m}_w$, the rate of flow of water, we have

$$\dot{m}_w = \dot{m}_r \frac{(h_i - h_e)_r}{(h_e - h_i)_w} = 0.016 \text{ kg/s} \times \frac{(232.91 - 69.55) \text{ kJ/kg}}{(83.95 - 42.00) \text{ kJ/kg}} = 0.0623 \text{ kg/s}$$

This problem can also be solved by considering two separate control volumes, one having the flow of R-12 across its control surface, and the other having the flow of water across its control surface. Furthermore, there is heat transfer from one control volume to the other. This is shown schematically in Fig. 6.8.

The heat transfer for the control volume using R-12 is calculated first. The SSSF energy equation, Eq. 6.16, reduces to

$$\dot{Q}_{\text{c.v.}} = \dot{m}_r(h_e - h_i)_r$$
$$\dot{Q}_{\text{c.v.}} = 0.016 \text{ kg/s } (69.55 - 232.91) \text{ kJ/kg} = -2.614 \text{ kW}$$

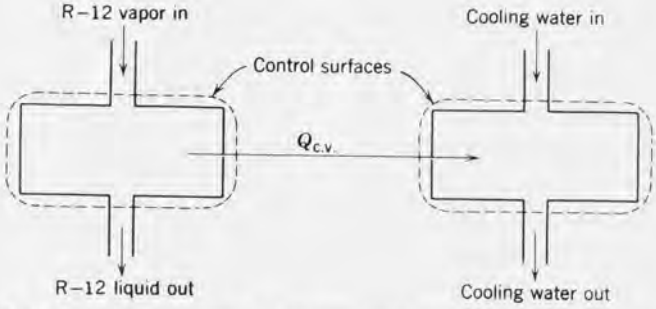


FIGURE 6.8 Schematic diagram of R-12 condenser considering two control surfaces.

This is also the heat transfer to the other control volume, for which $\dot{Q}_{c.v.} = +2.614$ kW.

$$\dot{Q}_{c.v.} = \dot{m}_w(h_e - h_i)_w$$

$$\dot{m}_w = \frac{2.614 \text{ kW}}{(83.95 - 42.00) \text{ kJ/kg}} = 0.0623 \text{ kg/s}$$

EXAMPLE 6.5

Consider the simple steam power plant, as shown in Fig. 6.9. The following data are for such a power plant.

Location	Pressure	Temperature or Quality
Leaving boiler	2.0 MPa	300°C
Entering turbine	1.9 MPa	290°C
Leaving turbine, entering condenser	15 kPa	90 percent
Leaving condenser, entering pump	14 kPa	45°C
Pump work = 4 kJ/kg		

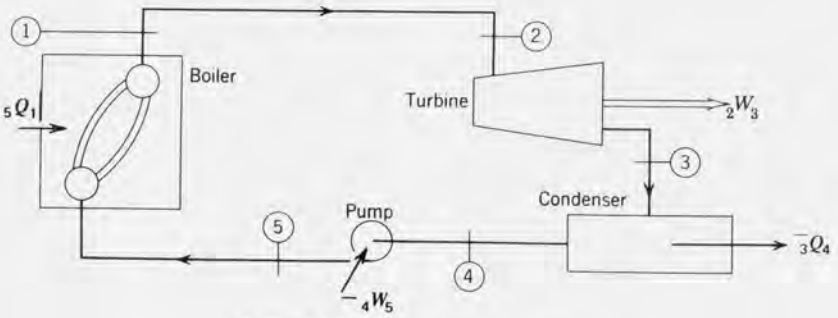


FIGURE 6.9 Simple steam power plant.

Determine the following quantities per kilogram flowing through the unit.

1. Heat transfer in line between boiler and turbine.
2. Turbine work.
3. Heat transfer in condenser.
4. Heat transfer in boiler.

There is a certain advantage in assigning a number to various points in the cycle. For this reason the subscripts i and e in the steady-state, steady-flow energy equation are often replaced by appropriate numbers.

Since there are several control volumes to be considered in the solution to this problem, let us consolidate our solution procedure somewhat. Using the notation of Fig. 6.9, we have

All processes: SSSF.

Model: Steam tables.

From the steam tables:

$$h_1 = 3023.5 \text{ kJ/kg}$$
$$h_2 = 3003.2 \text{ kJ/kg}$$
$$h_3 = 225.9 + 0.9(2373.2) = 2361.7 \text{ kJ/kg}$$
$$h_4 = 188.4 \text{ kJ/kg}$$

All analyses: No changes in kinetic or potential energy will be considered in the solution. In each case, the first law is given by Eq. 6.17.

Now we proceed to answer the specific questions raised in the problem statement.

1. *Control volume.* Pipe line between the boiler and the turbine.

   First law and solution:

$$ {}_1q_2 + h_1 = h_2$$
$$ {}_1q_2 = h_2 - h_1 = 3003.2 - 3023.5 = -20.3 \text{ kJ/kg}$$

2. *Control volume.* Turbine.

   First law and solution: A turbine is essentially an adiabatic machine. Therefore, it is reasonable to neglect heat transfer, so that

$$h_2 = h_3 + {}_2w_3$$
$$ {}_2w_3 = 3003.2 - 2361.7 = 641.5 \text{ kJ/kg}$$

3. *Control volume.* Condenser.

   First law and solution: There is no work for this control volume. Therefore,

$$ {}_3q_4 + h_3 = h_4$$
$$ {}_3q_4 = 188.4 - 2361.7 = -2173.3 \text{ kJ/kg}$$

4. *Control volume.* Boiler.

First law: The work is equal to zero, so that

$$_5q_1 + h_5 = h_1$$

A solution requires a value for h_5, which can be found by taking a control volume around the pump:

$$h_4 = h_5 + {}_4w_5$$
$$h_5 = 188.4 - (-4) = 192.4 \text{ kJ/kg}$$

Therefore, for the boiler,

$$_5q_1 + h_5 = h_1$$
$$_5q_1 = 3023.5 - 192.4 = 2831.1 \text{ kJ/kg}$$

EXAMPLE 6.6

The centrifugal air compressor of a gas turbine receives air from the ambient atmosphere where the pressure is 1 bar and the temperature is 300 K. At the discharge point of the compressor, the pressure is 4 bar, the temperature is 480 K, and the velocity is 100 m/s. The mass rate of flow into the compressor is 15 kg/s. Determine the power required to drive the compressor.

Control volume: We consider a control volume around the compressor, and locate the control volume at some distance from the compressor. The air crossing the control surface has a very low velocity and is essentially at ambient conditions. If we locate our control volume directly across the inlet section, we would need to know the temperature and velocity at the compressor inlet.

Sketch: Fig. 6.10.

Inlet and exit states: Both states fixed.

Process: SSSF.

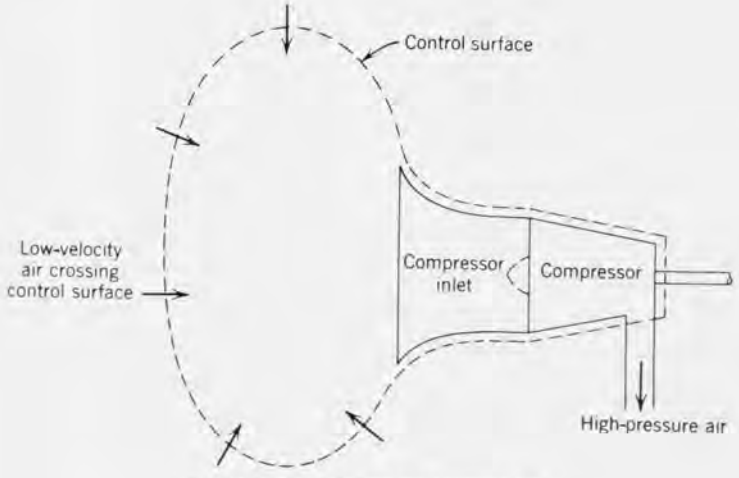


FIGURE 6.10 Sketch for Example 6.6.

Model: Ideal gas with constant specific heat, value from Table A.9 (300 K).

Analysis: A large, high-flow rate compressor such as this one is essentially an adiabatic machine, since the air passes through the compressor very quickly and no particular effort is made to promote any heat transfer. Therefore, we assume the process to be adiabatic. We also neglect any change in potential energy as well as the inlet kinetic energy. The first law, Eq. 6.17, reduces to

$$h_i = h_e + \frac{\mathbf{V}_e^2}{2} + w$$

Solution

$$-w = h_e - h_i + \frac{\mathbf{V}_e^2}{2} = C_{p0}(T_e - T_i) + \frac{\mathbf{V}_e^2}{2}$$

$$= 1.0035(480 - 300) + \frac{100 \times 100}{2 \times 1000}$$

$$= 180.6 + 5.0 = 185.6 \text{ kJ/kg}$$

$$-\dot{W}_{c.v.} = 15 \times 185.6 = 2784 \text{ kW}$$

A more accurate model for the behavior of the air in this process is given in the ideal gas air tables, Table A.11. For this model, the solution is

$$h_i = 300.47 \text{ kJ/kg}, \qquad h_e = 482.81 \text{ kJ/kg}$$

$$-w = h_e - h_i + \frac{\mathbf{V}_e^2}{2} = 482.81 - 300.47 + \frac{100 \times 100}{2 \times 1000}$$

$$= 182.3 + 5.0 = 187.3 \text{ kJ/kg}$$

$$-\dot{W}_{c.v.} = 15 \times 187.3 = 2810 \text{ kW}$$

6.4 THE JOULE–THOMSON COEFFICIENT AND THE THROTTLING PROCESS

The Joule–Thomson coefficient μ_J is defined by the relation

$$\mu_J \equiv \left(\frac{\partial T}{\partial P}\right)_h \tag{6.19}$$

As in the definition of specific heats in Section 5.6, this quantity is defined in terms of thermodynamic properties and is therefore itself a property of a substance.

The significance of the Joule–Thomson coefficient may be demonstrated by considering a throttling process that is a steady-state, steady-flow process across a restriction, with a resulting drop in pressure. A typical example is the flow through a partially opened valve or a restriction in the line. This usually occurs so rapidly and in such a small space that there is neither sufficient time, nor a large enough area for much heat transfer. Therefore, we usually assume such processes to be adiabatic.

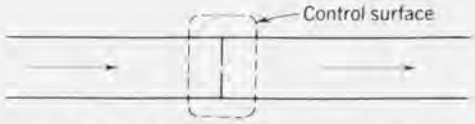


FIGURE 6.11 The throttling process.

If we consider the control surface shown in Fig. 6.11, we can write the SSSF energy equation for this process. There is no work, no change in potential energy, and we make the reasonable assumption that there is no heat transfer. The SSSF energy equation, Eq. 6.17, reduces to

$$h_i + \frac{\mathbf{V}_i^2}{2} = h_e + \frac{\mathbf{V}_e^2}{2}$$

If the fluid is a gas, the specific volume always increases in such a process and, therefore, if the pipe is of constant diameter, the kinetic energy of the fluid increases. In many situations, however, this increase in kinetic energy is small (or perhaps the diameter of the exit pipe is larger than that of the inlet pipe), and we can say with a high degree of accuracy that in this process the final and initial enthalpies are equal. Unless otherwise specified, we will make this assumption for throttling processes thorughout the remainder of this text.

It is for such a process that the Joule–Thomson coefficient, μ_J, is significant. A positive Joule–Thomson coefficient means that the temperature drops during throttling, and when the Joule–Thomson coefficient is negative the temperature rises during throttling.

EXAMPLE 6.7

Steam at 800 kPa, 300°C, is throttled to 200 kPa. Changes in kinetic energy are negligible for this process. Determine the final temperature of the steam and the average Joule–Thomson coefficient.

Control volume: Throttle valve (or other restriction).

Inlet state: P_i, T_i known; state fixed.

Exit state: P_e known.

Process: SSSF.

Model: Steam tables.

Analysis: First law, Eq. 6.17. Work equals zero. Neglect heat transfer and changes in kinetic and potential energies. Therefore, the first law reduces to

$$h_i = h_e$$

Solution

Since

$$h_e = h_i = 3056.4 \text{ kJ/kg}$$

and

$$P_e = 200 \text{ kPa}$$

these two properties determine the final state. From the superheat table for steam,

$$T_e = 292.4^\circ\text{C}$$

$$\mu_{J(\text{av})} = \left(\frac{\Delta T}{\Delta P}\right)_h = \frac{-7.6}{-600} = 0.0127 \text{ K/kPa}$$

A throttling process frequently involves a change in the phase of the fluid. A typical example is the flow through the expansion valve of a vapor-compression refrigeration system. The following example deals with this problem.

EXAMPLE 6.8

Consider the throttling process across the expansion valve or through the capillary tube in a vapor-compression refrigeration cycle. During this process the pressure of the refrigerant drops from the high pressure in the condenser to the low pressure in the evaporator and some of the liquid flashes into vapor. If we consider this process to be adiabatic, the quality of the refrigerant entering the evaporator can be calculated.

Consider the following process, in which ammonia is the refrigerant. The ammonia enters the expansion valve at a pressure of 1.50 MPa and a temperature of 32°C. Its pressure on leaving the expansion valve is 268 kPa. Calculate the quality of the ammonia leaving the expansion valve.

Control volume: Expansion valve or capillary tube.

Inlet state: P_i, T_i known, state therefore fixed.

Exit state: P_e known.

Process: SSSF.

Model: Ammonia tables.

Analysis: Standard throttling process analysis and assumptions, as in Example 6.7. The first law reduces to

$$h_i = h_e$$

Solution

From the ammonia tables

$$h_i = 332.3 \text{ kJ/kg}$$

(The enthalpy of a slightly compressed liquid is essentially equal to the enthalpy of a saturated liquid at the same temperature for the manual reading of tables that do not include a compressed-liquid-region table.)

$$h_e = h_i = 332.3 = 125.4 + x_e(1303.1)$$

$$x_e = 0.159 = 15.9 \text{ percent}$$

6.5 THE UNIFORM-STATE, UNIFORM-FLOW PROCESS

In Section 6.3 we considered the steady-state, steady-flow process and several examples of its application. Many processes of interest in thermodynamics involve unsteady flow and do not fit into this category. A certain group of these processes—for example, filling closed tanks with a gas or liquid, or discharge from closed vessels—can be reasonably represented to a first approximation by another simplified model, called the uniform-state, uniform-flow process, or for convenience, the USUF process. The basic assumptions are as follows.

1. The control volume remains constant relative to the coordinate frame.
2. The state of the mass within the control volume may change with time, but at any instant of time the state is uniform throughout the entire control volume (or over several identifiable regions that make up the entire control volume).
3. The state of the mass crossing each of the areas of flow on the control surface is constant with time, although the mass flow rates may vary with time.

Let us examine the consequence of these assumptions and derive an expression for the first law that applies to this process. The assumption that the control volume remains stationary relative to the coordinate frame has already been discussed in Section 6.3. The remaining assumptions lead to the following simplifications for the continuity equation and the first law.

The overall process occurs during time t. At any instant of time during the process, the continuity equation is

$$\frac{dm_{\text{c.v.}}}{dt} + \sum \dot{m}_e - \sum \dot{m}_i = 0$$

where the summation is over all areas on the control surface through which there is flow. Integrating over time t gives the change of mass in the control volume during the overall process.

$$\int_0^t \frac{dm_{\text{c.v.}}}{dt}\, dt = (m_2 - m_1)_{\text{c.v.}}$$

The total mass leaving the control volume during time t is

$$\int_0^t \sum \dot{m}_e\, dt = \sum m_e$$

and the total mass entering the control volume during time t is

$$\int_0^t \sum \dot{m}_i\, dt = \sum m_i$$

Therefore, for this period of time t, we can write the continuity equation for the USUF process as

$$(m_2 - m_1)_{\text{c.v.}} + \sum m_e - \sum m_i = 0 \tag{6.20}$$

In writing the first law for the USUF process, we consider Eq. 6.12, which applies at any instant of time during the process.

$$\dot{Q}_{\text{c.v.}} + \sum \dot{m}_i\left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) = \frac{dE_{\text{c.v.}}}{dt} + \sum \dot{m}_e\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right) + \dot{W}_{\text{c.v.}}$$

Since at any instant of time the state within the control volume is uniform, the first law for the USUF process becomes

$$\dot{Q}_{\text{c.v.}} + \sum \dot{m}_i\left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) = \sum \dot{m}_e\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right) + \frac{d}{dt}\left[(m)\left(u + \frac{\mathbf{V}^2}{2} + gZ\right)\right]_{\text{c.v.}} + \dot{W}_{\text{c.v.}}$$

Let us now integrate this equation over time t, during which time we have

$$\int_0^t \dot{Q}_{\text{c.v.}}\, dt = Q_{\text{c.v.}}$$

$$\int_0^t \left[\sum \dot{m}_i\left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right)\right] dt = \sum m_i\left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right)$$

$$\int_0^t \left[\sum \dot{m}_e\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right)\right] dt = \sum m_e\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right)$$

$$\int_0^t \dot{W}_{\text{c.v.}}\, dt = W_{\text{c.v.}}$$

$$\int_0^t \frac{d}{dt}\left[(m)\left(u + \frac{\mathbf{V}^2}{2} + gZ\right)\right]_{\text{c.v.}} dt = \left[m_2\left(u_2 + \frac{\mathbf{V}_2^2}{2} + gZ_2\right) - m_1\left(u_1 + \frac{\mathbf{V}_1^2}{2} + gZ_1\right)\right]_{\text{c.v.}}$$

Therefore, for this period of time t, we can write the first law for the uniform-state, uniform-flow process as

$$Q_{\text{c.v.}} + \sum m_i\left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) = \sum m_e\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right) + \left[m_2\left(u_2 + \frac{\mathbf{V}_2^2}{2} + gZ_2\right) - m_1\left(u_1 + \frac{\mathbf{V}_1^2}{2} + gZ_1\right)\right]_{\text{c.v.}} + W_{\text{c.v.}} \tag{6.21}$$

As an example of the type of problem for which these assumptions are valid and Eq. 6.21 is appropriate, let us consider the classic problem of flow into an evacuated vessel.

EXAMPLE 6.9

Steam at a pressure of 1.4 MPa, 300°C, is flowing in a pipe, as shown in Fig. 6.12. An evacuated tank is connected to this pipe through a valve. The valve is opened, the tank fills with steam until the pressure is 1.4 MPa, and then the valve is closed. The process takes place adiabatically. Kinetic energies and potential energies are negligible. Determine the final temperature of the steam.

Control volume: Tank, as shown in Fig. 6.12.

Initial state (in tank): Evacuated, mass $m_1 = 0$.

Final state: P_2 known.

Inlet state: P_i, T_i (in line) known.

Process: USUF.

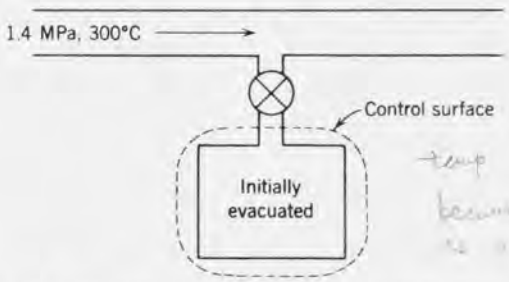


FIGURE 6.12 Flow into an evacuated vessel—control volume analysis.

Model: Steam tables.

Analysis:

First law, Eq. 6.21:

$$Q_{\text{c.v.}} + \sum m_i\left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) = \sum m_e\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right) + \left[m_2\left(u_2 + \frac{\mathbf{V}_2^2}{2} + gZ_2\right) - m_1\left(u_1 + \frac{\mathbf{V}_1^2}{2} + gZ_1\right)\right]_{\text{c.v.}} + W_{\text{c.v.}}$$

We note that $Q_{\text{c.v.}} = 0$, $W_{\text{c.v.}} = 0$, $m_e = 0$, and $(m_1)_{\text{c.v.}} = 0$. We further assume that changes in kinetic and potential energy are negligible. Therefore, the statement of the first law for this process reduces to

$$m_i h_i = m_2 u_2$$

From the continuity equation for this process, Eq. 6.20, we conclude that

$$m_2 = m_i$$

Therefore, combining the continuity equation with the first law, we have

$$h_i = u_2$$

That is, the final internal energy of the steam in the tank is equal to the enthalpy of the steam entering the tank.

Solution

From the steam tables

$$h_i = u_2 = 3040.4 \text{ kJ/kg}$$

Since the final pressure is given as 1.4 MPa, we know two properties at the final state and therefore the final state is determined. The temperature corresponding to a pressure of 1.4 MPa and an internal energy of 3040.4 kJ/kg is found to be 452°C. Had this problem involved a substance for which internal energies are not listed in the thermodynamic tables, it would have been necessary to calculate a few values for u before the final temperature could be interpolated. The same comment applies when using computer-based tables in which u and P are not a given table entry pair.

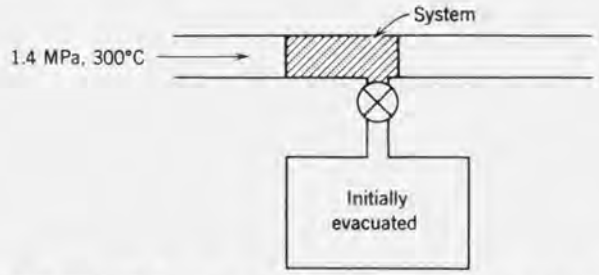


FIGURE 6.13 Flow into an evacuated vessel—system analysis.

This problem can also be solved by considering the steam that enters the tank and the evacuated space as a system, as indicated in Fig. 6.13.

The process is adiabatic, but we must examine the boundaries for work. If we visualize a piston between the steam that is included in the system and the steam that flows behind, we readily recognize that the boundaries of the system move and that the steam in the pipe does work on the steam that comprises the system. The amount of this work is

$$-W = P_1 V_1 = mP_1 v_1$$

Writing the first law for the system, Eq. 5.11, and noting that kinetic and potential energies can be neglected, we have

$$\begin{aligned} {}_1Q_2 &= U_2 - U_1 + {}_1W_2 \\ 0 &= U_2 - U_1 - P_1 V_1 \\ 0 &= mu_2 - mu_1 - mP_1 v_1 = mu_2 - mh_1 \end{aligned}$$

Therefore,

$$u_2 = h_1$$

which is the same conclusion that was reached using a control volume analysis.

The two following examples illustrate further the uniform-state, uniform-flow process.

EXAMPLE 6.10

Let the tank of the previous example have a volume of 0.4 m^3 and initially contain saturated vapor at 350 kPa. The valve is then opened and steam from the line at 1.4 MPa, 300°C, flows into the tank until the pressure is 1.4 MPa.

Calculate the mass of steam that flows into the tank.

Control volume: Tank, as in Fig. 6.12.

Initial state: P_1, saturated vapor; state fixed.

Final state: P_2.

Inlet state: P_i, T_i; state fixed.

Process: USUF.

Model: Steam tables.

Analysis: Same as in Example 6.9, except that the tank is not evacuated initially. Again, we note that $Q_{c.v.} = 0$, $W_{c.v.} = 0$, $m_e = 0$, and we assume that changes in kinetic energy and potential energy are zero. The statement of the first law for this process, Eq. 6.21, reduces to

$$m_i h_i = m_2 u_2 - m_1 u_1$$

The continuity equation, Eq. 6.20, reduces to

$$m_2 - m_1 = m_i$$

Therefore, combining the continuity equation and the first law, we have

$$(m_2 - m_1)h_i = m_2 u_2 - m_1 u_1$$

$$m_2(h_i - u_2) = m_1(h_i - u_1) \tag{a}$$

There are two unknowns in this equation—m_2 and u_2. However, we have one additional equation:

$$m_2 v_2 = V = 0.4 \text{ m}^3 \tag{b}$$

Substituting (b) into (a) and rearranging, we have

$$\frac{V}{v_2}(h_i - u_2) - m_1(h_i - u_1) = 0 \tag{c}$$

in which the only unknowns are v_2 and u_2, both functions of T_2 and P_2. Because T_2 is unknown, there is only one value of T_2 for which Eq. c will be satisfied. We must find it by trial and error.

Solution

$$v_1 = 0.5242 \text{ m}^3/\text{kg}, \qquad m_1 = \frac{0.4}{0.5242} = 0.763 \text{ kg}$$

$$h_i = 3040.4 \text{ kJ/kg}, \qquad u_1 = 2548.9 \text{ kJ/kg}$$

Assume

$$T_2 = 342°\text{C}$$

For this temperature and the known value of P_2,

$$v_2 = 0.1974 \text{ m}^3/\text{kg}, \qquad u_2 = 2855.8 \text{ kJ/kg}$$

Substituting into (c), we have

$$\frac{0.4}{0.1974}(3040.4 - 2855.8) - 0.763(3040.4 - 2548.9) \simeq 0$$

We conclude that the assumed value for $T_2 = 342°\text{C}$ is correct. The final mass inside the tank is

$$m_2 = \frac{0.4}{0.1974} = 2.026 \text{ kg}$$

and the mass of steam that flows into the tank is

$$m_i = m_2 - m_1 = 2.026 - 0.763 = 1.263 \text{ kg}$$

EXAMPLE 6.11

A tank of 2-m^3 volume contains saturated ammonia at a temperature of 40°C. Initially the tank contains 50 percent liquid and 50 percent vapor by volume. Vapor is withdrawn from the top of the tank until the temperature is 10°C. Assuming that only vapor (that is, no liquid) leaves and that the process is adiabatic, calculate the mass of ammonia that is withdrawn.

Control volume: Tank.

Initial state: T_1, V_{liq}, V_{vap}; state fixed.

Final state: T_2.

Exit state: Saturated vapor (temperature changing).

Process: USUF

Model: Ammonia tables.

Analysis: In the first law, Eq. 6.21, we note that $Q_{c.v.} = 0$, $W_{c.v.} = 0$, $m_i = 0$, and we assume that changes in kinetic and potential energy are negligible. However, the enthalpy of saturated vapor varies with temperature, and therefore we cannot simply assume that the enthalpy of the vapor leaving the tank remains constant. We note that at 40°C, $h_g = 1470.3$ kJ/kg, and at 10°C, $h_g = 1452.2$ kJ/kg. Since the change in h_g during this process is small, we may accurately assume that h_e is the average of the two values just given. Therefore,

$$(h_e)_{av} = 1461.2 \text{ kJ/kg}$$

and the first law reduces to

$$m_e h_e + m_2 u_2 - m_1 u_1 = 0$$

and the continuity equation (from Eq. 6.20),

$$(m_2 - m_1)_{c.v.} + m_e = 0$$

Combining these two equations, we have

$$m_2(h_e - u_2) = m_1 h_e - m_1 u_1$$

Solution

The following values are from the ammonia tables:

$$v_{f1} = 0.001\,725 \text{ m}^3/\text{kg}, \qquad v_{g1} = 0.083\,13 \text{ m}^3/\text{kg}$$
$$v_{f2} = 0.001\,60, \qquad v_{g2} = 0.205\,53$$
$$u_{f1} = 368.8 \text{ kJ/kg}$$
$$u_{g1} = 1341.1$$
$$u_{f2} = 226.1$$
$$u_{g2} = 1325.8$$
$$u_{fg2} = 1325.8 - 226.1 = 1099.7$$

Calculating first the initial mass, m_1, in the tank, we find that the mass of the liquid initially present, m_{f1}, is

$$m_{f1} = \frac{1.0}{0.001\ 725} = 579.7 \text{ kg}$$

Similarly, the initial mass of vapor, m_{g1}, is

$$m_{g1} = \frac{1.0}{0.083\ 13} = 12.0 \text{ kg}$$

Therefore,

$$\begin{aligned} m_1 &= m_{f1} + m_{g1} = 579.7 + 12.0 = 591.7 \text{ kg} \\ m_1 h_e &= 591.7 \times 1461.2 = 864\ 592 \text{ kJ} \\ m_1 u_1 &= (mu)_{f1} + (mu)_{g1} = 579.7 \times 368.8 + 12.0 \times 1341.1 \\ &= 229\ 945 \text{ kJ} \end{aligned}$$

Substituting these numbers into the first law, we have

$$m_2(h_e - u_2) = m_1 h_e - m_1 u_1 = 864\ 592 - 229\ 945 = 634\ 647 \text{ kJ}$$

There are two unknowns, m_2 and u_2, in this equation. However,

$$m_2 = \frac{V}{v_2} = \frac{2.0}{0.001\ 60 + x_2(0.203\ 93)}$$

and

$$u_2 = 226.1 + x_2(1099.7)$$

Both are functions only of x_2, the quality at the final state. Consequently,

$$\frac{2.0(1461.2 - 226.1 - 1099.7x_2)}{0.001\ 60 + 0.203\ 93x_2} = 634\ 647$$

Solving gives

$$x_2 = 0.011\ 05$$

Therefore,

$$v_2 = 0.001\ 60 + 0.011\ 05 \times 0.203\ 93 = 0.003\ 853 \text{ m}^3/\text{kg}$$

$$m_2 = \frac{2}{0.003\ 853} = 519.0 \text{ kg}$$

and the mass of ammonia withdrawn, m_e, is

$$m_e = m_1 - m_2 = 591.7 - 519.0 = 72.7 \text{ kg}$$

PROBLEMS

6.1 Air at 35°C, 105 kPa, flows in a 100 mm × 150 mm rectangular duct in a heating system. The volumetric flow rate is 0.015 m^3/s. What is the velocity of the air flowing in the duct?

6.1E Air at 95 F, 16 $lbf/in.^2$, flows in a 4 in. × 6 in. rectangular duct in a heating system. The volumetric flow rate is 30 cfm (ft^3/min). What is the velocity of the air flowing in the duct?

6.2 Nitrogen gas flowing in a 50-mm-diameter pipe at 15°C, 200 kPa, at the rate of 0.05 kg/s, encounters a partially closed valve. If there is a pressure drop of 30 kPa across the valve and essentially no temperature change, what are the velocities upstream and downstream of the valve?

6.3 Saturated vapor R-22 leaves the evaporator in a heat pump system at 10°C, with a steady mass flow rate of 0.2 kg/s. What is the smallest-diameter tubing that can be used at this location if the velocity of the refrigerant is not to exceed 10 m/s?

6.4 Nitrogen gas enters a steady-state, steady-flow heater at 600 kPa, 15°C, and exits at 550 kPa, 1200°C. Changes in kinetic and potential energies are negligible. Calculate the required heat transfer per kilogram of nitrogen flowing through the heater.

6.4E Nitrogen gas enters a steady-state, steady-flow heater at 90 $lbf/in.^2$, 60 F, and exits at 85 $lbf/in.^2$, 1800 F. Changes in kinetic and potential energies are negligible. Calculate the required heat transfer per pound-mass of nitrogen flowing through the heater.

6.5 The compressor of a large gas turbine receives air from the ambient at 95 kPa, 20°C, with a low velocity. At the compressor discharge, air exits at 1.52 MPa, 430°C, with a velocity of 90 m/s. The power input to the compressor is 5000 kW. Determine the mass flow rate of air through the unit.

6.6 The purpose of a nozzle is to produce a high-velocity stream of fluid (at the expense of its pressure). Superheated vapor ammonia enters an insulated nozzle at 20°C, 800 kPa, with a low velocity and at the steady rate of 0.01 kg/s. The ammonia exits at 300 kPa with a velocity of 450 m/s. Determine the temperature (or quality, if saturated) and the exit area of the nozzle.

6.7 A small, high-speed turbine operating on compressed air produces a power output of 0.1 kW. The inlet state is 400 kPa, 25°C, and the exit state is 100 kPa, −50°C. Assuming the velocities to be low, find the required mass flow rate of air through the turbine.

6.7E A small, high-speed turbine operating on compressed air produces a power output of 0.1 hp. The inlet state is 60 $lbf/in.^2$, 70 F, and the exit state is 14.7 $lbf/in.^2$, −60 F. Assuming the velocities to be low, find the required mass flow rate of air through the turbine.

6.8 A number of years ago, a well-known architect proposed a preliminary design for a 1600-m-tall building. Suppose that in such a building steam for the heating system enters a pipe at ground level as saturated vapor at 200 kPa. On the top floor the pressure in the pipe is 100 kPa, and the heat transfer from the steam as it flows up the pipe is 100 kJ/kg. What is the quality of the steam at the top of the pipe?

6.9 Consider a power plant steam generator in which compressed-liquid water at 10 MPa, 30°C, enters a 30-mm-diameter tube at the rate of 3 L/s. Saturated vapor exits this tube at 9 MPa. Calculate the rate of heat transfer to the water.

6.9E Consider a power plant steam generator in which compressed-liquid water at 1000 lbf/in.^{2}, 100 F, enters a 1-in.-diameter tube at the rate of 5 ft^3/min. Saturated vapor exits this tube at 900 lbf/in.^{2}. Calculate the rate of heat transfer to the water.

6.10 Consider a steady-state, steady-flow mixing process in which compressed-liquid R-22 at 1.5 MPa, 10°C, is mixed with saturated-vapor R-22 at 1.5 MPa. The two inlet stream mass flow rates are each 0.1 kg/s, and exiting the mixer is a stream of R-22 at 1.2 MPa with a quality of 85 percent. Calculate the rate of heat transfer to or from the mixer during this process.

6.11 Two steady streams of air enter a control volume: one enters at point 1 at 350 kPa, 150°C, with low velocity at the rate of 0.025 kg/s; the other enters at point 2 at 350 kPa, 15°C, with low velocity. A single stream of air exits the control volume at point 3 at 100 kPa, −40°C, through a 25-mm-diameter pipe. The control volume rejects heat to the surroundings at the rate of 1.2 kW and produces 4.5 kW of power. Determine the flow rate of air entering the control volume at point 2.

6.12 In certain situations, when only superheated vapor steam at a given state is available, saturated steam may be needed for a specific purpose. Saturated steam can be created in a steady-flow desuperheater. Liquid water is sprayed into the superheated steam of the desuperheater in an amount appropriate to make the steam exiting the unit a saturated vapor. Consider such a desuperheater, in which superheated steam at 3.5 MPa, 400°C, enters at the rate of 0.5 kg/s, and liquid water enters the unit at 3.5 MPa, 40°C. If saturated vapor exits at 3 MPa, determine the rate at which liquid water must be put into the unit.

6.13 The following data are for a simple steam power plant, as shown in Fig. 6.14.

$P_1 = 6.2$ MPa.
$P_2 = 6.1$ MPa, $T_2 = 45°C$
$P_3 = 5.9$ MPa, $T_3 = 175°C$
$P_4 = 5.7$ MPa, $T_4 = 500°C$
$P_5 = 5.5$ MPa, $T_5 = 490°C$

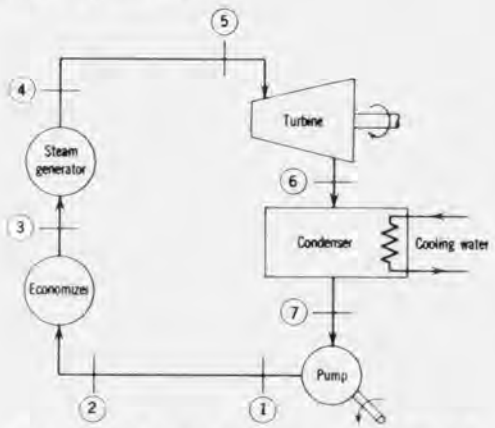


FIGURE 6.14 Sketch for Problems 6.13 and 6.13E.

$P_6 = 10$ kPa, $x_6 = 0.92$, $\mathbf{V}_6 = 200$ m/s
$P_7 = 9$ kPa, $T_7 = 40°C$.
Rate of steam flow = 25 kg/s
Power input to pump = 300 kW
Pipe diameters:
Steam generator to turbine: 200 mm
Condenser to steam generator: 75 mm

Calculate

(a) The power output of the turbine.
(b) Heat-transfer rates in the condenser, economizer, and steam generator.
(c) The flow rate of cooling water through the condenser, if the temperature of the cooling water increases from 15° to 25°C in the condenser.

6.13E The following data are for a simple steam power plant as shown in Fig. 6.14.

$P_1 = 900$ lbf/in.^{2}
$P_2 = 890$ lbf/in.^{2}, $T_2 = 115$ F
$P_3 = 860$ lbf/in.^{2}, $T_3 = 350$ F
$P_4 = 830$ lbf/in.^{2}, $T_4 = 920$ F
$P_5 = 800$ lbf/in.^{2}, $T_5 = 900$ F
$P_6 = 1.5$ lbf/in.^{2}, $x_6 = 0.92$, $\mathbf{V}_6 = 600$ ft/s
$P_7 = 1.4$ lbf/in.^{2}, $T_7 = 110$ F
Rate of steam flow = 200 000 lbm/h
Power input to pump = 400 hp
Pipe diameters:
Steam generator to turbine: 8 in.
Condenser to steam generator: 3 in.

Calculate

(a) The power output of the turbine.
(b) Heat-transfer rates in the condenser, economizer, and steam generator.
(c) The flow rate of cooling water through the condenser, if the temperature of the cooling water increases from 55 to 75 F in the condenser.

6.14 For a certain industrial process, it is necessary to have a 5-kg/s supply of steam at 0.5 MPa that contains no liquid. Rather than install a pump and a boiler solely for

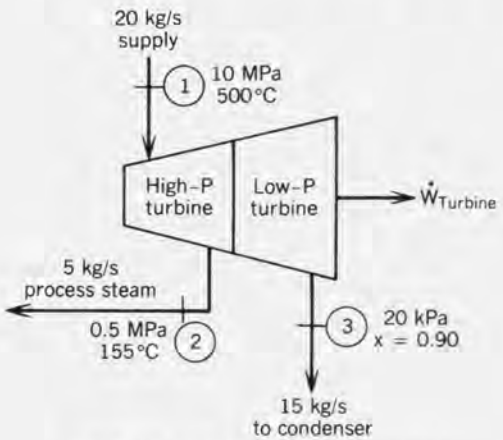


FIGURE 6.15 Sketch for Problem 6.14.

this purpose, the manufacturer decided to obtain it by cogeneration, that is, by bleeding the required steam from a steam turbine, which also produces power. The states are as shown in Fig. 6.15. Calculate the power output of the steam turbine in this cogeneration process.

6.15 A somewhat simplified flow diagram for the nuclear power plant shown in Fig. 1.5 is given in Fig. 6.16. Mass flow rates and the state of the water at various points in the cycle are shown in the accompanying table.

Point	m, kg/s	P, kPa	T, °C	h, kJ/kg
1	75.6	7240	Saturated vapor	
2	75.6	6900		2765
3	62.874	345		2517
4		310		
5		7		2279
6	75.6	7	33	
7		415		140
8	2.772	35		2459
9	4.662	310		558
10		35	54	
11	75.6	380	68	
12	8.064	345		2517
13	75.6	330		
14				349
15	4.662	965	139	584
16	75.6	7930		565
17	4.662	965		2593
18	75.6	7580		688
19	1386	7240	277	
20	1386	7410		1221
21	1386	7310		

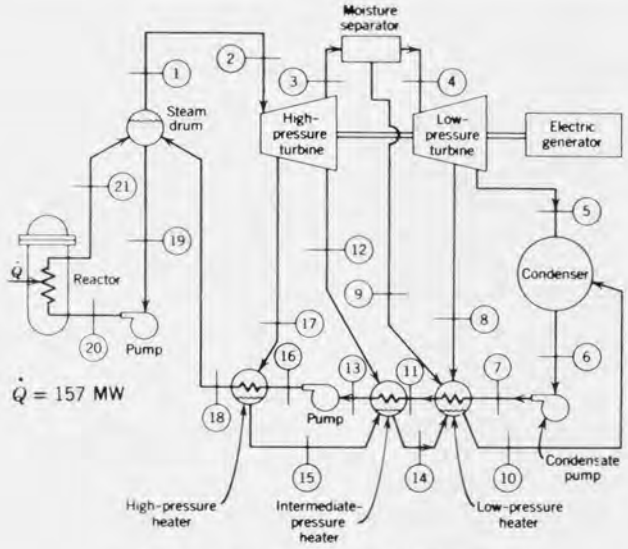


FIGURE 6.16 Sketch for Problem 6.15.

This cycle includes a number of "heaters," in which heat is transferred from steam, which leaves the turbine at some intermediate pressure, to liquid water, which is being pumped from the condenser to the steam drum. The rate of heat transfer to the water in the reactor is 157 MW.

(a) Assuming that there is no heat transfer from the moisture separator between the high-pressure and low-pressure turbines, determine the enthalpy per kilogram of steam and the quality of the steam entering the low-pressure turbine.

(b) Determine the power output of the high-pressure turbine. Assume no heat transfer from the steam as it flows through the turbine.

(c) Determine the power output of the low-pressure turbine. Assume no heat transfer from the steam as it flows through the turbine.

(d) Determine the quality of the steam leaving the reactor.

(e) Determine the temperature of the water leaving the intermediate-pressure heater. Assume no heat transfer from the heater to the surroundings.

(f) Determine the rate of heat transfer to the condenser cooling water.

(g) What is the ratio of the total power output of the two turbines to the heat transferred to the water in the reactor?

6.16 Helium is throttled from 1.2 MPa, 20 °C, to a pressure of 100 kPa. The diameter of the exit pipe is sufficiently larger than that of the inlet pipe to make the exit and inlet velocities equal. Determine the exit temperature of the helium and the ratio of the pipe diameters.

6.16E Helium is throttled from 175 lbf/in.^{2}, 70 F, to a pressure of 15 lbf/in.^{2}. The diameter of the exit pipe is sufficiently larger than that of the inlet pipe to make the exit and inlet velocities equal. Determine the exit temperature of the helium and the ratio of the pipe diameters.

6.17 Methane at 3 MPa, 300 K, is throttled to 100 kPa. Calculate the exit temperature assuming

(a) Ideal-gas behavior.
(b) Real-gas behavior.

6.18 Water at 1.5 MPa, 150°C, is throttled adiabatically through a valve to 200 kPa. The inlet velocity is 5 m/s, and the inlet and exit cross-sectional areas are the same Determine the state and velocity of the water at the exit.

6.19 A proposal is made to use a geothermal supply of hot water to operate a steam turbine, as shown in Fig. 6.17. The high-pressure water at 1.5 MPa, 180 °C, is throttled into an insulated flash evaporator, which forms liquid and vapor at a lower pressure, 400 kPa. The liquid exits at the bottom, while the vapor is drawn off and fed to the turbine as shown. Steam exits from the turbine at 10 kPa, 90 percent quality. If the turbine produces a power output of 1000 kW, how much hot water is required from the geothermal source per hour?

6.19E A proposal is made to use a geothermal supply of hot water to operate a steam turbine, as shown in Fig. 6.17. The high-pressure water at 200 lbf/in.^{2}, 350 F, is throttled into an insulated flash evaporator, which forms liquid and vapor at a lower pressure, 60 lbf/in.^{2}. The liquid exits at the bottom, while the vapor is drawn off and fed to the turbine as shown. Steam exits from the turbine at 1 lbf/in.^{2}, 90 percent quality. If the turbine produces a power output of 1000 hp, how much hot water is required from the geothermal source per hour?

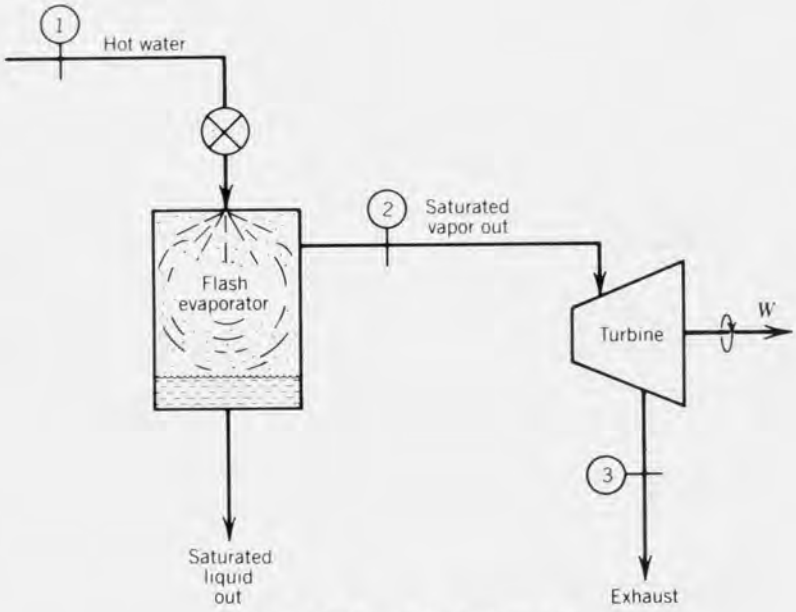


FIGURE 6.17 Sketch for Problem 6.19.

6.20 A small steam turbine operating at part load produces a 110-kW output with a steam flow rate of 0.25 kg/s. Steam at 1.4 MPa, 250°C, is throttled to 1.1 MPa before it enters the turbine. The turbine exhaust pressure is 10 kPa. Find the steam quality (or temperature, if superheated) at the turbine outlet.

6.21 The following data are for the R-12 heat pump cycle shown in Fig. 6.18.

$P_1 = 1250$ kPa, $T_1 = 120°C$
$P_2 = 1230$ kPa, $T_2 = 110°C$
$P_3 = 1200$ kPa, $T_3 = 45°C$
$P_4 = 320$ kPa.
$P_5 = 300$ kPa, $T_5 = 0°C$
$P_6 = 290$ kPa, $T_6 = 5°C$
Rate of flow of R-12 = 0.05 kg/s
Power input to compressor = 4 kW

Calculate

(a) The heat transfer from the compressor.
(b) The heat transfer from the R-12 in the condenser.
(c) The heat transfer to the R-12 in the evaporator.

6.22 A 25-L rigid tank that is initially evacuated is connected by a valve to an air supply line flowing air at 20°C, 800 kPa. The valve is opened, and air flows into the tank until the pressure inside reaches 600 kPa.

(a) Determine the final temperature and mass inside the tank. Assume that the process is adiabatic.

(b) Develop an expression for the relation between the line temperature and the final temperature in the tank.

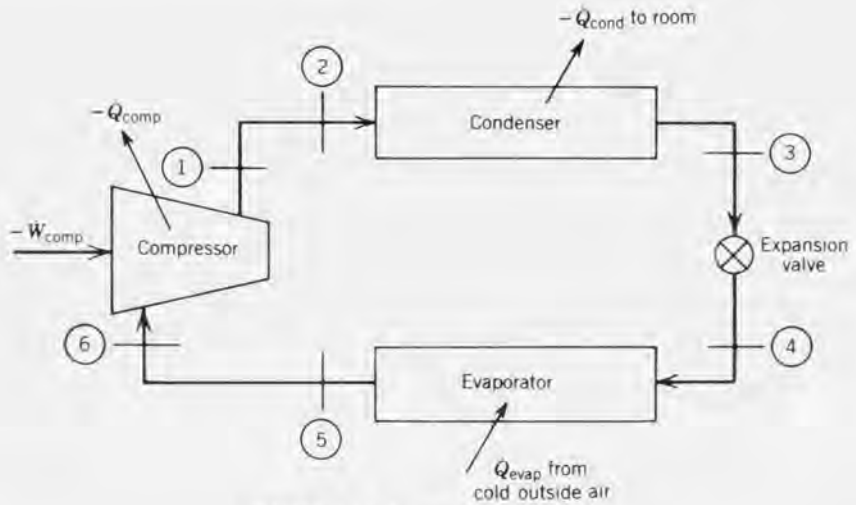


FIGURE 6.18 Sketch for Problem 6.21.

6.22E A 1-ft^3 rigid tank that is initially evacuated is connected by a valve to an air supply line flowing air at 70 F, 120 lbf/in.^{2}. The valve is opened, and air flows into the tank until the pressure inside reaches 90 lbf/in.^{2}.

(a) Determine the final temperature and mass inside the tank. Assume that the process is adiabatic.

(b) Develop an expression for the relation between the line temperature and the final temperature in the tank.

6.23 A 2-m^3 insulated tank containing ammonia at -20°C, 80 percent quality, is connected by a valve to a line flowing ammonia at 2 MPa, 60°C. The valve is opened, allowing ammonia to flow into the tank. At what pressure should the valve be closed if the manufacturer wishes to have 15 kg of ammonia inside at the final state?

6.24 A tank having a volume of 5 m^3 contains saturated vapor steam at a pressure of 200 kPa. Attached to this tank is a line flowing steam at 800 kPa, 300°C. The valve is opened, and steam flows into the tank until the pressure inside reaches 800 kPa. At this point the valve is closed. If there is no heat transfer from the tank during this process, find the mass of steam that enters the tank.

6.25 A 100-L rigid tank contains carbon dioxide gas at 1 MPa, 300 K. A valve is cracked open, and carbon dioxide escapes slowly until the tank pressure has dropped to 500 kPa. At this point the valve is closed. The gas remaining inside the tank may be assumed to have undergone a polytropic expansion, with polytropic exponent $n = 1.15$. Find the final mass inside and the heat transferred to the tank during the process.

6.26 A 1-m^3 tank contains ammonia at 150 kPa, 25°C. The tank is attached to a line flowing ammonia at 1200 kPa, 60°C. The valve is opened, and mass flows in until the tank is half full of liquid, by volume, at 25°C. Calculate the heat transferred from the tank during this process.

6.26E A 20-ft^3 tank contains ammonia at 20 lbf/in.^{2}, 80 F. The tank is attached to a line flowing ammonia at 180 lbf/in.^{2}, 140 F. The valve is opened, and mass flows in until

the tank is half full of liquid, by volume, at 80 F. Calculate the heat transferred from the tank during this process.

6.27 An evacuated 150-L tank is connected to a line flowing air at room temperature, 25°C, and 8-MPa pressure. The valve is opened, allowing air to flow into the tank until the pressure inside reaches 6 MPa. At this point the valve is closed. This filling process occurs rapidly and is essentially adiabatic. The tank is then allowed to sit for a long time with the valve closed, and eventually it returns to room temperature. What is the final pressure inside?

6.28 A 500-L insulated tank contains air at 40°C, 2 MPa. A valve on the tank is opened, and air escapes until half the original mass is gone, at which point the valve is closed. What is the pressure inside at this time?

6.29 A steam power plant proposed for an automotive vehicle is shown in Fig. 6.19. The boiler has a volume of 50 L and initially contains 90 percent liquid and 10 percent vapor by volume at 100 kPa. The burner is turned on, and when the pressure in the boiler reaches 700 kPa, the pressure-regulating valve holds the boiler pressure constant at this value. Saturated vapor at this pressure passes to the turbine. Saturated-vapor steam at 100 kPa exits the turbine and is discharged to the atmosphere. When the liquid in the boiler is depleted, the burner shuts off automatically. Find the total work output of the turbine and the total heat transfer for one charge of the boiler.

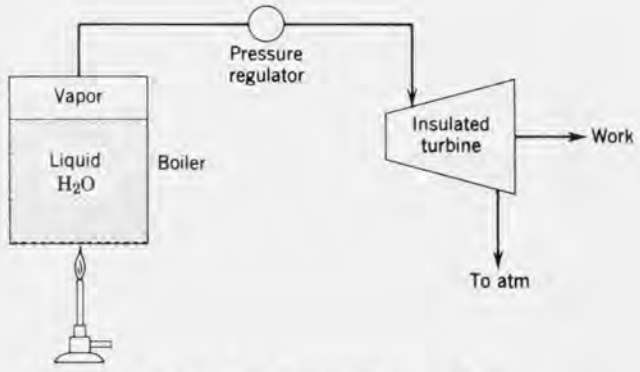


FIGURE 6.19 Sketch for Problem 6.29.

6.30 Air is contained in the insulated cylinder shown in Fig. 6.20. At this point the air is at 140 kPa, 25°C, and the cylinder volume is 15 L. The piston cross-sectional area is 0.045 m^2, and the spring force varies linearly with distance moved. The spring constant is 35 kN/m. The valve is opened, and air from the line at 700 kPa, 25°C, flows into the cylinder until the pressure inside reaches 700 kPa. At this point the valve is closed. What is the temperature inside the cylinder at the final state?

6.30E Air is contained in the insulated cylinder shown in Fig. 6.20. At this point the air is at 20 lbf/in.^{2}, 80 F, and the cylinder volume is 0.5 ft^3. The piston cross-sectional area is 0.5 ft^2, and the spring force varies linearly with distance moved. The spring constant is 200 lbf/in. The valve is opened, and air from the line at 100 lbf/in.^{2}, 80 F, flows into the cylinder until the pressure inside reaches 100 lbf/in.^{2}. At this point the valve is closed. What is the temperature inside the cylinder at the final state?

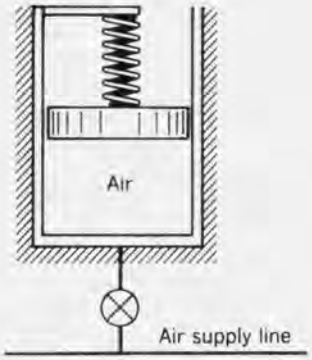


FIGURE 6.20 Sketch for Problems 6.30 and 6.30E.

6.31 A 2-m^3 insulated vessel contains saturated vapor steam at 4-MPa pressure. A valve on the top of the tank is opened, and steam is allowed to escape. During the process any liquid formed collects at the bottom of the vessel, so that only saturated vapor exits. Calculate the total mass that has escaped when the pressure inside reaches 1.0 MPa.

6.32 A 1-m^3 insulated, rigid steel tank having a mass of 40 kg contains air at 500 kPa, and both the tank and the air are at 20°C. The tank is connected by a valve to a line flowing air at 2 MPa, 20°C. The valve is opened, allowing air to flow into the tank until the pressure reaches 1.5 MPa, at which point the valve is closed. Assuming that the tank and the air inside are always at the same temperature, find the final temperature, at the moment when the valve is closed.

6.32E A 35-ft^3 insulated, rigid steel tank having a mass of 90 lbm contains air at 75 $lbf/in.^2$, and both the tank and the air are at 70 F. The tank is connected by a valve to a line flowing air at 300 $lbf/in.^2$, 70 F. The valve is opened, allowing air to flow into the tank until the pressure reaches 250 $lbf/in.^2$, at which point the valve is closed. Assuming that the tank and the air inside are always at the same temperature, find the final temperature at the moment when the valve is closed.

6.33 A certain elastic balloon supports an internal pressure equal to $P_0 = 100$ kPa until the balloon becomes spherical at a diameter of $D_0 = 1$ m. Above this diameter

$$P = P_0 + C(D^{*-1} - D^{*-7}), \qquad D^* = \frac{D}{D_0}$$

because of the offsetting effects of balloon curvature and elasticity. This balloon, initially flat and deflated, is connected to a supply line flowing saturated vapor R-22 at an ambient temperature of 10°C. The valve is opened, and the balloon slowly inflates at constant temperature to a final diameter of 2 m. During this process the maximum pressure inside the balloon at any point is measured to be 500 kPa. Calculate the heat transfer to or from the balloon during this inflation process.

6.34 A 750-L rigid tank initially contains water at 250°C, 50 percent liquid and 50 percent vapor, by volume. A valve on the bottom of the tank is opened, and liquid is withdrawn slowly. During the process enough heat is transferred that the temperature inside remains constant. Calculate the amount of heat transferred by the time half the initial mass has been withdrawn.

6.35 A cylinder fitted with a piston restrained by a linear spring contains 1 kg of R-12 at 100°C, 800 kPa. The spring constant is 50 kN/m, and the piston cross-sectional area is 0.05 m^2. A valve on the cylinder is opened and R-12 flows out. During this process enough heat is transferred that when half the initial mass has escaped, the temperature inside the cylinder is 10°C. Find

(a) The final state inside the cylinder.
(b) The heat transfer to or from the cylinder.

6.35E A cylinder fitted with a piston restrained by a linear spring contains 2 lbm of R-12 at 220 F, 125 lbf/in.^{2}. The spring constant is 285 lbf/in., and the piston cross-sectional area is 75 in.^{2}. A valve on the cylinder is opened and R-12 flows out. During this process enough heat is transferred that when half the initial mass has escaped, the temperature inside the cylinder is 50 F. Find

(a) The final state inside the cylinder.
(b) The heat transfer to or from the cylinder.

6.36 Liquids are often transferred from storage by pressurization with a gas. As an example of this procedure, consider the process shown in Fig. 6.21, in which tanks *A* and *B* both contain R-12. Tank *A* has a volume of 90 L and *B* has a volume of 75 L. The R-12 in *A* is initially at 25°C, saturated vapor, and that in *B* is at −40°C with a quality of 0.01. The valve is opened slightly, allowing gas to flow from *A* to *B*. When the pressure inside *B* has built up to 150 kPa, liquid begins to flow out. The liquid transfer continues until the pressure in *A* has dropped to 150 kPa. During the process enough heat is transferred to the gas inside tank *A* that its temperature always remains at 25°C. Tank *B* is insulated. Determine

(a) The quality in tank *B* at the end of the process.
(b) The mass of liquid transferred from tank *B*.

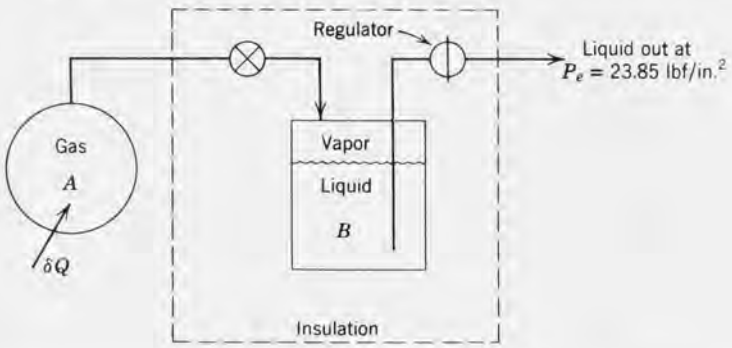


FIGURE 6.21 Sketch for Problem 6.36.

6.37 A 2-m^3 storage tank contains 90 percent liquid and 10 percent vapor, by volume, of liquified natural gas (LNG) at 160 K, as shown in Fig. 6.22. It may be assumed that LNG has the same properties as pure methane. Heat is transferred to the tank, and saturated vapor at 160 K flows into a steady-flow heater in which the vapor is heated at constant pressure to 300 K. The process continues until all the liquid in the storage tank is gone. Calculate the total amount of heat transferred to the tank and the total amount of heat transferred to the heater.

6.38 An uninsulated cylinder is fitted with a frictionless piston that is restrained by a variable external force. The cylinder initially contains 0.5 kg of water at 100 kPa,

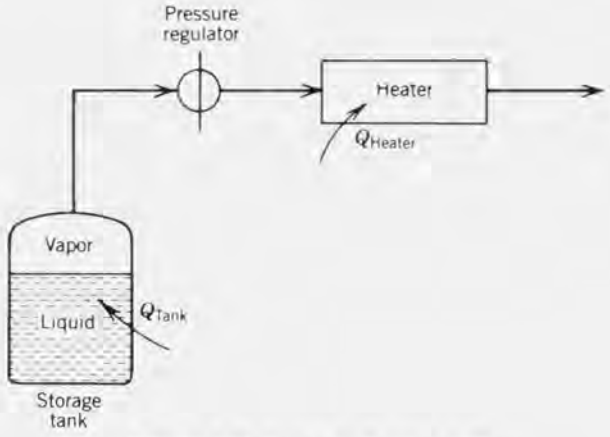


FIGURE 6.22 Sketch for Problem 6.37.

30 percent quality. A valve is opened to a line flowing steam at 2 MPa, 400°C, and steam flows into the cylinder. It is noted that when the cylinder volume is twice its initial value, the pressure inside the cylinder is 400 kPa. When the cylinder pressure reaches 1 MPa, the valve is closed, at which point the cylinder contains 3 kg of H_2O. During this process there is a heat transfer of 75 kJ from the cylinder to the ambient. Determine the final temperature inside the cylinder.

COMPUTER PROBLEMS

6.1C An insulated tank of volume V contains a specified ideal gas (with constant specific heat) at P_1, T_1. A valve is opened, allowing the gas to flow out until the pressure inside drops to P_2. Determine T_2 and m_2 using a stepwise solution in increments of pressure between P_1 and P_2; the number of increments is variable.

6.2C Write a program to solve the general case of Problem 6.8, in which all the parameters given in the problem are input variables.

6.3C Write a program to solve the general case of Problem 6.23, in which the final mass inside the tank is specified as a program input parameter.

6.4C We wish to solve Problem 6.31 using a stepwise solution, whereby the process is subdivided into several parts to minimize the effects of a linear average enthalpy approximation. Write a program to solve this problem, making the number of steps in the solution an input variable.

6.5C Write a program to solve the general case of the balloon inflation of Problem 6.33, using ammonia as the working fluid. Follow the path of the ammonia inside the balloon at all diameters during the process, and determine the pressure, the work, and the heat transfer up to this point.

6.6C Repeat Problem 6.5C, assuming that the balloon inflation process is adiabatic instead of isothermal.

6.7C Write a program to solve Problem 6.38, incorporating an empirical smooth curve for the relation between cylinder pressure and volume throughout the process.

7

THE SECOND LAW OF THERMODYNAMICS

The first law of thermodynamics states that during any cycle that a system undergoes, the cyclic integral of the heat is equal to the cyclic integral of the work. The first law, however, places no restrictions on the direction of flow of heat and work. A cycle in which a given amount of heat is transferred from the system and an equal amount of work is done on the system satisfies the first law just as well as a cycle in which the flows of heat and work are reversed. However, we know from our experience that because a proposed cycle does not violate the first law does not ensure that the cycle will actually occur. It is this kind of experimental evidence that led to the formulation of the second law of thermodynamics. Thus, a cycle will occur only if both the first and second laws of thermodynamics are satisfied.

In its broader significance the second law acknowledges that processes proceed in a certain direction but not in the opposite direction. A hot cup of coffee cools by virtue of heat transfer to the surroundings, but heat will not flow from the cooler surroundings to the hotter cup of coffee. Gasoline is used as a car drives up a hill, but the fuel level in the gasoline tank cannot be restored to its original level when the car coasts down the hill. Such familiar observations as these, and a host of others, are evidence of the validity of the second law of thermodynamics.

In this chapter, we consider the second law for a system undergoing a cycle, and in the next two chapters we extend the principles to a system undergoing a change of state and then to a control volume.

7.1 HEAT ENGINES AND REFRIGERATORS

Consider the system and the surroundings previously cited in the development of the first law, as shown in Fig. 7.1. Let the gas constitute the system and, as in our discussion of the first law, let this system undergo a cycle in which work is first done on the system by the paddle wheel as the weight is lowered. Then let the cycle be completed by transferring heat to the surroundings.

We know from our experience that we cannot reverse this cycle. That is, if we transfer heat to the gas, as shown by the dotted arrow, the temperature of the gas will increase, but the paddle wheel will not turn and raise the weight. With the given surroundings (the container, the paddle wheel, and the weight) this system can operate in a cycle in which the heat transfer and work are both negative, but

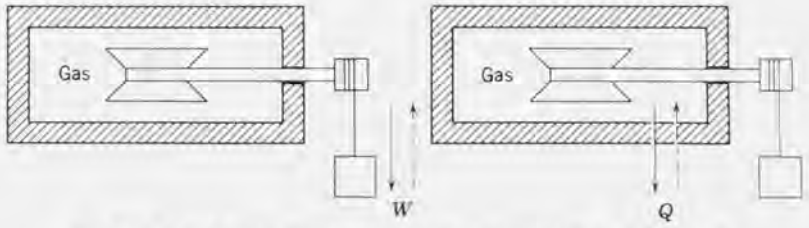


FIGURE 7.1 A system that undergoes a cycle involving work and heat.

it cannot operate in a cycle in which both the heat transfer and work are positive, even though this would not violate the first law.

Consider another cycle, which we know from our experience is impossible actually to complete. Let two systems, one at a high temperature and the other at a low temperature, undergo a process in which a quantity of heat is transferred from the high-temperature system to the low-temperature system. We know that this process can take place. We also know that the reverse process, in which heat is transferred from the low-temperature system to the high-temperature system, does not occur, and that it is impossible to complete the cycle by heat transfer only. This impossibility is illustrated in Fig. 7.2.

These two examples lead us to a consideration of the heat engine and the refrigerator, which is also referred to as a heat pump. With the heat engine we can have a system that operates in a cycle and performs a net positive work and a net positive heat transfer. With the heat pump we can have a system that operates in a cycle and has heat transferred to it from a low-temperature body and heat transferred from it to a high-temperature body, though work is required to do this. Three simple heat engines and two simple refrigerators will be considered.

The first heat engine is shown in Fig. 7.3. It consists of a cylinder fitted with appropriate stops and a piston. Let the gas in the cylinder constitute the system. Initially the piston rests on the lower stops, with a weight on the platform. Let the system now undergo a process in which heat is transferred from some high-temperature body to the gas, causing it to expand and raise the piston to the upper stops. At this point the weight is removed. Now let the system be restored to its initial state by transferring heat from the gas to a low-temperature body, thus

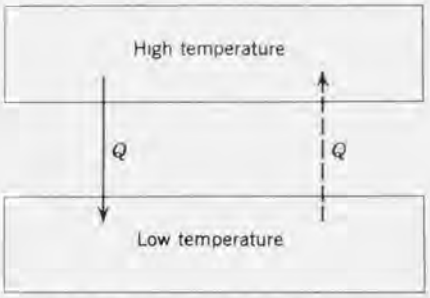


FIGURE 7.2 An example showing the impossibility of completing a cycle by transferring heat from a low-temperature body to a high-temperature body.

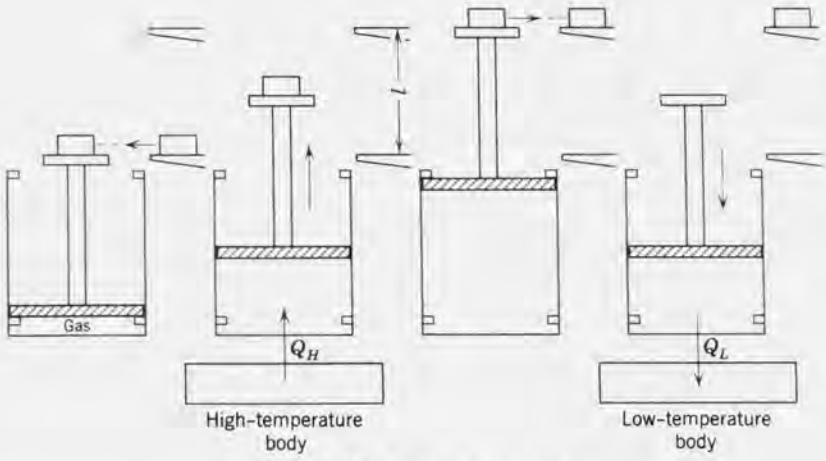


FIGURE 7.3 A simple heat engine.

completing the cycle. Since the weight was raised during the cycle, it is evident that work was done by the gas during the cycle. From the first law we conclude that the net heat transfer was positive and equal to the work done during the cycle.

Such a device is called a heat engine, and the substance to which and from which heat is transferred is called the working substance or working fluid. A heat engine may be defined as a device that operates in a thermodynamic cycle and does a certain amount of net positive work through the transfer of heat from a high-temperature body and to a low-temperature body. Often the term heat engine is used in a broader sense to include all devices that produce work, either through heat transfer or through combustion, even though the device does not operate in a thermodynamic cycle. The internal-combustion engine and the gas turbine are examples of such devices, and calling them heat engines is an acceptable use of the term. In this chapter, however, we are concerned with the more restricted form of heat engine, as just defined, one which operates on a thermodynamic cycle.

A simple steam power plant is an example of a heat engine in this restricted sense. Each component in this plant may be analyzed individually as a steady-state, steady-flow process, but as a whole it may be considered a heat engine (Fig. 7.4) in which water (steam) is the working fluid. An amount of heat, Q_H, is transferred from a high-temperature body, which may be the products of combustion in a furnace, a reactor, or a secondary fluid that in turn has been heated in a reactor. In Fig. 7.4 the turbine is shown schematically as driving the pump. What is significant, however, is the net work that is delivered during the cycle. The quantity of heat Q_L is rejected to a low-temperature body, which is usually the cooling water in a condenser. Thus, the simple steam power plant is a heat engine in the restricted sense, for it has a working fluid, to which and from which heat is transferred, and which does a certain amount of work as it undergoes a cycle.

Another example of a heat engine is the thermoelectric power generation device that was discussed in Chapter 1 and shown schematically in Fig. 1.11. Heat is transferred from a high-temperature body to the hot junction (Q_H), and heat is transferred from the cold junction to the surroundings (Q_L). Work is done in the

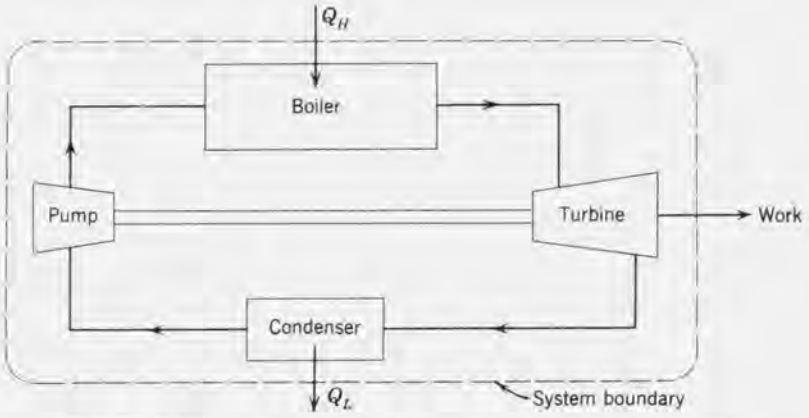


FIGURE 7.4 A heat engine involving steady-state, steady-flow processes.

form of electrical energy. Since there is no working fluid, we do not usually think of this as a device that operates in a cycle. However, if we adopt a microscopic point of view, we could regard a cycle as the flow of electrons. Furthermore, as with the steam power plant, the state at each point in the thermoelectric power generator does not change with time under steady-state conditions.

Thus, by means of a heat engine, we are able to have a system operate in a cycle and have both the net work and the net heat transfer positive, which we were not able to do with the system and surroundings of Fig. 7.1.

We note that in using the symbols Q_H and Q_L, we have departed from our sign connotation for heat, because for a heat engine Q_L is negative when the working fluid is considered as the system. In this chapter it will be advantageous to use the symbol Q_H to represent the heat transfer to or from the high-temperature body, and Q_L to represent the heat transfer to or from the low-temperature body. The direction of the heat transfer will be evident from the context.

At this point it is appropriate to introduce the concept of thermal efficiency of a heat engine. In general, we say that efficiency is the ratio of output, the energy sought, to input, the energy that costs, but these output and input must be clearly defined. At the risk of oversimplification, we may say that in a heat engine the energy sought is the work, and the energy that costs money is the heat from the high-temperature source (indirectly, the cost of the fuel). Thermal efficiency is defined as

$$\eta_{\text{thermal}} = \frac{W(\text{energy sought})}{Q_H(\text{energy that costs})} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \tag{7.1}$$

The second cycle that we were not able to complete was the one indicating the impossibility of transferring heat directly from a low-temperature body to a high-temperature body. This can of course be done with a refrigerator or heat pump. A vapor-compression refrigerator cycle, which was introduced in Chapter 1 and shown in Fig. 1.8, is shown again in Fig. 7.5. The working fluid is the refrigerant, such as R-12 or ammonia, which goes through a thermodynamic cycle. Heat is

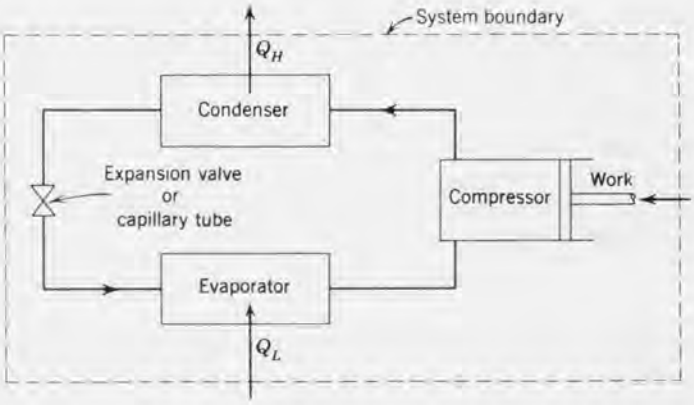


FIGURE 7.5 A simple refrigeration cycle.

transferred to the refrigerant in the evaporator, where its pressure and temperature are low. Work is done on the refrigerant in the compressor and heat is transferred from it in the condenser, where its pressure and temperature are high. The pressure drops as the refrigerant flows through the throttle valve or capillary tube.

Thus, in a refrigerator or heat pump, we have a device that operates in a cycle, that requires work, and that accomplishes the objective of transferring heat from a low-temperature body to a high-temperature body.

The thermoelectric refrigerator, which was discussed in Chapter 1 and is shown schematically in Fig. 1.10, is another example of a device that meets our definition of a refrigerator. The work input to the thermoelectric refrigerator is in the form of electrical energy, and heat is transferred from the refrigerated space to the cold junction (Q_L) and from the hot junction to the surroundings (Q_H).

The "efficiency" of a refrigerator is expressed in terms of the coefficient of performance, which we designate with the symbol β. For a refrigerator the objective, that is, the energy sought, is Q_L, the heat transferred from the refrigerated space. The energy that costs is the work W. Thus, the coefficient of performance, β,[1] is

$$\beta = \frac{Q_L(\text{energy sought})}{W(\text{energy that costs})} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1} \tag{7.2}$$

[1] It should be noted that a refrigeration or heat pump cycle can be used with either of two objectives. It can be used as a refrigerator, in which case the primary objective is Q_L, the heat transferred to the refrigerant from the refrigerated space. It can also be used as a heating system (in which case it is usually referred to as a heat pump), the objective being Q_H, the heat transferred from the refrigerant to the high-temperature body, which is the space to be heated. Q_L is transferred to the refrigerant from the ground, the atmospheric air, or well water. The coefficient of performance for this case, β' is

$$\beta' = \frac{Q_H(\text{energy sought})}{W(\text{energy that costs})} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$

It also follows that for a given cycle,

$$\beta' - \beta = 1$$

Unless otherwise specified, the term coefficient of performance will always refer to a refrigerator as defined by Eq. 7.2.

Before we state the second law, the concept of a thermal reservoir should be introduced. A thermal reservoir is a body to which and from which heat can be transferred indefinitely without change in the temperature of the reservoir. Thus, a thermal reservoir always remains at constant temperature. The ocean and the atmosphere approach this definition very closely. Frequently it will be useful to designate a high-temperature reservoir and a low-temperature reservoir. Sometimes a reservoir from which heat is transferred is called a source, and a reservoir to which heat is transferred is called a sink.

7.2 SECOND LAW OF THERMODYNAMICS

On the basis of the matter considered in the previous section, we are now ready to state the second law of thermodynamics. There are two classical statements of the second law, known as the Kelvin–Planck statement and the Clausius statement.

The Kelvin–Planck statement: It is impossible to construct a device that will operate in a cycle and produce no effect other than the raising of a weight and the exchange of heat with a single reservoir.

This statement ties in with our discussion of the heat engine. In effect, it states that it is impossible to construct a heat engine that operates in a cycle, receives a given amount of heat from a high-temperature body, and does an equal amount of work. The only alternative is that some heat must be transferred from the working fluid at a lower temperature to a low-temperature body. Thus, work can be done by the transfer of heat only if there are two temperature levels, and heat is transferred from the high-temperature body to the heat engine and also from the heat engine to the low-temperature body. This implies that it is impossible to build a heat engine that has a thermal efficiency of 100 percent.

The Clausius statement: It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.

This statement is related to the refrigerator or heat pump. In effect, it states that it is impossible to construct a refrigerator that operates without an input of work. This also implies that the coefficient of performance is always less than infinity.

Three observations should be made about these two statements. The first observation is that both are negative statements. It is of course impossible to "prove" a negative statement. However, we can say that the second law of thermodynamics (like every other law of nature) rests on experimental evidence. Every relevant experiment that has been conducted either directly or indirectly verifies the second law, and no experiment has ever been conducted that contradicts the second law. The basis of the second law is therefore experimental evidence.

A second observation is that these two statements of the second law are equivalent. Two statements are equivalent if the truth of each statement implies the truth of the other, or if the violation of each statement implies the violation of the other. That a violation of the Clausius statement implies a violation of the Kelvin–

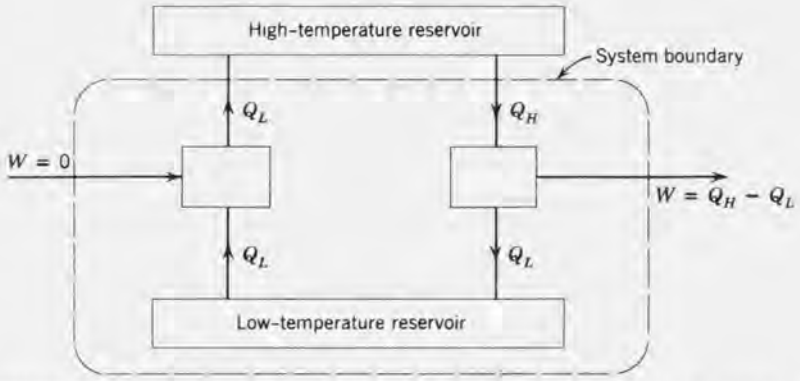


FIGURE 7.6 Demonstration of the equivalence of the two statements of the second law.

Planck statement may be shown. The device at the left in Fig. 7.6 is a refrigerator that requires no work and thus violates the Clausius statement. Let an amount of heat Q_L be transferred from the low-temperature reservoir to this refrigerator, and let the same amount of heat Q_L be transferred to the high-temperature reservoir. Let an amount of heat Q_H that is greater than Q_L be transferred from the high-temperature reservoir to the heat engine, and let the engine reject the amount of heat Q_L as it does an amount of work W, which equals $Q_H - Q_L$. Because there is no net heat transfer to the low-temperature reservoir, the low-temperature reservoir, the heat engine, and the refrigerator can be considered together as a device that operates in a cycle and produces no effect other than the raising of a weight (work) and the exchange of heat with a single reservoir. Thus, a violation of the Clausius statement implies a violation of the Kelvin–Planck statement. The complete equivalence of these two statements is established when it is also shown that a violation of the Kelvin–Planck statement implies a violation of the Clausius statement. This is left as an exercise for the student.

The third observation is that frequently the second law of thermodynamics has been stated as the impossibility of constructing a perpetual-motion machine of the second kind. A perpetual-motion machine of the first kind would create work from nothing or create mass or energy, thus violating the first law. A perpetual-motion machine of the second kind would extract heat from a source and then convert this heat completely into other forms of energy, thus violating the second law. A perpetual-motion machine of the third kind would have no friction, and thus would run indefinitely but produce no work.

A heat engine that violated the second law could be made into a perpetual-motion machine of the second kind by taking the following steps. Consider Fig. 7.7, which might be the power plant of a ship. An amount of heat Q_L is transferred from the ocean to a high-temperature body by means of a heat pump. The work required is W', and the heat transferred to the high-temperature body is Q_H. Let the same amount of heat be transferred to a heat engine that violates the Kelvin–Planck statement of the second law and does an amount of work $W = Q_H$. Of this

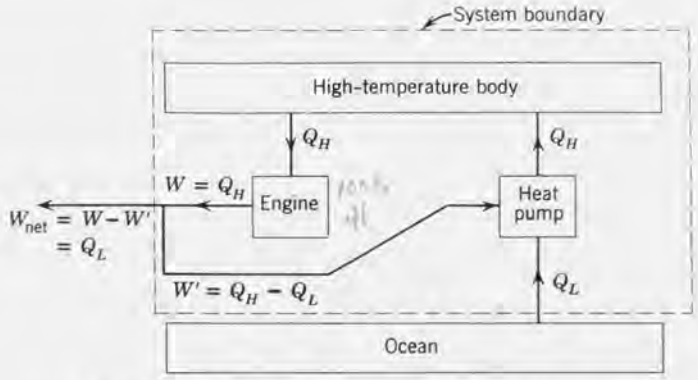


FIGURE 7.7 A perpetual-motion machine of the second kind.

work an amount $Q_H - Q_L$ is required to drive the heat pump, leaving the net work ($W_{net} = Q_L$) available for driving the ship. Thus, we have a perpetual-motion machine in the sense that work is done by utilizing freely available sources of energy such as the ocean or atmosphere.

7.3 THE REVERSIBLE PROCESS

The question that can now logically be posed is this. If it is impossible to have a heat engine of 100 percent efficiency, what is the maximum efficiency one can have? The first step in the answer to this question is to define an ideal process, which is called a reversible process.

A reversible process for a system is defined as a process that once having taken place can be reversed and in so doing leave no change in either system or surroundings.

Let us illustrate the significance of this definition for a gas contained in a cylinder that is fitted with a piston. Consider first Fig. 7.8, in which a gas, which we define as the system, is restrained at high pressure by a piston that is secured by a pin. When the pin is removed, the piston is raised and forced abruptly against the stops.

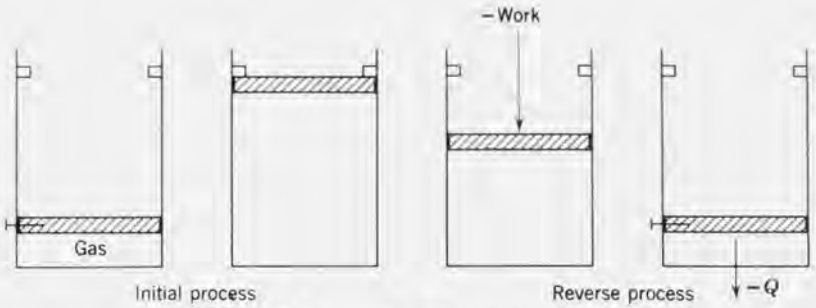


FIGURE 7.8 An example of an irreversible process.

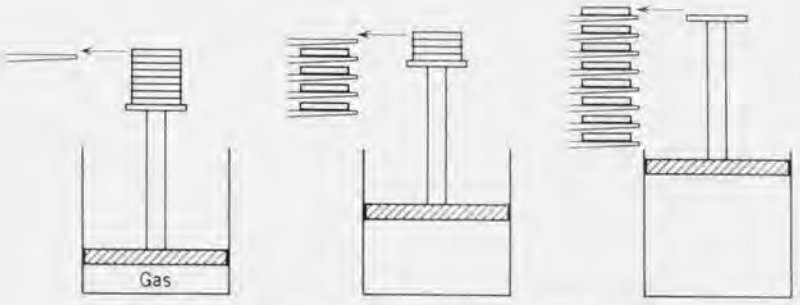


FIGURE 7.9 An example of a process that approaches being reversible.

Some work is done by the system, since the piston has been raised a certain amount. Suppose we wish to restore the system to its initial state. One way of doing this would be to exert a force on the piston and thus compress the gas until the pin can be reinserted in the piston. Since the pressure on the face of the piston is greater on the return stroke than on the initial stroke, the work done on the gas in this reverse process is greater than the work done by the gas in the initial process. An amount of heat must be transferred from the gas during the reverse stroke so that the system has the same internal energy as it had originally. Thus, the system is restored to its initial state, but the surroundings have changed by virtue of the fact that work was required to force the piston down and heat was transferred to the surroundings. The initial process therefore is an irreversible one because it could not be reversed without leaving a change in the surroundings.

In Fig. 7.9 let the gas in the cylinder comprise the system, and let the piston be loaded with a number of weights. Let the weights be slid off horizontally one at a time, allowing the gas to expand and do work in raising the weights that remain on the piston. As the size of the weights is made smaller and their number is increased, we approach a process that can be reversed, for at each level of the piston during the reverse process there will be a small weight that is exactly at the level of the platform and thus can be placed on the platform without requiring work. In the limit, therefore, as the weights become very small, the reverse process can be accomplished in such a manner that both the system and surroundings are in exactly the same state they were initially. Such a process is a reversible process.

7.4 FACTORS THAT RENDER PROCESSES IRREVERSIBLE

There are many factors that make processes irreversible. Four—friction, unrestrained expansion, heat transfer through a finite temperature difference, and mixing of two different substances—are considered in this section.

FRICTION

It is readily evident that friction makes a process irreversible, but a brief illustration may amplify the point. Let a block and an inclined plane make up a system, as

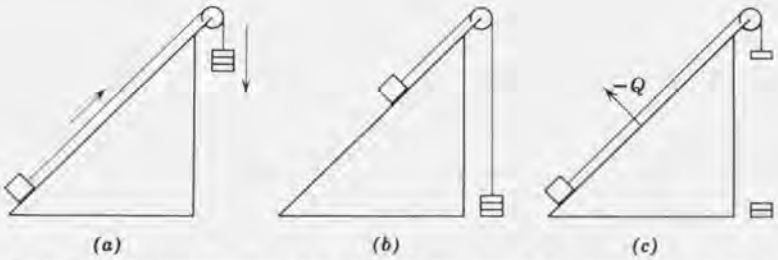


FIGURE 7.10 Demonstration of the fact that friction makes processes irreversible.

in Fig. 7.10, and let the block be pulled up the inclined plane by weights that are lowered. A certain amount of work is needed to do this. Some of this work is required to overcome the friction between the block and the plane, and some is required to increase the potential energy of the block. The block can be restored to its initial position by removing some of the weights and thus allowing the block to slide back down the plane. Some heat transfer from the system to the surroundings will no doubt be required to restore the block to its initial temperature. Since the surroundings are not restored to their initial state at the conclusion of the reverse process, we conclude that friction has rendered the process irreversible. Another type of frictional effect is that associated with the flow of viscous fluids in pipes and passages and in the movement of bodies through viscous fluids.

UNRESTRAINED EXPANSION

The classic example of an unrestrained expansion, as shown in Fig. 7.11, is a gas separated from a vacuum by a membrane. Consider what happens when the membrane breaks and the gas fills the entire vessel. It can be shown that this is an irreversible process by considering what would be necessary to restore the system to its original state. The gas would have to be compressed and heat transferred from the gas until its initial state is reached. Since the work and heat transfer involve a change in the surroundings, the surroundings are not restored to their initial state, indicating that the unrestrained expansion was an irreversible process. The process described in Fig. 7.8 is also an example of an unrestrained expansion.

In the reversible expansion of a gas there must be only an infinitesimal difference between the force exerted by the gas and the restraining force, so that the rate at which the boundary moves will be infinitesimal. In accordance with our previous definition, this is a quasi-equilibrium process. However, actual systems have a finite

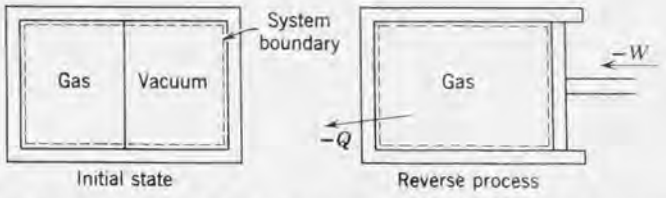


FIGURE 7.11 Demonstration of the fact that unrestrained expansion makes processes irreversible.

difference in forces, which causes a finite rate of movement of the boundary, and thus the processes are irreversible in some degree.

HEAT TRANSFER THROUGH A FINITE TEMPERATURE DIFFERENCE

Consider as a system a high-temperature body and a low-temperature body, and let heat be transferred from the high-temperature body to the low-temperature body. The only way in which the system can be restored to its initial state is to provide refrigeration, which requires work from the surroundings, and some heat transfer to the surroundings will also be necessary. Because of the heat transfer and the work, the surroundings are not restored to their original state, indicating that the process was irreversible.

An interesting question is now posed. Heat is defined as energy that is transferred through a temperature difference. We have just shown that heat transfer through a temperature difference is an irreversible process. Therefore, how can we have a reversible heat-transfer process? A heat-transfer process approaches a reversible process as the temperature difference between the two bodies approaches zero. Therefore, we define a reversible heat-transfer process as one in which the heat is transferred through an infinitesimal temperature difference. We realize of course that to transfer a finite amount of heat through an infinitesimal temperature difference would require an infinite amount of time or infinite area. Therefore, all actual heat transfers are through a finite temperature difference and hence are irreversible; the greater the temperature difference, the greater the irreversibility. We will find, however, that the concept of reversible heat transfer is very useful in describing ideal processes.

MIXING OF TWO DIFFERENT SUBSTANCES

Figure 7.12 illustrates the process of mixing two different gases separated by a membrane. When the membrane is broken, a homogeneous mixture of oxygen and nitrogen fills the entire volume. This process will be considered in some detail in Chapter 11. We can say here that this may be considered a special case of an unrestrained expansion, for each gas undergoes an unrestrained expansion as it fills the entire volume. A certain amount of work is necessary to separate these gases. Thus, an air separation plant such as described in Chapter 1 requires an input of work to accomplish the separation.

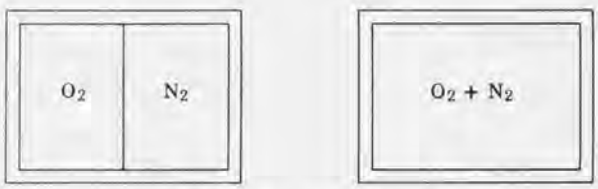


FIGURE 7.12 Demonstration of the fact that the mixing of two different substances is an irreversible process.

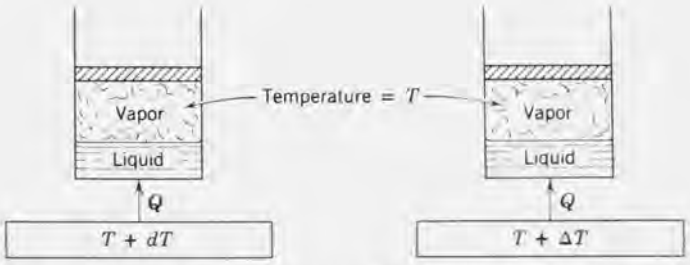


FIGURE 7.13 Illustration of the difference between an internally and externally reversible process

OTHER FACTORS

There are a number of other factors that make processes irreversible, but they will not be considered in detail here. Hysteresis effects and the i^2R loss encountered in electrical circuits are both factors that make processes irreversible. Ordinary combustion is also an irreversible process.

It is frequently advantageous to distinguish between internal and external irreversibility. Figure 7.13 shows two identical systems to which heat is transferred. Assuming each system to be a pure substance, the temperature remains constant during the heat-transfer process. In one system the heat is transferred from a reservoir at a temperature $T + dT$, and in the other the reservoir is at a much higher temperature, $T + \Delta T$, than the system. The first is a reversible heat-transfer process and the second is an irreversible heat-transfer process. However, as far as the system itself is concerned, it passes through exactly the same states in both processes, which we assume are reversible. Thus, we can say for the second system that the process is internally reversible but externally irreversible because the irreversibility occurs outside the system.

We should also note the general interrelation of reversibility, equilibrium, and time. In a reversible process, the deviation from equilibrium is infinitesimal, and therefore it occurs at an infinitesimal rate. Since it is desirable that actual processes proceed at a finite rate, the deviation from equilibrium must be finite, and therefore the actual process is irreversible in some degree. The greater the deviation from equilibrium, the greater the irreversibility, and the more rapidly the process will occur. It should also be noted that the quasi-equilibrium process, which was described in Chapter 2, is a reversible process, and hereafter the term reversible process will be used.

7.5 THE CARNOT CYCLE

Having defined the reversible process and considered some factors that make processes irreversible, let us again pose the question raised in Section 7.3. If the efficiency of all heat engines is less than 100 percent, what is the most efficient cycle we can have? Let us answer this question for a heat engine that receives heat from a high-temperature reservoir and rejects heat to a low-temperature reservoir. Since we are dealing with reservoirs, we recognize that both the high temperature

and the low temperature of the reservoirs are constant and remain constant regardless of the amount of heat transferred.

Let us assume that this heat engine, which operates between the given high-temperature and low-temperature reservoirs, does so in a cycle in which every process is reversible. If every process is reversible, the cycle is also reversible; and if the cycle is reversed, the heat engine becomes a refrigerator. In the next section we will show that this is the most efficient cycle that can operate between two constant-temperature reservoirs. It is called the Carnot cycle and is named after a French engineer, Nicolas Leonard Sadi Carnot (1796–1832), who expressed the foundations of the second law of thermodynamics in 1824.

We now turn our attention to the Carnot cycle. Figure 7.14 shows a power plant that is similar in many respects to a simple steam power plant and, we assume, operates on the Carnot cycle. Consider the working fluid to be a pure substance, such as steam. Heat is transferred from the high-temperature reservoir to the water (steam) in the boiler. For this process to be a reversible heat transfer, the temperature of the water (steam) must be only infinitesimally lower than the temperature of the reservoir. This result also implies, since the temperature of the reservoir remains constant, that the temperature of the water must remain constant. Therefore, the first process in the Carnot cycle is a reversible isothermal process in which heat is transferred from the high-temperature reservoir to the working fluid. A change of phase from liquid to vapor at constant pressure is of course an isothermal process for a pure substance.

The next process occurs in the turbine without heat transfer and is therefore adiabatic. Since all processes in the Carnot cycle are reversible, this must be a reversible adiabatic process, during which the temperature of the working fluid decreases from the temperature of the high-temperature reservoir to the temperature of the low-temperature reservoir.

In the next process heat is rejected from the working fluid to the low-temperature reservoir. This must be a reversible isothermal process in which the temperature of

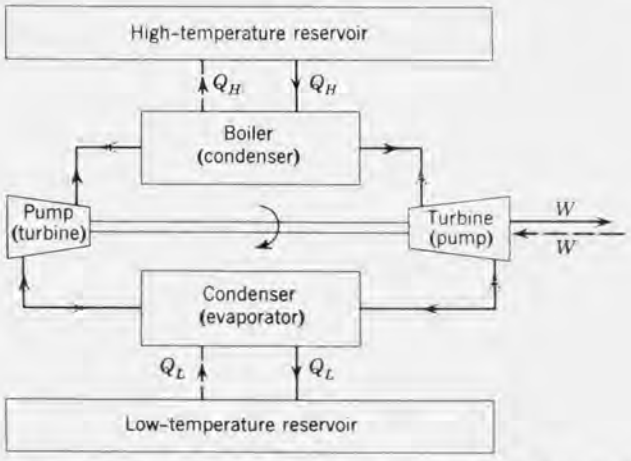


FIGURE 7.14 Example of a heat engine that operates on a Carnot cycle.

the working fluid is infinitesimally higher than that of the low-temperature reservoir. During this isothermal process some of the steam is condensed.

The final process, which completes the cycle, is a reversible adiabatic process in which the temperature of the working fluid increases from the low temperature to the high temperature. If this were to be done with water (steam) as the working fluid, a mixture of liquid and vapor would have to be taken from the condenser and compressed. (This would be very inconvenient in practice, and therefore in all power plants the working fluid is completely condensed in the condenser. The pump handles only the liquid phase.)

Since the Carnot heat engine cycle is reversible, every process could be reversed, in which case it would become a refrigerator. The refrigerator is shown by the dotted lines and parentheses in Fig. 7.14. The temperature of the working fluid in the evaporator would be infinitesimally less that the temperature of the low-temperature reservoir, and in the condenser it is infinitesimally higher than that of the high-temperature reservoir.

It should be emphasized that the Carnot cycle can be executed in many different ways. Many different working substances can be used, such as a gas, a thermoelectric device, or a paramagnetic substance in a magnetic field such as described in Chapter 4. There are also various possible arrangements of machinery. For example, a Carnot cycle can be devised that takes place entirely within a cylinder, using a gas as a working substance, as shown in Fig. 7.15.

The important point to be made here is that the Carnot cycle, regardless of what the working substance may be, always has the same four basic processes. These processes are

1. A reversible isothermal process in which heat is transferred to or from the high-temperature reservoir.
2. A reversible adiabatic process in which the temperature of the working fluid decreases from the high temperature to the low temperature.
3. A reversible isothermal process in which heat is transferred to or from the low-temperature reservoir.
4. A reversible adiabatic process in which the temperature of the working fluid increases from the low temperature to the high temperature.

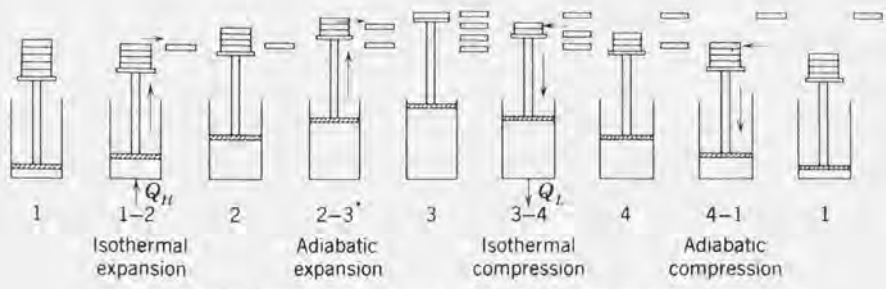


FIGURE 7.15 Example of a gaseous system operating on a Carnot cycle.

7.6 TWO PROPOSITIONS REGARDING THE EFFICIENCY OF A CARNOT CYCLE

There are two important propositions regarding the efficiency of a Carnot cycle.

FIRST PROPOSITION

It is impossible to construct an engine that operates between two given reservoirs and is more efficient than a reversible engine operating between the same two reservoirs.

The proof of this statement is accomplished through a "thought experiment." An initial assumption is made, and it is then shown that this assumption leads to impossible conclusions. The only possible conclusion is that the initial assumption was incorrect.

Let us assume that there is an irreversible engine operating between two given reservoirs that has a greater efficiency than a reversible engine operating between the same two reservoirs. Let the heat transfer to the irreversible engine be Q_H, the heat rejected be Q'_L, and the work be W_{IE} (which equals $Q_H - Q'_L$) as shown in Fig. 7.16. Let the reversible engine operate as a refrigerator (this is possible since it is reversible). Finally, let the heat transfer with the low-temperature reservoir be Q_L, the heat transfer with the high-temperature reservoir be Q_H, and the work required be W_{RE} (which equals $Q_H - Q_L$).

Since the initial assumption was that the irreversible engine is more efficient, it follows (because Q_H is the same for both engines) that $Q'_L < Q_L$ and $W_{IE} > W_{RE}$. Now the irreversible engine can drive the reversible engine and still deliver the net work W_{net}, which equals $W_{IE} - W_{RE} = Q_L - Q'_L$. If we consider the two engines and the high-temperature reservoir as a system, as indicated in Fig. 7.16, it is a system that operates in a cycle, exchanges heat with a single reservoir, and does a certain amount of work. However, this would constitute a violation of the second

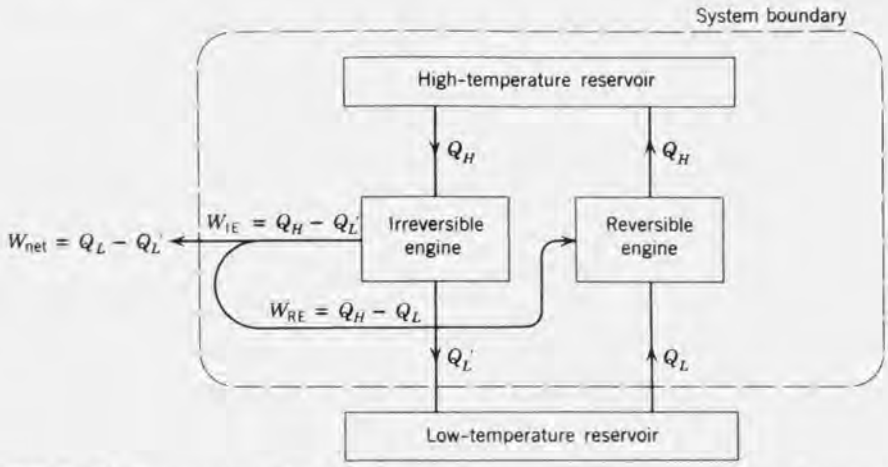


FIGURE 7.16 Demonstration of the fact that the Carnot cycle is the most efficient cycle operating between two fixed-temperature reservoirs.

law, and we conclude that our initial assumption (that the irreversible engine is more efficient than the reversible engine) is incorrect. Therefore, we cannot have an irreversible engine that is more efficient than a reversible engine operating between the same two reservoirs.

SECOND PROPOSITION

All engines that operate on the Carnot cycle between two given constant-temperature reservoirs have the same efficiency. The proof of this proposition is similar to the proof just outlined, which assumes that there is one Carnot cycle that is more efficient than another Carnot cycle operating between the same temperature reservoirs. Let the Carnot cycle with the higher efficiency replace the irreversible cycle of the previous argument, and the Carnot cycle with the lower efficiency operate as the refrigerator. The proof proceeds with the same line of reasoning as in the first proposition. The details are left as an exercise for the student.

7.7 THE THERMODYNAMIC TEMPERATURE SCALE

In discussing the matter of temperature in Chapter 2, we pointed out that the zeroth law of thermodynamics provides a basis for temperature measurement, but that a temperature scale must be defined in terms of a particular thermometer substance and device. A temperature scale that is independent of any particular substance, which might be called an absolute temperature scale, would be most desirable. In the last paragraph we noted that the efficiency of a Carnot cycle is independent of the working substance and depends only on the temperature. This fact provides the basis for such an absolute temperature scale, which we call the thermodynamic scale.

The concept of this temperature scale may be developed with the help of Fig. 7.17, which shows three reservoirs and three engines that operate on the Carnot

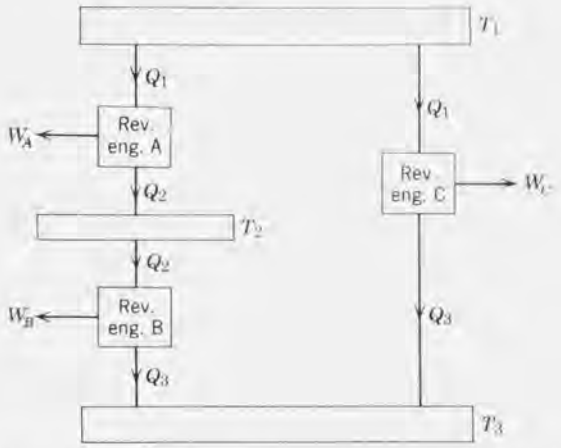


FIGURE 7.17 Arrangement of heat engines to demonstrate the thermodynamic temperature scale

cycle. T_1 is the highest temperature, T_3 is the lowest temperature, and T_2 is an intermediate temperature, and the engines operate between the various reservoirs as indicated. Q_1 is the same for both A and C and, since we are dealing with reversible cycles, Q_3 is the same for B and C.

Since the efficiency of a Carnot cycle is a function only of the temperature, we can write

$$\eta_{\text{thermal}} = 1 - \frac{Q_L}{Q_H} = \psi(T_L, T_H) \tag{7.3}$$

where ψ designates a functional relation.

Let us apply this functional relation to the three Carnot cycles of Fig. 7.17.

$$\frac{Q_1}{Q_2} = \psi(T_1, T_2)$$

$$\frac{Q_2}{Q_3} = \psi(T_2, T_3)$$

$$\frac{Q_1}{Q_3} = \psi(T_1, T_3)$$

Since

$$\frac{Q_1}{Q_3} = \frac{Q_1 Q_2}{Q_2 Q_3}$$

it follows that

$$\psi(T_1, T_3) = \psi(T_1, T_2) \times \psi(T_2, T_3) \tag{7.4}$$

Note that the left side is a function of T_1 and T_3 (and not of T_2), and therefore the right side of this equation must also be a function of T_1 and T_3 (and not of T_2). From this fact we can conclude that the form of the function ψ must be such that

$$\psi(T_1, T_2) = \frac{f(T_1)}{f(T_2)}$$

$$\psi(T_2, T_3) = \frac{f(T_2)}{f(T_3)}$$

for in this way $f(T_2)$ will cancel from the product of $\psi(T_1, T_2) \times \psi(T_2, T_3)$. Therefore, we conclude that

$$\frac{Q_1}{Q_3} = \psi(T_1, T_3) = \frac{f(T_1)}{f(T_3)} \tag{7.5}$$

In general terms,

$$\frac{Q_H}{Q_L} = \frac{f(T_H)}{f(T_L)} \tag{7.6}$$

Now there are several functional relations that will satisfy this equation. For the thermodynamic scale of temperature, which was originally proposed by Lord

Kelvin, the selected relation is

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \tag{7.7}$$

With absolute temperatures so defined, the efficiency of a Carnot cycle may be expressed in terms of the absolute temperatures.[2]

$$\eta_{\text{thermal}} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H} \tag{7.8}$$

This means that if the thermal efficiency of a Carnot cycle operating between two given constant-temperature reservoirs is known, the ratio of the two absolute temperatures is also known.

It should be noted that Eq. 7.7 gives us a ratio of absolute temperatures, but it does not give us information about the magnitude of the degree. Let us first consider a qualitative approach to this matter and then a more rigorous statement.

Suppose we had a heat engine operating on the Carnot cycle that received heat at the temperature of the steam point and rejected heat at the temperature of the ice point. (Because a Carnot cycle involves only reversible processes, it is impossible to construct such a heat engine and perform the proposed experiment. However, we can follow the reasoning as a "thought experiment" and gain additional understanding of the thermodynamic temperature scale.) If the efficiency of such an engine could be measured, we would find it to be 26.80 percent. Therefore, from Eq. 7.8,

$$\eta_{\text{th}} = 1 - \frac{T_L}{T_H} = 1 - \frac{T_{\text{ice point}}}{T_{\text{steam point}}} = 0.2680$$

$$\frac{T_{\text{ice point}}}{T_{\text{steam point}}} = 0.7320$$

[2] Lord Kelvin also proposed a logarithmic scale of the form

$$\frac{Q_H}{Q_L} = \frac{e^{"T_H"}}{e^{"T_L"}}$$

where "T_H" and "T_L" designate the absolute temperatures on this proposed logarithmic scale. This relation can also be written

$$\ln \frac{Q_H}{Q_L} = "T_H" - "T_L"$$

The form Kelvin actually proposed was

$$\log_{10} \frac{Q_H}{Q_L} = "T_H" - "T_L"$$

Thus, the relation between the scale in use and the proposed logarithmic scale is

$$"T" = \log_{10} T + L$$

where L is a constant that determines the level of temperature that corresponds to zero on the logarithmic scale. On this logarithmic scale temperatures range from $-\infty$ to $+\infty$, whereas on the thermodynamic scale in use they vary from 0 to $+\infty$ for ordinary systems.

This gives us one equation concerning the two unknowns T_H and T_L. The second equation comes from an arbitrary decision regarding the magnitude of the degree on the thermodynamic temperature scale. If we wish to have the magnitude of the degree on the absolute scale correspond to the magnitude of the degree on the Celsius scale, we can write

$$T_{\text{steam point}} - T_{\text{ice point}} = 100$$

Solving these two equations simultaneously, we find

$$T_{\text{steam point}} = 373.15 \text{ K}, \qquad T_{\text{ice point}} = 273.15 \text{ K}$$

It follows that

$$T(^\circ\text{C}) + 273.15 = T(\text{K})$$

The absolute scale related to the Fahrenheit scale is the Rankine scale, designated by R. On both these scales there are 180 degrees between the ice point and the steam point. Therefore, for a Carnot cycle heat engine operating between the steam point and the ice point, we would have the two relations

$$T_{\text{steam point}} - T_{\text{ice point}} = 180$$

$$\frac{T_{\text{ice point}}}{T_{\text{steam point}}} = 0.7320$$

Solving these two equations simultaneously, we find

$$T_{\text{steam point}} = 671.67 \text{ R}, \qquad T_{\text{ice point}} = 491.67 \text{ R}$$

It follows that temperatures on the Fahrenheit and Rankine scales are related as follows:

$$T(\text{F}) + 459.67 = T(\text{R})$$

As already noted, the measurement of efficiencies of Carnot cycles is, however, not a practical way to approach the problem of temperature measurement on the thermodynamic scale of temperature. The actual approach is based on the ideal-gas thermometer and an assigned value for the triple point of water. At the Tenth Conference on Weights and Measures, which was held in 1954, the temperature of the triple point of water was assigned the value 273.16 K. [The triple point of water is approximately 0.01°C above the ice point. The ice point is defined as the temperature of a mixture of ice and water at a pressure of 1 atm (101.3 kPa) of air that is saturated with water vapor.] The ideal-gas thermometer is discussed in the following section.

7.8 THE IDEAL-GAS TEMPERATURE SCALE

In this section we consider the ideal-gas scale of temperature. This scale is based on the observation that as the pressure of a gas approaches zero, its equation of state approaches that of an ideal gas:

$$Pv = RT$$

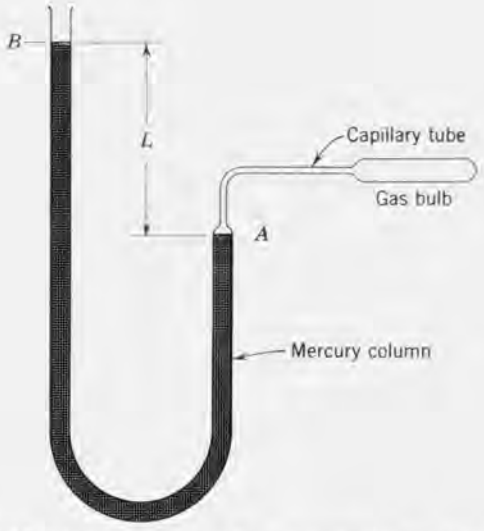


FIGURE 7.18 Schematic diagram of a constant-volume gas thermometer.

Consider how an ideal gas might be used to measure temperature in a constant-volume gas thermometer, which is shown schematically in Fig. 7.18. Let the gas bulb be placed in the location where the temperature is to be measured, and let the mercury column be adjusted so that the level of mercury stands at the reference mark A. Thus, the volume of the gas remains constant. Assume that the gas in the capillary tube is at the same temperature as the gas in the bulb. Then the pressure of the gas, which is indicated by the height L of the mercury column, is a measure of the temperature.

Let the pressure that is associated with the temperature of the triple point of water (273.16 K) also be measured, and let us designate this pressure $P_{\text{t.p.}}$. Then, from the definition of an ideal gas, any other temperature T could be determined from a pressure measurement P by the relation

$$T = 273.16\left(\frac{P}{P_{\text{t.p.}}}\right)$$

The temperature so measured is referred to as the ideal-gas temperature, and it can be shown that the temperature so measured is exactly equal to the thermodynamic temperature.

From a practical point of view, we have the problem that no gas behaves exactly like an ideal gas. However, we do know that as the pressure approaches zero, the behavior of all gases approaches that of an ideal gas. Suppose then that a series of measurements is made with varying amounts of gas in the gas bulb. This means that the pressure measured at the triple point, and also the pressure at any other temperature, will vary. If the indicated temperature T_i (obtained by assuming that the gas is ideal) is plotted against the pressure of gas with the bulb at the triple point of water, a curve like the one shown in Fig. 7.19 is obtained. When this curve is extrapolated to zero pressure, the correct ideal-gas temperature is obtained.

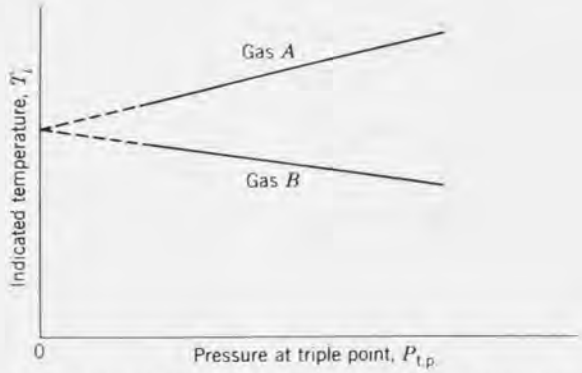


FIGURE 7.19 Sketch showing how the ideal-gas temperature is determined.

Different curves might result from different gases, but they would all indicate the same temperature at zero pressure.

We have outlined only the general features and principles for measuring temperature on the ideal-gas scale of temperatures. Precision work in this field is difficult and laborious, and there are only a few laboratories in the world where this precision work is carried on. The International Temperature Scale, which was presented in Chapter 2, closely approximates the thermodynamic temperature scale and is much easier to work with in actual temperature measurement.

7.9 EQUIVALENCE OF IDEAL-GAS AND THERMODYNAMIC TEMPERATURE SCALES

In this section we demonstrate that the ideal-gas temperature scale discussed in the previous section is, in fact, identical to the thermodynamic temperature scale, which was defined in the discussion of the Carnot cycle and the second law. Our objective can be achieved by using an ideal gas as the working fluid for a Carnot-cycle heat engine and analyzing the four processes that make up the cycle. The four state points, 1, 2, 3, 4, and the four processes are as shown in Fig. 7.15. For convenience, let us consider a unit mass of gas inside the cylinder. Now for each of the four processes, the reversible work done at the moving boundary is given by Eq. 4.2.

$$\delta w = P\, dv$$

Similarly, for each process the gas behavior is, from the ideal-gas relation, Eq. 3.2,

$$Pv = RT$$

and the internal energy change, from Eq. 5.20, is

$$du = C_{v0}\, dT$$

Assuming no changes in kinetic or potential energies, the first law is, from Eq. 5.7 at unit mass,

$$\delta q = du + \delta w$$

Substituting the three previous expressions into this equation, we have for each of the four processes

$$\delta q = C_{v0}\, dT + \frac{RT}{v}\, dv \tag{7.9}$$

We now proceed to integrate Eq. 7.9 for each of the four processes that make up the Carnot cycle. For the isothermal heat addition process 1–2, we have

$$q_H = {}_1q_2 = 0 + RT_H \ln \frac{v_2}{v_1} \tag{7.10}$$

For the adiabatic expansion process 2–3,

$$0 = \int_{T_H}^{T_L} \frac{C_{v0}}{T}\, dT + R \ln \frac{v_3}{v_2} \tag{7.11}$$

For the isothermal heat rejection process 3–4,

$$q_L = -{}_3q_4 = -0 - RT_L \ln \frac{v_4}{v_3}$$

$$= +RT_L \ln \frac{v_3}{v_4} \tag{7.12}$$

and for the adiabatic compression process 4–1,

$$0 = \int_{T_L}^{T_H} \frac{C_{v0}}{T}\, dT + R \ln \frac{v_1}{v_4} \tag{7.13}$$

From Eqs. 7.11 and 7.13,

$$\int_{T_L}^{T_H} \frac{C_{v0}}{T}\, dT = R \ln \frac{v_3}{v_2} = -R \ln \frac{v_1}{v_4}$$

Therefore,

$$\frac{v_3}{v_2} = \frac{v_4}{v_1} \qquad \text{or} \qquad \frac{v_3}{v_4} = \frac{v_2}{v_1} \tag{7.14}$$

Thus, from Eqs. 7.10 and 7.12 and substituting Eq. 7.14, we find that

$$\frac{q_H}{q_L} = \frac{R\, T_H \ln \dfrac{v_2}{v_1}}{R\, T_L \ln \dfrac{v_3}{v_4}} = \frac{T_H}{T_L}$$

which is Eq. 7.7, the definition of the thermodynamic temperature scale in connection with the second law.

A final point needs to be made about the significance of absolute-zero temperature in connection with the second law and the thermodynamic temperature scale. Consider a Carnot-cycle heat engine that receives a given amount of heat from a given high-temperature reservoir. As the temperature at which heat is rejected from the cycle is lowered, the net work output increases and the amount of heat rejected

decreases. In the limit, the heat rejected is zero, and the temperature of the reservoir corresponding to this limit is absolute zero.

Similarly, for a Carnot-cycle refrigerator, the amount of work required to produce a given amount of refrigeration increases as the temperature of the refrigerated space decreases. Absolute zero represents the limiting temperature that can be achieved, and the amount of work required to produce a finite amount of refrigeration approaches infinity as the temperature at which refrigeration is provided approaches zero.

PROBLEMS

7.1 Calculate the thermal efficiency of the steam power plant cycle described in Problem 6.13.

7.2 Calculate the coefficient of performance of the R-12 heat pump cycle described in Problem 6.21.

7.3 Prove that a cyclic device that violates the Kelvin–Planck statement of the second law also violates the Clausius statement of the second law.

7.4 Discuss the factors that would make the power plant cycle described in Problem 6.13 an irreversible cycle.

7.5 Discuss the factors that would make the heat pump cycle described in Problem 6.21 an irreversible cycle.

7.6 Calculate the thermal efficiency of a Carnot-cycle heat engine operating between 500° and 40°C. Compare the result with that of Problem 7.1.

7.7 Calculate the coefficient of performance of a Carnot-cycle heat pump operating between 0° and 45°C. Compare the result with that of Problem 7.2.

7.8 The application of geothermal power, whereby an underground source of hot water or steam is utilized as the energy source for a power plant, has received increased attention in recent years. Consider a supply of saturated-liquid water at 150°C. What is the maximum possible thermal efficiency of a cyclic heat engine using this source of energy and operating in a 20°C environment? Would it be better to locate a source of saturated vapor at 150°C than use this saturated-liquid water at 150°C?

7.9 We propose to heat a house during the winter using a heat pump. The house is to be maintained at 20°C at all times. When the ambient temperature outside drops to −10°C, the rate at which heat is lost from the house is estimated to be 25 kW. What is the minimum electrical power required to drive the heat pump unit?

7.9E We propose to heat a house during the winter using a heat pump. The house is to be maintained at 68 F at all times. When the ambient temperature outside drops to 15 F, the rate at which heat is lost from the house is estimated to be 80 000 Btu/h. What is the minimum electrical power required to drive the heat pump unit?

7.10 A household refrigerator operates in a room whose temperature is 20°C. Heat must be transferred from the cold space at the rate of 5 kW to maintain its temperature at −30°C. What is the theoretically smallest (power) motor required to operate this refrigerator?

7.11 An electric utility company proposed constructing a cyclic heat engine that will operate in the ocean at a location where the water temperature is 20°C near the surface and 5°C at some greater depth. What is the maximum possible thermal efficiency of such an engine?

7.12 An inventor claims to have developed a refrigeration unit that maintains the refrigerated space at −10°C. The unit, which operates in a room whose temperature is 25°C, has a coefficient of performance of 8.5. How do you evaluate this claim? How would you evaluate a claim of a coefficient of performance of 7.0?

7.13 A certain solar-energy collector produces a maximum temperature of 100°C. The energy collected is to be used as the heat source in a cyclic heat engine. What is the maximum thermal efficiency of the engine if it operates in a 10°C environment? What is it if the collector is designed to focus and concentrate the energy to produce a maximum temperature of 300°C?

7.14 Liquid sodium leaves a nuclear reactor at 800°C. It is to be used as the energy source in a steam power plant. The condenser cooling water is recirculated using a cooling tower and leaves the tower at 15°C. Determine the maximum possible thermal efficiency of this power plant. Is it misleading to use the 800° and 15°C temperatures to calculate this value?

7.14E Liquid sodium leaves a nuclear reactor at 1500 F. It is to be used as the energy source in a steam power plant. The condenser cooling water is recirculated using a cooling tower and leaves the tower at 60 F. Determine the maximum possible thermal efficiency of this power plant. Is it misleading to use the 1500 and 60 F temperatures to calculate this value?

7.15 A cyclic machine transfers heat from a higher-temperature to a lower-temperature reservoir, as shown in Fig. 7.20. With the energy transfer values as shown, determine whether this machine is reversible, irreversible, or impossible.

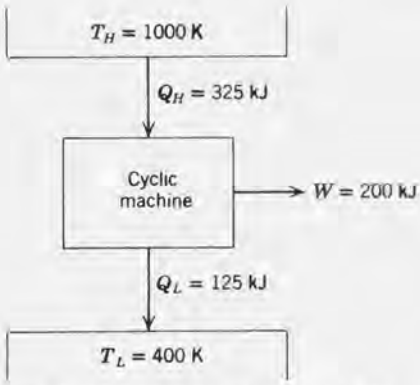


FIGURE 7.20 Sketch for Problem 7.15

7.16 For several different winter outdoor temperatures, we wish to estimate the percent of household electrical energy that can be saved by heating a house to only 20°C instead of 24°C. An electric heat pump supplies the heat. It may be assumed that the rate of heat loss from the house is directly proportional to the difference between the inside and outdoor temperatures.

7.16E For several different winter outdoor temperatures, we wish to estimate the percent of household electrical energy that can be saved by heating a house to only 68 F instead of 75 F. An electric heat pump supplies the heat. It may be assumed that the rate of heat loss from the house is directly proportional to the difference between the inside and outdoor temperatures.

7.17 For several different summer outdoor temperatures, we wish to estimate the percent of household electrical energy that can be saved by cooling a house to only 25°C instead of 20°C. The house has an electric air-conditioning system. It may be assumed that the rate of heat leak into the house is directly proportional to the difference between the outdoor and inside temperatures.

7.17E For several different summer outdoor temperatures, we wish to estimate the percent of household electrical energy that can be saved by cooling a house to only 77 F instead of 68 F. The house has an electric air-conditioning system. It may be assumed that the rate of heat leak into the house is directly proportional to the difference between the outdoor and inside temperatures.

7.18 Helium has the lowest normal boiling point of any of the elements, namely 4.2 K. At this temperature helium has an enthalpy of evaporation of 83.3 kJ/kmol. A Carnot refrigeration cycle is analyzed for the production of 1 kmol of liquid helium at 4.2 K from saturated vapor at the same temperature. What is the work input to the refrigerator and the coefficient of performance of this refrigeration cycle, assuming that the ambient temperature is 300 K?

7.19 A temperature of about 0.01 K can be achieved by magnetic cooling, which was described in Section 4.5. In this process a strong magnetic field is imposed on a paramagnetic salt that is maintained at 1 K by transferring heat to liquid helium, which is boiling at very low pressure. The salt is then thermally isolated from the helium, the magnetic field is removed, and the temperature of the salt drops. Assume that 1 mJ of energy is to be removed from the paramagnetic salt at an average temperature of 0.1 K, and, to establish the theoretical limit, the necessary refrigeration is produced by a Carnot-cycle refrigerator. Calculate the work input to the refrigerator and the coefficient of performance for this refrigeration cycle, assuming that the ambient temperature is 300 K.

7.20 The lowest temperature that has been achieved at the present time is about 1×10^{-6} K. Lowering a specimen to this temperature requires an additional stage to that described in Problem 7.19, namely nuclear cooling. This process is similar to magnetic cooling, but it involves the magnetic moment associated with the nucleus rather than that associated with certain ions in the paramagnetic salt. Suppose that 10 J of energy is to be removed from a specimen at an average temperature of 10^{-5} K. (Ten joules is about the amount of energy spent by a pin dropping through a distance of 3 mm. Ten joules is also about the amount of energy transferred as heat at this temperature in some experiments.) Consider that a Carnot-cycle refrigerator produces this amount of refrigeration at an average temperature of 10^{-5} K (for the purpose of determining the theoretical limit). Determine the work input and the coefficient of performance for the refrigeration cycle, assuming that the ambient temperature is 300 K.

7.21 We wish to produce refrigeration at −30°C. A reservoir is available at a temperature of 200°C and the ambient temperature is 30°C. Thus, work can be done by a cyclic heat engine operating between the 200°C reservoir and the ambient. This work can

be used to drive the refrigerator. Determine the ratio of the heat transferred from the high-temperature reservoir to the heat transferred from the refrigerated space, assuming that all processes are reversible.

7.21E We wish to produce refrigeration at −20 F. A reservoir is available at a temperature of 400 F, and the ambient temperature is 80 F. Thus, work can be done by a cyclic heat engine operating between the 400 F reservoir and the ambient. This work can be used to drive the refrigerator. Determine the ratio of the heat transferred from the high-temperature reservoir to the heat transferred from the refrigerated space, assuming that all processes are reversible.

7.22 Consider a Carnot-cycle heat engine operating in outer space. Heat can be rejected from this engine only by thermal radiation. The rate at which heat is transferred by thermal radiation is proportional to the fourth power of the absolute temperature and to the area of the radiating surface. Show that for a given output of engine power and a given T_H, the area of the radiator will be minimum when the ratio $T_L/T_H = 3/4$.

7.23 A heat pump heats a house in the winter and is then reversed to cool the house in the summer. The interior temperature is to be maintained at 20°C in the winter and 25°C in the summer. Heat transfer through the walls and roof is estimated to be 2400 kJ per hour per degree temperature difference between the inside and outside.

(a) If the outside temperature in the winter is 0°C, what is the minimum power required to drive the heat pump?

(b) If the power input is the same as in part a, what is the maximum outside summer temperature for which the inside of the house can be maintained at 25°C?

7.24 We propose to build a 1000-MW electric power plant with steam as the working fluid. The condensers are to be cooled with river water (see Fig. 7.21). The maximum steam temperature will be 550°C, and the pressure in the condensers will be 10 kPa. As an engineering consultant, you are asked to estimate the temperature rise of the river downstream from the power plant. What is your estimate?

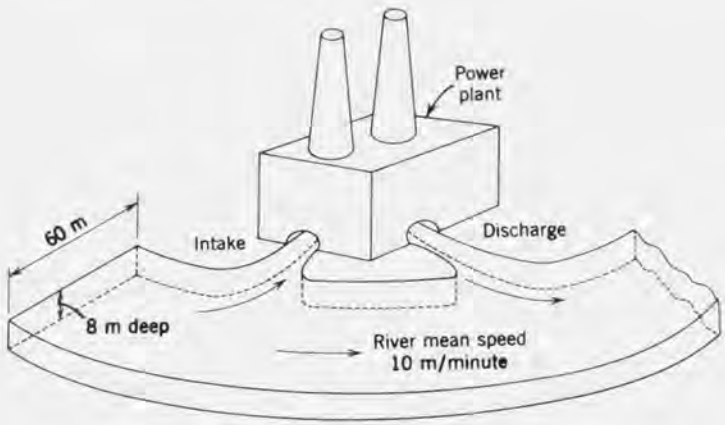


FIGURE 7.21 Sketch for Proble 7.21

8

ENTROPY

Up to this point in our consideration of the second law of thermodynamics, we have dealt only with thermodynamic cycles. Although this is a very important and useful approach, we are often concerned with processes rather than cycles. Thus, we might be interested in the second-law analysis of processes we encounter daily, such as the combustion process in an automobile engine, the cooling of a cup of coffee, or the chemical processes that take place in our bodies. It would also be beneficial to be able to deal with the second law quantitatively as well as qualitatively.

In our consideration of the first law, we initially stated the law in terms of a cycle, but then defined a property, the internal energy, which enabled us to use the first law quantitatively for processes. Similarly, we have stated the second law for a cycle, and we now find that the second law leads to a property, entropy, which enables us to treat the second law quantitatively for processes. Energy and entropy are both abstract concepts that help to describe certain observations. As we noted in Chapter 2, thermodynamics can be described as the science of energy and entropy. The significance of this statement will become increasingly evident.

8.1 INEQUALITY OF CLAUSIUS

The first step in our consideration of the property we call entropy is to establish the inequality of Clausius, which is

$$\oint \frac{\delta Q}{T} \leqslant 0$$

The inequality of Clausius is a corollary or a consequence of the second law of thermodynamics. It will be demonstrated to be valid for all possible cycles, including both reversible and irreversible heat engines and refrigerators. Since any reversible cycle can be represented by a series of Carnot cycles, in this analysis we need consider only a Carnot cycle that leads to the inequality of Clausius.

Consider first a reversible (Carnot) heat engine cycle operating between reservoirs at temperatures T_H and T_L, as shown in Fig. 8.1. For this cycle, the cyclic integral of the heat transfer, $\oint \delta Q$, is greater than zero.

$$\oint \delta Q = Q_H - Q_L > 0$$

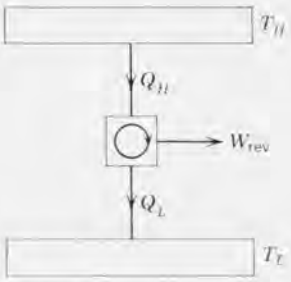


FIGURE 8.1 Reversible heat engine cycle for demonstration of the inequality of Clausius.

Since T_H and T_L are constant, from the definition of the absolute temperature scale and from the fact this is a reversible cycle, it follows that

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

If $\oint \delta Q$, the cyclic integral of δQ, approaches zero (by making T_H approach T_L) and the cycle remains reversible, the cyclic integral of $\delta Q/T$ remains zero. Thus, we conclude that for all reversible heat engine cycles

$$\oint \delta Q \geqslant 0$$

and

$$\oint \frac{\delta Q}{T} = 0$$

Now consider an irreversible cyclic heat engine operating between the same T_H and T_L as the reversible engine of Fig. 8.1 and receiving the same quantity of heat Q_H. Comparing the irreversible cycle with the reversible one, we conclude from the second law that

$$W_{\text{irr}} < W_{\text{rev}}$$

Since $Q_H - Q_L = W$ for both the reversible and irreversible cycles, we conclude that

$$Q_H - Q_{L\,\text{irr}} < Q_H - Q_{L\,\text{rev}}$$

and therefore

$$Q_{L\,\text{irr}} > Q_{L\,\text{rev}}$$

Consequently, for the irreversible cyclic engine,

$$\oint \delta Q = Q_H - Q_{L\,\text{irr}} > 0$$

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_{L\,\text{irr}}}{T_L} < 0$$

Suppose that we cause the engine to become more and more irreversible, but keep Q_H, T_H, and T_L fixed. The cyclic integral of δQ then approaches zero, and

that for $\delta Q/T$ becomes a progressively larger negative value. In the limit, as the work output goes to zero,

$$\oint \delta Q = 0$$

$$\oint \frac{\delta Q}{T} < 0$$

Thus, we conclude that for all irreversible heat engine cycles

$$\oint \delta Q \geqslant 0$$

$$\oint \frac{\delta Q}{T} < 0$$

To complete the demonstration of the inequality of Clausius, we must perform similar analyses for both reversible and irreversible refrigeration cycles. For the reversible refrigeration cycle shown in Fig. 8.2,

$$\oint \delta Q = -Q_H + Q_L < 0$$

and

$$\oint \frac{\delta Q}{T} = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$$

As the cyclic integral of δQ approaches zero reversibly (T_H approaches T_L), the cyclic integral of $\delta Q/T$ remains at zero. In the limit,

$$\oint \delta Q = 0$$

$$\oint \frac{\delta Q}{T} = 0$$

Thus, for all reversible refrigeration cycles,

$$\oint \delta Q \leqslant 0$$

$$\oint \frac{\delta Q}{T} = 0$$

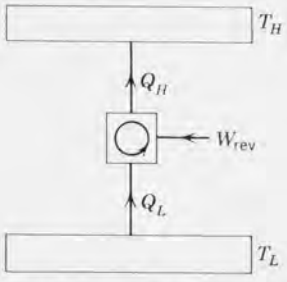


FIGURE 8.2 Reversible refrigeration cycle for demonstration of the inequality of Clausius.

Finally, let an irreversible cyclic refrigerator operate between temperatures T_H and T_L and receive the same amount of heat Q_L as the reversible refrigerator of Fig. 8.2. From the second law, we conclude that the work input required will be greater for the irreversible refrigerator, or

$$W_{\text{irr}} > W_{\text{rev}}$$

Since $Q_H - Q_L = W$ for each cycle, it follows that

$$Q_{H\,\text{irr}} - Q_L > Q_{H\,\text{rev}} - Q_L$$

and therefore,

$$Q_{H\,\text{irr}} > Q_{H\,\text{rev}}$$

That is, the heat rejected by the irreversible refrigerator to the high-temperature reservoir is greater than the heat rejected by the reversible refrigerator. Therefore, for the irreversible refrigerator,

$$\oint \delta Q = -Q_{H\,\text{irr}} + Q_L < 0$$

$$\oint \frac{\delta Q}{T} = -\frac{Q_{H\,\text{irr}}}{T_H} + \frac{Q_L}{T_L} < 0$$

As we make this machine progressively more irreversible, but keep Q_L, T_H, and T_L constant, the cyclic integrals of δQ and $\delta Q/T$ both become larger in the negative direction. Consequently, a limiting case as the cyclic integral of δQ approaches zero does not exist for the irreversible refrigerator.

Thus, for all irreversible refrigeration cycles,

$$\oint \delta Q < 0$$

$$\oint \frac{\delta Q}{T} < 0$$

Summarizing, we note that, in regard to the sign of $\oint \delta Q$, we have considered all possible reversible cycles (that is, $\oint \delta Q \lesseqgtr 0$), and for each of these reversible cycles

$$\oint \frac{\delta Q}{T} = 0$$

We have also considered all possible irreversible cycles for the sign of $\oint \delta Q$ (that is, $\oint \delta Q \lesseqgtr 0$), and for all these irreversible cycles

$$\oint \frac{\delta Q}{T} < 0$$

Thus, for all cycles we can write

$$\oint \frac{\delta Q}{T} \leqslant 0 \tag{8.1}$$

where the equality holds for reversible cycles and the inequality for irreversible cycles. This relation, Eq. 8.1, is known as the inequality of Clausius.

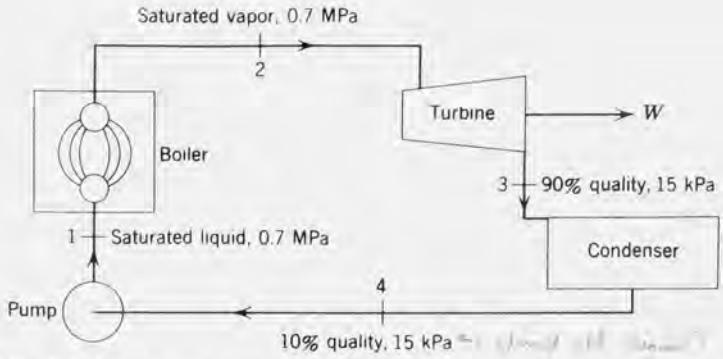


FIGURE 8.3 A simple steam power plant that demonstrates the inequality of Clausius.

The significance of the inequality of Clausius may be illustrated by considering the simple steam power plant cycle shown in Fig. 8.3. This cycle is slightly different from the usual cycle for steam power plants in that the pump handles a mixture of liquid and vapor in such proportions that saturated liquid leaves the pump and enters the boiler. Suppose that someone reports that the pressure and quality at various points in the cycle are as given in Fig. 8.3. Does this cycle satisfy the inequality of Clausius?

Heat is transferred in two places, the boiler and the condenser. Therefore,

$$\oint \frac{\delta Q}{T} = \int \left(\frac{\delta Q}{T}\right)_{\text{boiler}} + \int \left(\frac{\delta Q}{T}\right)_{\text{condenser}}$$

Since the temperature remains constant in both the boiler and condenser, this may be integrated as follows:

$$\oint \frac{\delta Q}{T} = \frac{1}{T_1}\int_1^2 \delta Q + \frac{1}{T_3}\int_3^4 \delta Q = \frac{{}_1Q_2}{T_1} + \frac{{}_3Q_4}{T_3}$$

Let us consider a 1-kg mass as the working fluid.

$${}_1q_2 = h_2 - h_1 = 2066.3 \text{ kJ/kg}, \qquad T_1 = 164.97^\circ\text{C}$$
$${}_3q_4 = h_4 - h_3 = 463.4 - 2361.8 = -1898.4 \text{ kJ/kg}, \qquad T_3 = 53.97^\circ\text{C}$$

Therefore,

$$\oint \frac{\delta Q}{T} = \frac{2066.3}{164.97 + 273.15} - \frac{1898.4}{53.97 + 273.15} = -1.087 \text{ kJ/kg K}$$

Thus, this cycle satisfies the inequality of Clausius, which is equivalent to saying that it does not violate the second law of thermodynamics.

8.2 ENTROPY—A PROPERTY OF A SYSTEM

By applying Eq. 8.1 and Fig. 8.4, we can demonstrate that the second law of thermodynamics leads to a property of a system that we call entropy. Let a system

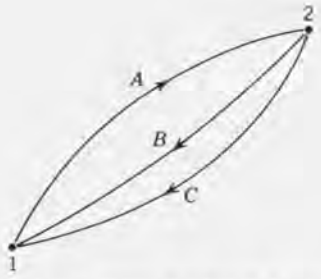


FIGURE 8.4 *Two reversible cycles demonstrating the fact that entropy is a property of a substance.*

undergo a reversible process from state 1 to state 2 along path A, and let the cycle be completed along path B, which is also reversible.

Because this is a reversible cycle, we can write

$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left(\frac{\delta Q}{T}\right)_A + \int_2^1 \left(\frac{\delta Q}{T}\right)_B$$

Now consider another reversible cycle, which has the same initial process, but let the cycle be completed along path C. For this cycle we can write

$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left(\frac{\delta Q}{T}\right)_A + \int_2^1 \left(\frac{\delta Q}{T}\right)_C$$

Subtracting the second equation from the first, we have

$$\int_2^1 \left(\frac{\delta Q}{T}\right)_B = \int_2^1 \left(\frac{\delta Q}{T}\right)_C$$

Since the $\int \delta Q/T$ is the same for all reversible paths between states 2 and 1, we conclude that this quantity is independent of the path and is a function of the end states only; it is therefore a property. This property is called entropy and is designated S. It follows that entropy may be defined as a property of a substance in accordance with the relation

$$dS \equiv \left(\frac{\delta Q}{T}\right)_{\text{rev}} \tag{8.2}$$

Entropy is an extensive property, and the entropy per unit mass is designated s. It is important to note that entropy is defined here in terms of a reversible process.

The change in the entropy of a system as it undergoes a change of state may be found by integrating Eq. 8.2. Thus,

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{rev}} \tag{8.3}$$

To perform this integration, we must know the relation between T and Q, and illustrations will be given subsequently. The important point is that since entropy is a property, the change in the entropy of a substance in going from one state to another is the same for all processes, both reversible and irreversible, between these two states. Equation 8.3 enables us to find the change in entropy only along a

reversible path. However, once the change has been evaluated, this value is the magnitude of the entropy change for all processes between these two states.

Equation 8.3 enables us to determine changes of entropy, but it tells us nothing about absolute values of entropy. However, from the third law of thermodynamics, which is discussed in Chapter 13, it follows that the entropy of all pure substances can be assigned the value of zero at the absolute zero of temperature. This value allows in turn the assignment of absolute values of entropy and is particularly important when chemical reactions are involved.

However, when there is no change of composition, it is quite adequate to give values of entropy relative to some arbitrarily selected reference state. This is the procedure followed in most tables of thermodynamic properties, such as the steam tables and ammonia tables. Therefore, until absolute entropy is introduced in Chapter 13, values of entropy will always be given relative to some arbitrary reference state.

A word should be added here regarding the role of T as an integrating factor. We noted in Chapter 4 that Q is a path function, and therefore δQ is an inexact differential. However, since $(\delta Q/T)_{rev}$ is a thermodynamic property, it is an exact differential. From a mathematical perspective, we note that an inexact differential may be converted to an exact differential by the introduction of an integrating factor. Therefore, $1/T$ serves as the integrating factor in converting the inexact differential δQ to the exact differential $\delta Q/T$ for a reversible process.

8.3 THE ENTROPY OF A PURE SUBSTANCE

Entropy is an extensive property of a system. Values of specific entropy (entropy per unit mass) are given in tables of thermodynamic properties in the same manner as specific volume and specific enthalpy. The units of specific entropy in the steam tables, R-12 tables, and ammonia tables are kJ/kg K, and the values are given relative to an arbitrary reference state. In the steam tables the entropy of saturated liquid at 0.01°C is given the value of zero. For many refrigerants, such as R-12 and ammonia, the entropy of saturated liquid at −40°C is assigned the value of zero.

In general, we use the term "entropy" to refer to both total entropy and entropy per unit mass, since the context or appropriate symbol will clearly indicate the precise meaning of the term.

In the saturation region the entropy may be calculated using the quality. The relations are similar to those for specific volume and enthalpy.

$$s = (1 - x)s_f + xs_g$$
$$s = s_f + xs_{fg} \tag{8.4}$$

The entropy of a compressed liquid is tabulated in the same manner as the other properties. These properties are primarily a function of the temperature, and are not greatly different from those for saturated liquid at the same temperature. Table 4 of the steam tables, which is summarized in Table A.1.4, gives the entropy of compressed-liquid water in the same manner as for other properties.

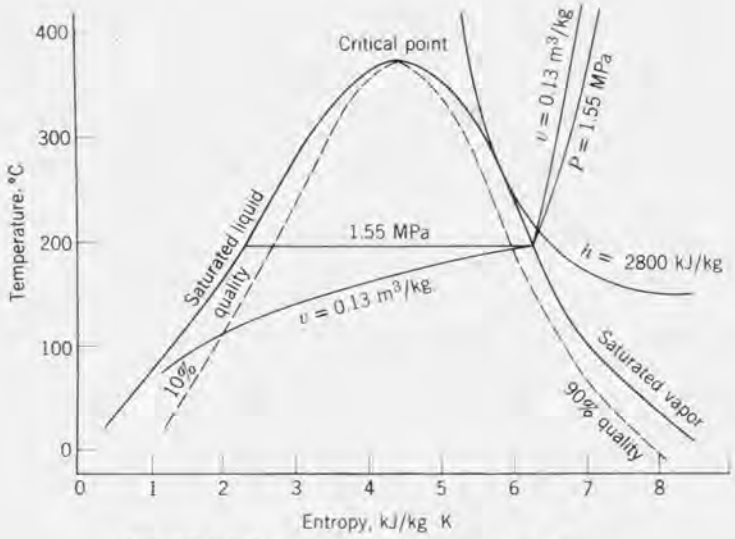


FIGURE 8.5 Temperature-entropy diagram for steam.

The thermodynamic properties of a substance are often shown on a temperature–entropy diagram and on an enthalpy–entropy diagram, which is also called a Mollier diagram, after Richard Mollier (1863–1935) of Germany. Figures 8.5 and 8.6 show the essential elements of temperature–entropy and enthalpy–entropy diagrams for steam. The general features of such diagrams are the same for all pure substances. A more complete temperature–entropy diagram for steam is shown in Fig. A.1.

These diagrams are valuable both because they present thermodynamic data and because they enable us to visualize the changes of state that occur in various

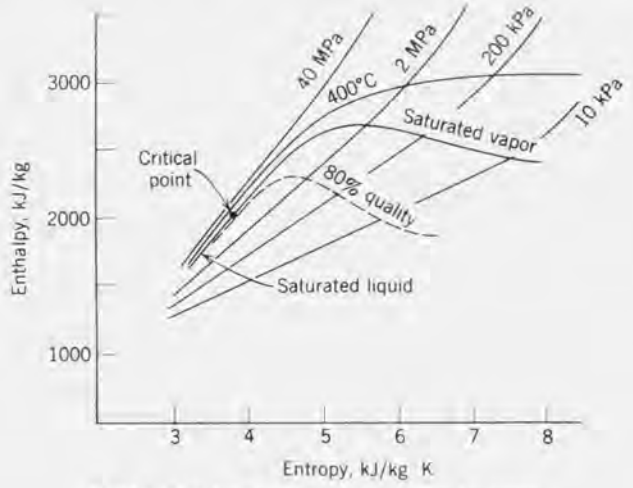


FIGURE 8.6 Enthalpy-entropy diagram for steam.

processes. As our study progresses, the student should acquire facility in visualizing thermodynamic processes on these diagrams. The temperature–entropy diagram is particularly useful for this purpose.

One more observation should be made here concerning the compressed-liquid lines on the temperature–entropy diagram for water. Reference to Table 4 of the steam tables (Table A.1.4) indicates that the entropy of the compressed liquid is less than that of saturated liquid at the same temperature for all the temperatures listed except 0°C. It can be shown that each constant-pressure line crosses the saturated-liquid line at the point of maximum density, which is about 4°C for water (the exact temperature at which maximum density occurs varies with pressure). For temperatures less than the temperature at which the density is a maximum, the entropy of compressed liquid is greater than that of the saturated liquid. Thus, lines of constant pressure in the compressed-liquid region appear (on a magnified scale) as shown in Fig. 8.7*a*. It is important to understand the general shape of these lines when showing the pumping process for liquids.

Having made this observation for water, we should state that for most substances the difference in the entropy of a compressed liquid and a saturated liquid at the

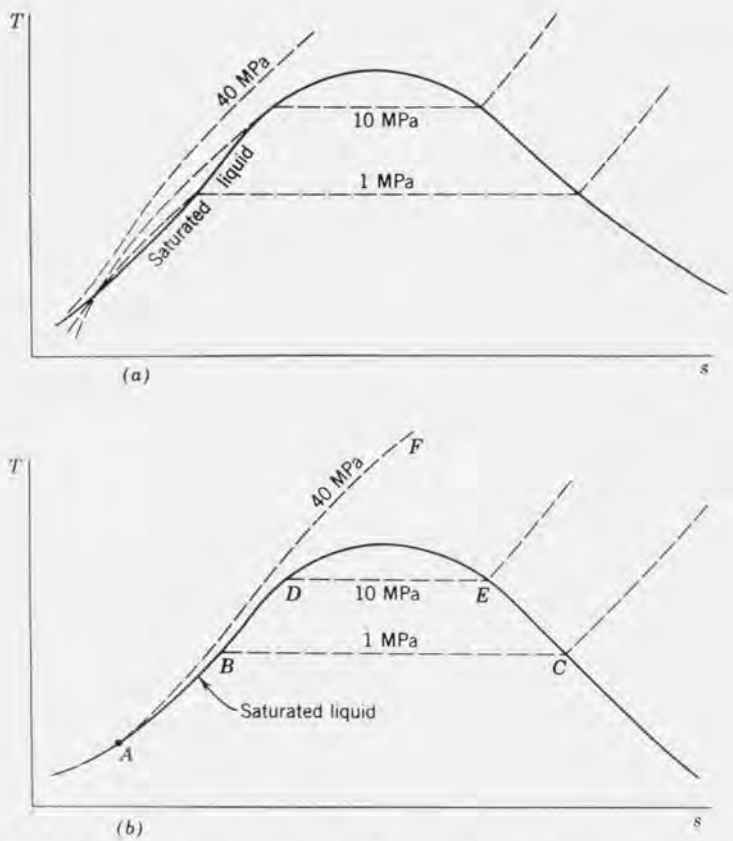


FIGURE 8.7 Temperature-entropy diagram to show properties of a compressed liquid, water.

same temperature is so small that a process in which liquid is heated at constant pressure nearly coincides with the saturated-liquid line until the saturation temperature is reached (Fig. 8.7*b*). Thus, if water at 10 MPa is heated from 0°C to the saturation temperature, it would be shown by line *ABD*, which coincides with the saturated-liquid line.

8.4 ENTROPY CHANGE IN REVERSIBLE PROCESSES

Having established that entropy is a thermodynamic property of a system, we now consider its significance in various processes. In this section we will limit ourselves to systems that undergo reversible processes and consider the Carnot cycle, reversible heat-transfer processes, and reversible adiabatic processes.

Let the working fluid of a heat engine operating on the Carnot cycle make up the system. The first process is the isothermal transfer of heat to the working fluid from the high-temperature reservoir. For this process we can write

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{rev}}$$

Since this is a reversible process in which the temperature of the working fluid remains constant, the equation can be integrated to give

$$S_2 - S_1 = \frac{1}{T_H}\int_1^2 \delta Q = \frac{{}_1Q_2}{T_H}$$

This process is shown in Fig. 8.8*a*, and the area under line 1–2, area 1–2–*b*–*a*–1, represents the heat transferred to the working fluid during the process.

The second process of a Carnot cycle is a reversible adiabatic one. From the definition of entropy,

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{rev}}$$

it is evident that the entropy remains constant in a reversible adiabatic process. A constant-entropy process is called an isentropic process. Line 2–3 represents this process, and this process is concluded at state 3 when the temperature of the working fluid reaches T_L.

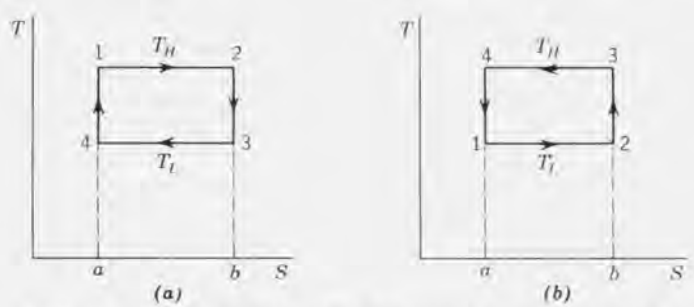


FIGURE 8.8 The Carnot cycle on the temperature-entropy diagram.

The third process is the reversible isothermal process in which heat is transferred from the working fluid to the low-temperature reservoir. For this process we can write

$$S_4 - S_3 = \int_3^4 \left(\frac{\delta Q}{T}\right)_{\text{rev}} = \frac{{}_3Q_4}{T_L}$$

Because during this process the heat transfer is negative (in regard to the working fluid), the entropy of the working fluid decreases. Moreover, because the final process 4–1, which completes the cycle, is a reversible adiabatic process (and therefore isentropic), it is evident that the entropy decrease in process 3–4 must exactly equal the entropy increase in process 1–2. The area under line 3–4, area 3–4–*a*–*b*–3, represents the heat transferred from the working fluid to the low-temperature reservoir.

Since the net work of the cycle is equal to the net heat transfer, it is evident that area 1–2–3–4–1 represents the net work of the cycle. The efficiency of the cycle may also be expressed in terms of areas.

$$\eta_{\text{th}} = \frac{W_{\text{net}}}{Q_H} = \frac{\text{area } 1\text{–}2\text{–}3\text{–}4\text{–}1}{\text{area } 1\text{–}2\text{–}b\text{–}a\text{–}1}$$

Some statements made earlier about efficiencies may now be understood graphically. For example, increasing T_H while T_L remains constant increases the efficiency. Decreasing T_L as T_H remains constant increases the efficiency. It is also evident that the efficiency approaches 100 percent as the absolute temperature at which heat is rejected approaches zero.

If the cycle is reversed, we have a refrigerator or heat pump. The Carnot cycle for a refrigerator is shown in Fig. 8.8*b*. Notice that the entropy of the working fluid increases at T_L, since heat is transferred to the working fluid at T_L. The entropy decreases at T_H because of heat transfer from the working fluid.

Let us next consider reversible heat-transfer processes. Actually, we are concerned here with processes that are internally reversible, that is, processes that have no irreversibilities within the boundary of the system. For such processes the heat transfer to or from a system can be shown as an area on a temperature–entropy diagram. For example, consider the change of state from saturated liquid to saturated vapor at constant pressure. This process would correspond to the process 1–2 on the T–s diagram of Fig. 8.9 (note that absolute temperature is required here), and the area 1–2–*b*–*a*–1 represents the heat transfer. Since this is a constant-pressure process, the heat transfer per unit mass is equal to h_{fg}. Thus,

$$s_2 - s_1 = s_{fg} = \frac{1}{m}\int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{rev}} = \frac{1}{mT}\int_1^2 \delta Q = \frac{{}_1q_2}{T} = \frac{h_{fg}}{T}$$

This relation gives a clue about how s_{fg} is calculated for tabulation in tables of thermodynamic properties. For example, consider steam at 10 MPa. From the steam tables we have

$$h_{fg} = 1317.1 \text{ kJ/kg}$$
$$T = 311.06 + 273.15 = 584.21 \text{ K}$$

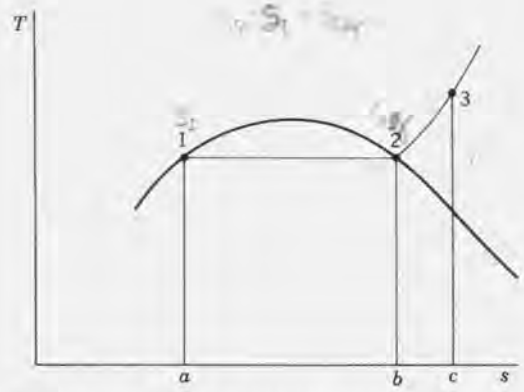


FIGURE 8.9 A temperature-entropy diagram to show areas that represent heat transfer for an internally reversible process.

Therefore,

$$s_{fg} = \frac{h_{fg}}{T} = \frac{1317.1}{584.21} = 2.2544 \text{ kJ/kg K}$$

This is the value listed for s_{fg} in the steam tables.

If heat is transferred to the saturated vapor at constant pressure, the steam is superheated along line 2–3. For this process we can write

$$_2q_3 = \frac{1}{m}\int_2^3 \delta Q = \int_2^3 T\, ds$$

Since T is not constant, this equation cannot be integrated unless we know a relation between temperature and entropy. However, we do realize that the area under line 2–3, area 2–3–c–b–2, represents $\int_2^3 T\,ds$, and therefore represents the heat transferred during this reversible process.

The important conclusion to draw here is that for processes that are internally reversible, the area underneath the process line on a temperature–entropy diagram represents the quantity of heat transferred. This is not true for irreversible processes, as will be demonstrated later.

There are many situations in which essentially adiabatic processes take place. We have already noted that in such cases the ideal process, which is a reversible adiabatic process, is isentropic. We will consider here an example of this ideal process for a system and then consider in the next chapter the reversible adiabatic process for a control volume. We will also note in a later section of Chapter 9 that by comparing an actual process with the ideal or isentropic process, we have a basis for defining the efficiency of certain classes of machines.

EXAMPLE 8.1

Consider a cylinder fitted with a piston that contains saturated R-12 vapor at $-10°C$. Let this vapor be compressed in a reversible adiabatic process until the pressure is 1.6 MPa. Determine the work per kilogram of R-12 for this process.

System: R-12.
Initial state: T_1, saturated vapor; state fixed.
Final state: P_2 known.
Process: Reversible and adiabatic.
Model: R-12 tables.
Analysis:

First law, adiabatic:

$$ {}_1q_2 = u_2 - u_1 + {}_1w_2 = 0 $$
$$ {}_1w_2 = u_1 - u_2 $$

Second law, reversible and adiabatic:

$$ s_1 = s_2 $$

Therefore, we know entropy and pressure in the final state, which is sufficient to specify the final state, since we are dealing with a pure substance.

Solution

From the R-12 tables,

$$ u_1 = 166.40 \text{ kJ/kg} $$
$$ s_1 = s_2 = 0.7014 \text{ kJ/kg K} $$
$$ P_2 = 1.6 \text{ MPa} $$

Therefore, from the superheat tables for R-12,

$$ \text{Interpolate} \rightarrow T_2 = 72.2^\circ\text{C}, \qquad u_2 = 200.57 $$
$$ {}_1w_2 = u_1 - u_2 = 166.40 - 200.57 = -34.17 \text{ kJ/kg} $$

8.5 TWO IMPORTANT THERMODYNAMIC RELATIONS

At this point we derive two important thermodynamic relations for a simple compressible substance. These relations are

$$ T\,dS = dU + P\,dV $$
$$ T\,dS = dH - V\,dP $$

The first of these relations can be derived by considering a simple compressible substance in the absence of motion or gravitational effects. The first law for a change of state under these conditions can be written

$$ \delta Q = dU + \delta W $$

The equations we are deriving here deal first with the changes of state in which the state of the substance can be identified at all times. Thus, we must consider a quasi-equilibrium process or, to use the term introduced in the last chapter, a

reversible process. For a reversible process of a simple compressible substance, we can write

$$\delta Q = T\,dS \qquad \text{and} \qquad \delta W = P\,dV$$

Substituting these relations into the first-law equation, we have

$$T\,dS = dU + P\,dV \tag{8.5}$$

which is the first equation we set out to derive. Note that this equation was derived by assuming a reversible process, and this equation can therefore be integrated for any reversible process, for during such a process the state of the substance can be identified at any point during the process. We also note that Eq. 8.5 deals only with properties. Suppose we have an irreversible process taking place between the given initial and final states. The properties of a substance depend only on the state, and therefore the change in the properties during a given change of state are the same for an irreversible process as for a reversible process. Therefore, Eq. 8.5 is often applied to an irreversible process between two given states, but the integration of Eq. 8.5 is performed along a reversible path between the same two states.

Since enthalpy is defined as

$$H = U + PV$$

it follows that

$$dH = dU + P\,dV + V\,dP$$

Substituting this relation into Eq. 8.5, we have

$$T\,dS = dH - V\,dP \tag{8.6}$$

which is the second equation that we set out to derive.

These equations can also be written for a unit mass,

$$\begin{aligned} T\,ds &= du + P\,dv \\ T\,ds &= dh - v\,dP \end{aligned} \tag{8.7}$$

or on a mole basis,

$$\begin{aligned} T\,d\bar{s} &= d\bar{u} + P\,d\bar{v} \\ T\,d\bar{s} &= d\bar{h} - \bar{v}\,dP \end{aligned} \tag{8.8}$$

These equations will be used extensively in certain subsequent sections of this book.

If we consider substances of fixed composition other than a simple compressible substance, we can write "$T\,dS$" equations other than those just given for a simple compressible substance. In Eq. 4.16 we noted that for a reversible process we can write the following expression for work:

$$\delta W = P\,dV - \mathcal{T}\,dL - \mathcal{S}\,d\mathcal{A} - \mu_0 \mathcal{H}\,d(V\mathcal{M}) - \mathcal{E}\,dZ + \cdots$$

It follows that a more general expression for the "$T\,dS$" equation would be

$$T\,dS = dU + P\,dV - \mathcal{T}\,dL - \mathcal{S}\,d\mathcal{A} - \mu_0 \mathcal{H}\,d(V\mathcal{M}) - \mathcal{E}\,dZ + \cdots \tag{8.9}$$

8.6 ENTROPY CHANGE OF A SYSTEM DURING AN IRREVERSIBLE PROCESS

Consider a system that undergoes the cycles shown in Fig. 8.10. The cycle made up of the reversible processes A and B is a reversible cycle. Therefore, we can write

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T}\right)_A + \int_2^1 \left(\frac{\delta Q}{T}\right)_B = 0$$

The cycle made up of the reversible process A and the irreversible process C is an irreversible cycle. Therefore, for this cycle the inequality of Clausius may be applied, giving the result

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T}\right)_A + \int_2^1 \left(\frac{\delta Q}{T}\right)_C < 0$$

Subtracting the second equation from the first and rearranging, we have

$$\int_2^1 \left(\frac{\delta Q}{T}\right)_B > \int_2^1 \left(\frac{\delta Q}{T}\right)_C$$

Since path B is reversible, and since entropy is a property,

$$\int_2^1 \left(\frac{\delta Q}{T}\right)_B = \int_2^1 dS_B = \int_2^1 dS_C$$

Therefore,

$$\int_2^1 dS_C > \int_2^1 \left(\frac{\delta Q}{T}\right)_C$$

For the general case we can write

$$dS \geq \frac{\delta Q}{T}$$

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T} \tag{8.10}$$

In these equations the equality holds for a reversible process and the inequality for an irreversible process.

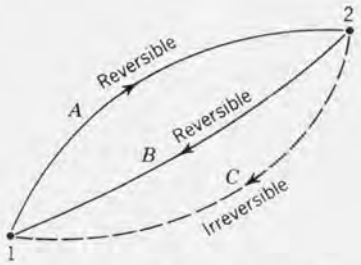


FIGURE 8.10 Entropy change of a system during an irreversible process.

This is one of the most important equations of thermodynamics. It is used to develop a number of concepts and definitions. In essence, this equation states the influence of irreversibility on the entropy of a system. Thus, if an amount of heat δQ is transferred to a system at temperature T in a reversible process, the change of entropy is given by the relation

$$dS = \frac{\delta Q}{T}$$

If any irreversible effects occur while the amount of heat δQ is transferred to the system at temperature T, however, the change of entropy will be greater than for the reversible process. We would then write

$$dS > \frac{\delta Q}{T}$$

Equation 8.10 holds when $\delta Q = 0$, when $\delta Q < 0$, and when $\delta Q > 0$. If δQ is negative, the entropy will tend to decrease as the result of the heat transfer. However, the influence of irreversibilities is still to increase the entropy of the system, and from the absolute numerical perspective we can still write for $\delta Q < 0$:

$$dS \geqslant \frac{\delta Q}{T}$$

8.7 LOST WORK

The significance of the change of entropy for an irreversible process can be amplified by introducing the concept of lost work, to which we give the symbol LW. This concept can be described with the help of Fig. 8.11, in which a gas is separated from a vacuum by a membrane. Let the membrane have a small rupture so that the gas fills the entire volume, and let the necessary heat transfer take place so that the final temperature is the same as the initial temperature. (How much heat would have to be transferred if this were an ideal gas?) Since the work is zero for this process, we conclude from the first law that

$$\delta Q = dU$$

We would like to compare this irreversible process with a reversible process between the same two states. This objective could be achieved by allowing the gas

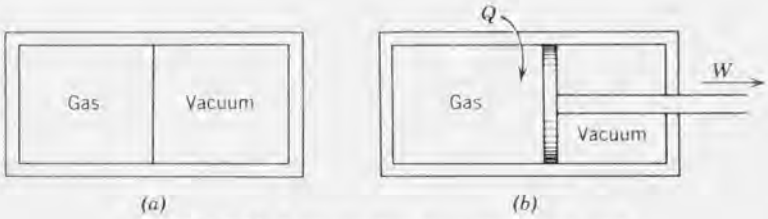


FIGURE 8.11 A process that demonstrates lost work.

to expand against a frictionless piston while heat is transferred to the gas in the amount necessary to maintain constant temperature. For this process we conclude from the first law that

$$\delta Q = dU + \delta W$$

and, because this is a reversible process, we can write

$$\delta Q = T\,dS \qquad \text{and} \qquad \delta W = P\,dV$$

The major difference between these two processes is that in the irreversible process the work is zero, whereas in the reversible process the greatest possible work is done. Thus, we speak of the lost work for an irreversible process. Every irreversible process has associated with it a certain amount of lost work. In Fig. 8.11 we show the two extreme cases, a reversible process and one in which the work is zero. Between these two extremes are processes that have various degrees of irreversibility, that is, the lost work may vary from zero to some maximum value. For a simple compressible substance we can therefore write

$$P\,dV = \delta W + \delta LW \tag{8.11}$$

where δLW is the lost work and δW the actual work.

Substituting the relation, Eq. 8.5,

$$T\,dS = dU + P\,dV$$

into Eq. 8.11, we have

$$T\,dS = dU + \delta W + \delta LW$$

But from the first law,

$$\delta Q = dU + \delta W$$

Therefore,

$$T\,dS = \delta Q + \delta LW$$

and

$$dS = \frac{\delta Q}{T} + \frac{\delta LW}{T} \tag{8.12}$$

Thus, we have an expression for the change of entropy for an irreversible process as an equality, whereas in the last section we had the inequality

$$dS \geqslant \frac{\delta Q}{T} \tag{8.13}$$

In a reversible process the lost work is zero, and therefore both Eqs. 8.12 and 8.13 reduce to

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{rev}}$$

for a reversible process.

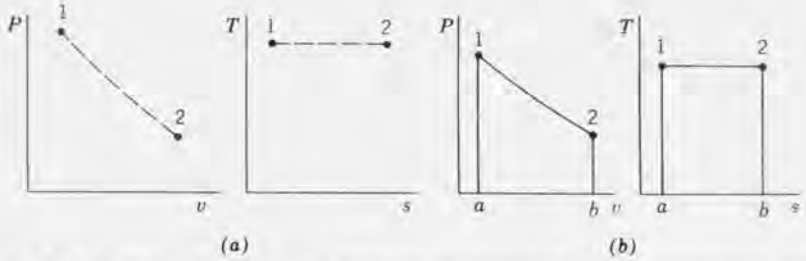


FIGURE 8.12 Reversible and irreversible processes on pressure-volume and temperature-entropy diagrams.

Some important conclusions can now be drawn from Eqs. 8.12 and 8.13. First, there are two ways in which the entropy of a system can be increased—by transferring heat to it and by having it undergo an irreversible process. Since the lost work cannot be less than zero, there is only one way in which the entropy of a system can be decreased, and that is to transfer heat from the system.

Second, the change in entropy of a system can be separated into the change that is due to heat transfer and the change that is due to internal irreversibilities. Frequently the increase in entropy caused by irreversibilities is called the irreversible production of entropy.

Finally, as we have already noted for an adiabatic process, $\delta Q = 0$, and therefore the increase in entropy is always associated with the irreversibilities.

One other point, concerning the representation of irreversible processes on P–V and T–S diagrams should be made. The work for an irreversible process is not equal to $\int P\,dV$, and the heat transfer is not equal to $\int T\,dS$. Therefore, the area underneath the path does not represent work and heat on the P–V and T–S diagrams, respectively. In fact, in many situations we are not certain of the exact state through which a system passes when it undergoes an irreversible process. For this reason it is advantageous to show irreversible processes as dotted lines and reversible processes as solid lines. Thus, the area underneath the dotted line will never represent work or heat. For example, the processes of Fig. 8.11 would be shown on P–V and T–S diagrams, as in Fig. 8.12.

Figure 8.12*a* shows an irreversible process and, because the heat transfer and work for this process are zero, the area underneath the dashed line has no significance. Figure 8.12*b* shows the reversible process, and area 1–2–*b*–*a*–1 represents the work on the P–V diagram and the heat transfer on the T–S diagram.

8.8 PRINCIPLE OF THE INCREASE OF ENTROPY

In this section we consider the total change in the entropy of a system and its surroundings when the system undergoes a change of state. This consideration leads to the principle of the increase of entropy.

Consider the process shown in Fig. 8.13, in which a quantity of heat δQ is transferred from the surroundings at temperature T_0 to the system at temperature T. Let the work done by the system during this process be δW. For this process

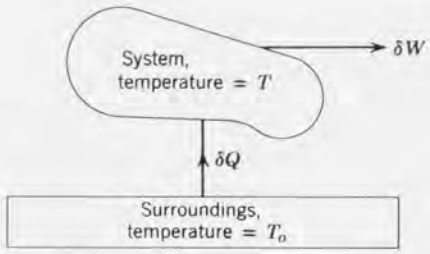


FIGURE 8.13 Entropy change for the system plus surroundings.

we can apply Eq. 8.10 to the system and write

$$dS_{\text{system}} \geqslant \frac{\delta Q}{T}$$

For the surroundings, δQ is negative and we can write

$$dS_{\text{surr}} = \frac{-\delta Q}{T_0}$$

The total net change of entropy is therefore

$$\begin{aligned} dS_{\text{net}} = dS_{\text{system}} + dS_{\text{surr}} &\geqslant \frac{\delta Q}{T} - \frac{\delta Q}{T_0} \\ &\geqslant \delta Q\left(\frac{1}{T} - \frac{1}{T_0}\right) \end{aligned} \tag{8.14}$$

Since $T_0 > T$, the quantity $\left(\frac{1}{T} - \frac{1}{T_0}\right)$ is positive and we conclude that

$$dS_{\text{net}} = dS_{\text{system}} + dS_{\text{surr}} \geqslant 0$$

If $T > T_0$, the heat transfer is from the system to the surroundings, and both δQ and the quantity $\left(\frac{1}{T} - \frac{1}{T_0}\right)$ are negative, thus yielding the same result.

Thus, we conclude that for all possible processes a system in a given surroundings can undergo,

$$dS_{\text{net}} = dS_{\text{system}} + dS_{\text{surr}} \geqslant 0 \tag{8.15}$$

where the equality holds for reversible processes and the inequality for irreversible processes. This is a very important equation, not only for thermodynamics but also for philosophical thought. This equation is referred to as the principle of the increase of entropy. The great significance is that the only processes that can take place are those in which the net change in entropy of the system plus its surroundings increases (or in the limit, remains constant). The reverse process, in which both the system and surroundings are returned to their original state, can never be made to occur. In other words, Eq. 8.15 dictates the single direction in which any process can proceed. Thus, the principle of the increase of entropy can be considered a quantitative general statement of the second law from the macroscopic point of

view and applies to the combustion of fuel in our automobile engines, the cooling of our coffee, and the processes that take place in our body.

Sometimes this principle of the increase of entropy is stated in terms of an isolated system, one in which there is no interaction between the system and its surroundings. Then there is no change in entropy of the surroundings, and we then conclude that

$$dS_{\text{isolated system}} \geq 0 \tag{8.16}$$

That is, in an isolated system, the only processes that can occur are those that have an associated increase in entropy.

EXAMPLE 8.2

Suppose that 1 kg of saturated water vapor at 100°C is condensed to a saturated liquid at 100°C in a constant-pressure process by heat transfer to the surrounding air, which is at 25°C. What is the net increase in entropy of the system plus surroundings?

Solution

For the system, from the steam tables,

$$\Delta S_{\text{system}} = -ms_{fg} = -1 \times 6.0480 = -6.0480 \text{ kJ/K}$$

Concerning the surroundings, we have

$$Q_{\text{to surroundings}} = mh_{fg} = 1 \times 2257.0 = 2257 \text{ kJ}$$

$$\Delta S_{\text{surr}} = \frac{Q}{T_0} = \frac{2257}{298.15} = 7.5700 \text{ kJ/K}$$

$$\Delta S_{\text{net}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = -6.0480 + 7.5700 = 1.5220 \text{ kJ/K}$$

This increase in entropy is in accordance with the principle of the increase of entropy, and tells us, as does our experience, that this process can take place.

It is interesting to note how this heat transfer from the water to the surroundings might have taken place reversibly. Suppose that an engine operating on the Carnot cycle received heat from the water and rejected heat to the surroundings, as shown in Fig. 8.14. The decrease in the entropy of the water is equal to the increase in

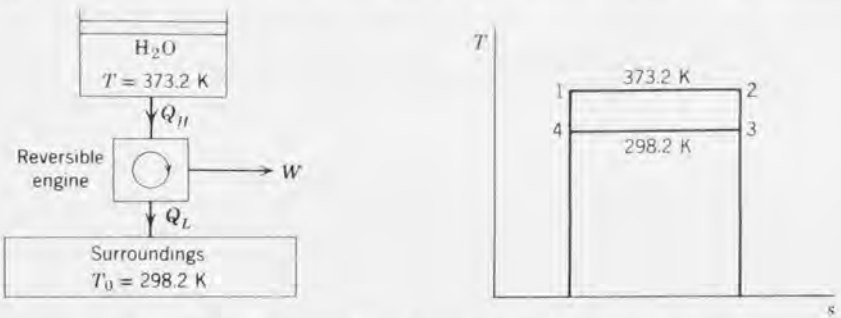


FIGURE 8.14 Reversible heat transfer with the surroundings.

the entropy of the surroundings.

$$\Delta S_{\text{system}} = -6.0480 \text{ kJ/K}$$
$$\Delta S_{\text{surr}} = 6.0480 \text{ kJ/K}$$
$$Q_{\text{to surroundings}} = T_0 \, \Delta S = 298.15(6.0480) = 1803.2 \text{ kJ}$$
$$W = Q_H - Q_L = 2257 - 1803.2 = 453.8 \text{ kJ}$$

Since this is a reversible cycle, the engine could be reversed and operated as a heat pump. For this cycle the work input to the heat pump would be 453.8 kJ.

8.9 ENTROPY CHANGE OF A SOLID OR LIQUID

In Section 5.6 we considered the calculation of the internal energy and enthalpy changes with temperature for solids and liquids and found that, in general, it is possible to express both in terms of the specific heat, in the simple manner of Eq. 5.17, and in most instances in the integrated form of Eq. 5.18. We can now use this result and the thermodynamic property relation, Eq. 8.7, to calculate the entropy change for a solid or liquid. Note that for such a phase the specific volume term in Eq. 8.7 is very small, so that substituting Eq. 5.17 yields

$$ds \simeq \frac{du}{T} \simeq \frac{C}{T} dT \tag{8.17}$$

Now, as was mentioned in Section 5.6, for many processes involving a solid or liquid, we may assume that the specific heat remains constant, in which case Eq. 8.17 can be integrated. The result is

$$s_2 - s_1 \simeq C \ln \frac{T_2}{T_1} \tag{8.18}$$

If the specific heat is not constant, then commonly C is known as a function of T, in which case Eq. 8.17 can also be integrated to find the entropy change.

EXAMPLE 8.3

One kilogram of liquid water is heated from 20°C to 90°C. Calculate the entropy change, assuming constant specific heat, and compare the result with that found when using the steam tables.

System: Water.

Initial and final states: Known.

Model: Constant specific heat, value at room temperature.

Solution

For constant specific heat, from Eq. 8.18,

$$s_2 - s_1 = 4.184 \ln\left(\frac{363.2}{293.2}\right) = 0.8958 \text{ kJ/kg K}$$

Comparing this result with that obtained by using the steam tables, we have

$$s_2 - s_1 = s_{f\,90^\circ C} - s_{f\,20^\circ C} = 1.1925 - 0.2966$$
$$= 0.8959 \text{ kJ/kg K}$$

8.10 ENTROPY CHANGE OF AN IDEAL GAS

Two very useful equations for computing the entropy change of an ideal gas can be developed from Eq. 8.7 by substituting Eqs. 5.20 and 5.24:

$$T\,ds = du + P\,dv$$

For an ideal gas

$$du = C_{v0}\,dT \qquad \text{and} \qquad \frac{P}{T} = \frac{R}{v}$$

Therefore,

$$ds = C_{v0}\frac{dT}{T} + \frac{R\,dv}{v} \tag{8.19}$$

$$s_2 - s_1 = \int_1^2 C_{v0}\frac{dT}{T} + R\ln\frac{v_2}{v_1} \tag{8.20}$$

Similarly,

$$T\,ds = dh - v\,dP$$

For an ideal gas

$$dh = C_{p0}\,dT \qquad \text{and} \qquad \frac{v}{T} = \frac{R}{P}$$

Therefore,

$$ds = C_{p0}\frac{dT}{T} - R\frac{dP}{P} \tag{8.21}$$

$$s_2 - s_1 = \int_1^2 C_{p0}\frac{dT}{T} - R\ln\frac{P_2}{P_1} \tag{8.22}$$

To integrate Eqs. 8.20 and 8.22, we must know the temperature dependence of the specific heats. However, if we recall that their difference is always constant as expressed by Eq. 5.27, we realize that we need to examine the temperature dependence of only one of the specific heats.

As in Section 5.7, let us consider the specific heat C_{p0}. Again, there are three possibilities to examine, the simplest of which is the assumption of constant specific heat. In this instance it is possible to integrate Eq. 8.22 directly, to

$$s_2 - s_1 = C_{p0}\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1} \tag{8.23}$$

Similarly, integrating Eq. 8.20 for constant specific heat, we have

$$s_2 - s_1 = C_{v0} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \tag{8.24}$$

The second possibility for the specific heat is to use an analytical equation for C_{p0} as a function of temperature, for example, one of those listed in Table A.10. The third possibility is to integrate the results of the calculations of statistical thermodynamics from reference temperature T_0 to any other temperature T and define a function

$$s_T^0 = \int_{T_0}^{T} \frac{C_{p0}}{T} dT \tag{8.25}$$

This function can then be tabulated in the single-entry (temperature) ideal-gas table, as for air in Table A.11 or for other gases in Table A.12. The entropy change between any two states 1 and 2 is then given by

$$s_2 - s_1 = (s_{T2}^0 - s_{T1}^0) - R \ln \frac{P_2}{P_1} \tag{8.26}$$

As with the energy functions discussed in Section 5.7, the ideal-gas tables, Tables A.11 and A.12, would give the most accurate results, and the equations listed in Table A.10 would give a close empirical approximation. Constant specific heat would be less accurate, except for monatomic gases and for other gases below room temperature. Again, it should be remembered that all these results are part of the ideal-gas model, which may or may not be appropriate in any particular problem.

EXAMPLE 8.4

Consider Example 5.6, in which oxygen is heated from 300 to 1500 K. Assume that during this process the pressure dropped from 200 to 150 kPa. Calculate the change in entropy per kilogram.

Solution

The most accurate answer for the entropy change, assuming ideal-gas behavior, would be from the ideal-gas tables, Table A.12. This result is, using Eq. 8.26,

$$\bar{s}_2 - \bar{s}_1 = (258.068 - 205.329) - 8.3144 \ln\left(\frac{150}{200}\right)$$

$$= 52.739 + 2.392 = 55.131 \text{ kJ/kmol K}$$

$$s_2 - s_1 = \frac{55.131}{32} = 1.7228 \text{ kJ/kg K}$$

The empirical equation from Table A.10 should give a good approximation to this result. Integrating Eq. 8.22, we have

$$\bar{s}_2 - \bar{s}_1 = \int_{T_1}^{T_2} \bar{C}_{p0} \frac{dT}{T} - \bar{R} \ln \frac{P_2}{P_1}$$

$$\bar{s}_2 - \bar{s}_1 = \left(37.432 \ln \theta + \frac{0.020\,102}{1.5} \theta^{1.5} + \frac{178.57}{1.5} \theta^{-1.5} - \frac{236.88}{2} \theta^{-2} \right)\Bigg|_{\theta_1 = 3}^{\theta_2 = 1.5} - 8.3144 \ln\left(\frac{150}{200}\right)$$

$$= 52.726 + 2.392 = 55.118 \text{ kJ/kmol K}$$

$$s_2 - s_1 = \frac{\bar{s}_2 - \bar{s}_1}{M} = \frac{55.118}{32} = 1.7224 \text{ kJ/kg K}$$

which is within 0.1 percent of the previous value. For constant specific heat, using the value at 300 K from Table A.9, we have

$$s_2 - s_1 = 0.9216 \ln\left(\frac{1500}{300}\right) - 0.259\,83 \ln\left(\frac{150}{200}\right)$$

$$= 1.4833 + 0.0747 = 1.558 \text{ kJ/kg K}$$

which is too low by 9.6 percent. If, on the other hand, we assume that the specific heat is constant at its value at 900 K, the average temperature, as in Example 5.6, then

$$s_2 - s_1 = 1.0714 \ln\left(\frac{1500}{300}\right) + 0.0747 = 1.7991 \text{ kJ/kg K}$$

which is high by 4.4 percent.

EXAMPLE 8.5

Calculate the change in entropy per kilogram as air is heated from 300 to 600 K while pressure drops from 400 to 300 kPa. Assume:

1. Constant specific heat.
2. Variable specific heat.

Solution

1. From Table A.9 for air at 300 K,

$$C_{p0} = 1.0035 \text{ kJ/kg K}$$

Therefore, using Eq. 8.23, we have

$$s_2 - s_1 = 1.0035 \ln\left(\frac{600}{300}\right) - 0.287 \ln\left(\frac{300}{400}\right) = 0.7781 \text{ kJ/kg K}$$

2. From Table A.11,

$$s^0_{T1} = 6.8693 \text{ kJ/kg K}, \qquad s^0_{T2} = 7.5764 \text{ kJ/kg K}$$

Using Eq. 8.26 gives

$$s_2 - s_1 = 7.5764 - 6.8693 - 0.287 \ln\left(\frac{300}{400}\right) = 0.7897 \text{ kJ/kg K}$$

The air tables can be used for reversible adiabatic processes by employing the relative pressure P_r and relative specific volume v_r. The definition of these terms and the derivation follow.

For the reversible adiabatic process

$$T\,ds = dh - v\,dP = 0$$

Therefore,

$$dh = C_{p0}\,dT = v\,dP = RT\frac{dP}{P}$$

$$\frac{dP}{P} = \frac{C_{p0}}{R}\frac{dT}{T}$$

Let this equation be integrated between a reference state having a temperature T_0 and a pressure P_0, and a given arbitrary state having a temperature T and a pressure P. Then

$$\ln\frac{P}{P_0} = \frac{1}{R}\int_{T_0}^{T} C_{p0}\frac{dT}{T}$$

The right side of this equation is a function of temperature only. The relative pressure P_r is defined as

$$\ln P_r \equiv \ln\frac{P}{P_0} = \frac{1}{R}\int_{T_0}^{T} C_{p0}\frac{dT}{T} = \frac{s_T^0}{R} \tag{8.27}$$

Thus, a value of P_r can be tabulated as a function of temperature.

If we consider two states, 1 and 2, along a constant-entropy line, it follows from Eq. 8.27 that

$$\frac{P_1}{P_2} = \left(\frac{P_{r1}}{P_{r2}}\right)_{s\,=\,\text{constant}} \tag{8.28}$$

This equation states that the ratio of the relative pressures for two states having the same entropy is equal to the ratio of the absolute pressures.

The development of the relative specific volume is similar, and the ratio of the relative specific volumes v_r in an isentropic process is equal to the ratio of the specific volumes. That is,

$$\frac{v_1}{v_2} = \left(\frac{v_{r1}}{v_{r2}}\right)_{s\,=\,\text{constant}} \tag{8.29}$$

The isentropic functions P_r and v_r are tabulated for air, Table A.11, but are not listed in the other gas tables in the Appendix, Table A.12. In analyzing an isentropic process for these gases, we need to use Eq. 8.26 with the left side of the equation equal to zero and the standard-state entropies from Table A.12.

EXAMPLE 8.6

One kilogram of air is contained in a cylinder fitted with a piston at a pressure of 400 kPa and a temperature of 600 K. The air is expanded to 150 kPa in a reversible, adiabatic process. Calculate the work done by the air.

System: Air.
Initial state: P_1, T_1; state 1 fixed.
Final state: P_2.
Process: Reversible and adiabatic.
Model: Ideal-gas and air tables, Table A.11.
Analysis:

First law: $$0 = u_2 - u_1 + w$$

Second law: $$s_2 = s_1$$

Solution

From Table A.11,

$$u_1 = 435.10 \text{ kJ/kg}; \qquad P_{r1} = 13.0923$$

From Eq. 8.28,

$$P_{r2} = P_{r1} \times \frac{P_2}{P_1} = 13.0923 \times \frac{150}{400} = 4.9096$$

From Table A.11,

$$T_2 = 457 \text{ K}, \qquad u_2 = 328.14$$

Therefore,

$$w = 435.10 - 328.14 = 106.96 \text{ kJ/kg}$$

At this point it is advantageous to introduce the specific heat ratio k, which is defined as the ratio of the constant-pressure specific heat to the constant-volume specific heat at zero pressure.

$$k = \frac{C_{p0}}{C_{v0}} \tag{8.30}$$

Because the difference between C_{p0} and C_{v0} is a constant, Eq. 5.27, and because C_{p0} and C_{v0} are functions of temperature, it follows that k is also a function of temperature. However, when we consider the specific heat to be constant, k is also constant.

From the definition of k and Eq. 5.27, it follows that

$$C_{v0} = \frac{R}{k-1}, \qquad C_{p0} = \frac{kR}{k-1} \tag{8.31}$$

Some very useful and simple relations for the reversible adiabatic process can be developed when the specific heats are assumed to be constant.

For the reversible adiabatic process, $ds = 0$. Therefore,

$$T\,ds = du + P\,dv = C_{v0}\,dT + P\,dv = 0$$

From the equation of state for an ideal gas,

$$dT = \frac{1}{R}(P\,dv + v\,dP)$$

Therefore,

$$\frac{C_{v0}}{R}(P\,dv + v\,dP) + P\,dv = 0$$

Substituting Eq. 8.31 into the expression and rearranging gives

$$\frac{1}{k-1}(P\,dv + v\,dP) + P\,dv = 0$$

$$v\,dP + kP\,dv = 0$$

$$\frac{dP}{P} + k\frac{dv}{v} = 0$$

Because k is constant when the specific heat is constant, this equation can be integrated under these conditions to give

$$Pv^k = \text{constant} \tag{8.32}$$

Equation 8.32 holds for all reversible adiabatic processes that involve an ideal gas with constant specific heat. It is usually advantageous to express this constant in terms of the initial and final states.

$$Pv^k = P_1v_1^k = P_2v_2^k = \text{constant} \tag{8.33}$$

From this equation and the ideal-gas equation of state, the following expressions relating the initial and final states of an isentropic process can be derived.

$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^k = \left(\frac{V_1}{V_2}\right)^k \tag{8.34}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} = \left(\frac{v_1}{v_2}\right)^{k-1} \tag{8.35}$$

With the assumption of constant specific heat, some convenient equations can be derived for the work done by an ideal gas during an adiabatic process. Consider a system consisting of an ideal gas that undergoes a process in which work is done only at the moving boundary.

$${}_1Q_2 = m(u_2 - u_1) + {}_1W_2 = 0$$

$${}_1W_2 = -m(u_2 - u_1) = -mC_{v0}(T_2 - T_1)$$

$$= \frac{mR}{1-k}(T_2 - T_1) = \frac{P_2V_2 - P_1V_1}{1-k} \tag{8.36}$$

It should be noted that Eq. 8.36 applies to adiabatic processes only. Since no assumption was made regarding reversibility, it applies to both reversible and

irreversible processes. Equation 8.36 is frequently derived for reversible processes by starting with the relation

$$ {}_1W_2 = \int_1^2 P\, dV $$

for the system.

8.11 THE REVERSIBLE POLYTROPIC PROCESS FOR AN IDEAL GAS

When a gas undergoes a reversible process in which there is heat transfer, the process frequently takes place in such a manner that a plot of log P versus log V is a straight line, as shown in Fig. 8.15. For such a process PV^n is a constant.

A process having this relation between pressure and volume is called a polytropic process. An example is the expansion of the combustion gases in the cylinder of a water-cooled reciprocating engine. If the pressure and volume are measured during the expansion stroke of a polytropic process, as might be done with an engine indicator, and the logarithms of the pressure and volume are plotted, the result would be similar to the straight line in Fig. 8.15. From this figure it follows that

$$ \frac{d \ln P}{d \ln V} = -n $$

$$ d \ln P + n d \ln V = 0 $$

If n is a constant (which implies a straight line on the log P versus log V plot), this equation can be integrated to give the following relation:

$$ PV^n = \text{constant} = P_1 V_1^n = P_2 V_2^n \tag{8.37} $$

From this equation it is evident that the following relations can be written for a polytropic process.

$$ \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^n $$

$$ \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(n-1)/n} = \left(\frac{V_1}{V_2}\right)^{n-1} \tag{8.38} $$

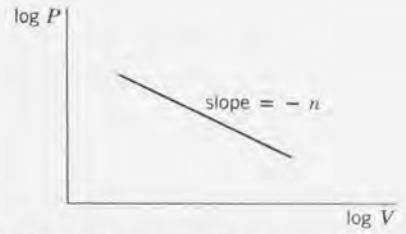


FIGURE 8.15 Example of a polytropic process.

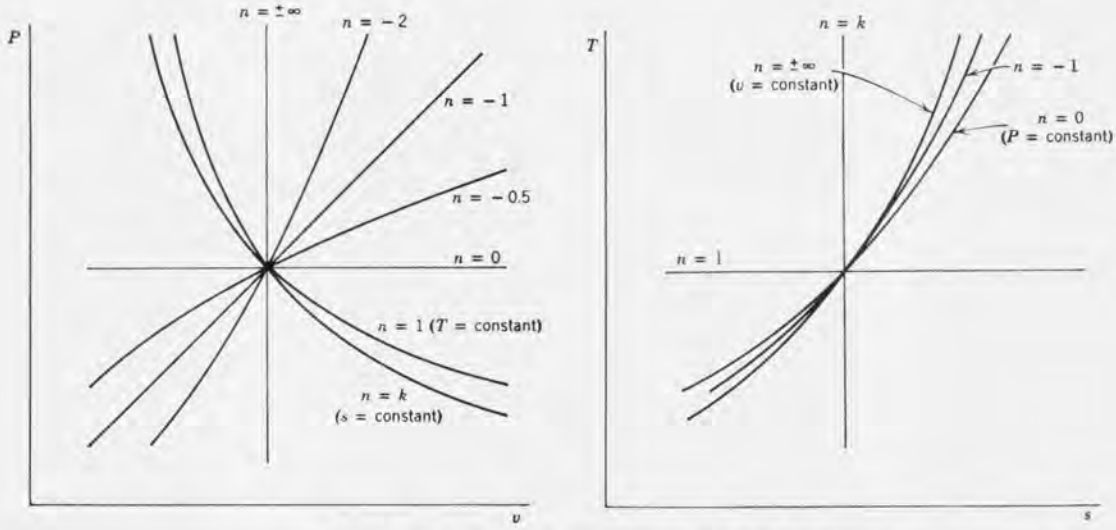


FIGURE 8.16 Polytropic processes on P–v and T–s diagrams.

For a system consisting of an ideal gas, the work done at the moving boundary during a reversible polytropic process can be derived from the relations

$$
\begin{aligned}
{}_1W_2 &= \int_1^2 P\,dV \qquad \text{and} \qquad PV^n = \text{constant} \\
{}_1W_2 &= \int_1^2 P\,dV = \text{constant} \int_1^2 \frac{dV}{V^n} \\
&= \frac{P_2V_2 - P_1V_1}{1-n} = \frac{mR(T_2 - T_1)}{1-n}
\end{aligned} \tag{8.39}
$$

for any value of n except $n = 1$.

The polytropic processes for various values of n are shown in Fig. 8.16 on P–v and T–s diagrams. The values of n for some familiar processes are

Isobaric process	$n = 0$
Isothermal process	$n = 1$
Isentropic process	$n = k$
Isochoric process	$n = \infty$

EXAMPLE 8.7

In a reversible process nitrogen is compressed in a cylinder from 100 kPa, 20°C to 500 kPa. During the compression process the relation between pressure and volume is $PV^{1.3} = \text{constant}$. Calculate the work and heat transfer per kilogram, and show this process on P–v and T–s diagrams.

System: Nitrogen.

Initial state: P_1, T_1; state 1 known.

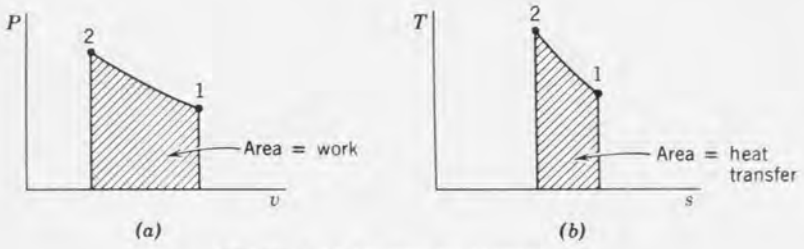


FIGURE 8.17 Diagram for Example 8.7.

Final state: P_2.

Process: Reversible, polytropic with exponent $n < k$.

Diagram: Fig. 8.17.

Model: Ideal gas, constant specific heat—value at 300 K.

Analysis: Boundary movement work. From Eq. 8.39,

$$ {}_1W_2 = \int_1^2 P\,dV = \frac{P_2V_2 - P_1V_1}{1-n} = \frac{mR(T_2 - T_1)}{1-n} $$

First law: $$ {}_1q_2 = u_2 - u_1 + {}_1w_2 = C_{v0}(T_2 - T_1) + {}_1w_2 $$

Solution

From Eq. 8.38,

$$ \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(n-1)/n} = \left(\frac{500}{100}\right)^{(1.3-1)/1.3} = 1.4498 $$

$$ T_2 = 293.2 \times 1.4498 = 425 \text{ K} $$

Then

$$ {}_1w_2 = \frac{R(T_2 - T_1)}{1-n} = \frac{0.2968(425 - 293.2)}{(1 - 1.3)} = -130.4 \text{ kJ/kg} $$

and from the first law,

$$ {}_1q_2 = C_{v0}(T_2 - T_1) + {}_1w_2 $$
$$ = 0.7448(425 - 293.2) - 130.4 = -32.2 \text{ kJ/kg} $$

The reversible isothermal process for an ideal gas is of particular interest. In this process

$$ PV = \text{constant} = P_1V_1 = P_2V_2 \tag{8.40} $$

The work done at the boundary of a simple compressible system during a reversible isothermal process can be found by integrating the equation

$$ {}_1W_2 = \int_1^2 P\,dV $$

The integration is

$$ {}_1W_2 = \int_1^2 P\,dV = \text{constant} \int_1^2 \frac{dV}{V} = P_1V_1 \ln \frac{V_2}{V_1} = P_1V_1 \ln \frac{P_1}{P_2} \tag{8.41} $$

or

$$ {}_1W_2 = mRT \ln \frac{V_2}{V_1} = mRT \ln \frac{P_1}{P_2} \tag{8.42} $$

Because there is no change in internal energy or enthalpy in an isothermal process, the heat transfer is equal to the work (neglecting changes in kinetic and potential energy). Therefore, we could have derived Eq. 8.41 by calculating the heat transfer.

For example, using Eq. 8.7, we have

$$ \int_1^2 T\,ds = {}_1q_2 = \int_1^2 du + \int_1^2 P\,dv $$

But $du = 0$ and $Pv = \text{constant} = P_1v_1 = P_2v_2$, such that

$$ {}_1q_2 = \int_1^2 P\,dv = P_1v_1 \ln \frac{v_2}{v_1} $$

which yields the same result as Eq. 8.41.

PROBLEMS

8.1 Consider a Carnot-cycle heat engine with water as the working fluid. The heat transfer to the working fluid takes place at 300°C; during this process the water changes from saturated liquid to saturated vapor. Heat is rejected from the working fluid at 40°C.

(a) Show this cycle on a T–s diagram.

(b) Calculate the quality of the working fluid at the beginning and at the end of the isothermal heat rejection process.

(c) Determine the net work output per kilogram of water and the thermal efficiency of the cycle.

8.2 Consider a Carnot-cycle heat pump with R-22 as the working fluid. Heat is rejected from the working fluid at 40°C. During this process the R-12 changes from saturated vapor to saturated liquid. Heat is transferred to the R-22 at 0°C.

(a) Show this cycle on a T–s diagram.

(b) Calculate the quality of the working fluid at the beginning and at the end of the isothermal heat addition process at 0°C.

(c) Determine the coefficient of performance for the cycle.

8.3 A cylinder fitted with a frictionless piston contains ammonia at 50°C, 20 percent quality, and under these conditions the cylinder volume is 1 L. The ammonia expands slowly, and during this process heat is transferred to the system to maintain a constant temperature. The process continues until all the liquid is gone. Determine the work and heat transfer for this process.

8.3E A cylinder fitted with a frictionless piston contains ammonia at 120 F, 20 percent quality, and under these conditions the cylinder volume is 60 $in.^3$. The ammonia expands slowly, and during this process heat is transferred to the system to maintain a constant temperature. The process continues until all the liquid is gone. Determine the work and heat transfer for this process.

8.4 An insulated cylinder fitted with a frictionless piston contains 0.1 kg of water at 100°C, 90 percent quality. The piston is moved, compressing the water until it reaches a pressure of 1.2 MPa. How much work is required in this process?

8.5 A cylinder containing R-22 at 10°C, 100 kPa, has an initial volume of 20 L. A piston compresses the R-22 in a reversible, isothermal process until it reaches the saturated-vapor point. Calculate the required work and heat transfer needed to accomplish this change of state.

8.6 One kilogram of water at 300°C expands against a piston in a cylinder until it reaches ambient pressure, 100 kPa, at which point the water has a quality of 90 percent. It may be assumed that the expansion is reversible and adiabatic.

(a) What was the initial pressure in the cylinder?
(b) How much work is done by the water?

8.6E One pound-mass of water at 600 F expands against a piston in a cylinder until it reaches ambient pressure, 14.7 $lbf/in.^2$, at which point the water has a quality of 90 percent. It may be assumed that the expansion is reversible and adiabatic.

(a) What was the initial pressure in the cylinder?
(b) How much work is done by the water?

8.7 A heavily insulated cylinder fitted with a piston contains ammonia at 10°C. The piston is moved, compressing the ammonia in a reversible process until the pressure reaches 2 MPa; at this point the temperature is 70°C. During the process 400 kJ of work is done on the system. What was the initial volume of the cylinder?

8.8 A rigid, insulated vessel contains superheated vapor steam at 1.8 MPa, 350°C. A valve on the vessel is opened, allowing steam to escape. It may be assumed that at any instant the steam remaining inside the vessel has undergone a reversible, adiabatic expansion. Determine the fraction of steam that has escaped when the steam remaining inside the vessel reaches the saturated vapor line.

8.8E A rigid, insulated vessel contains superheated vapor steam at 200 $lbf/in.^2$, 700 F. A valve on the vessel is opened, allowing steam to escape. It may be assumed that at any instant the steam remaining inside the vessel has undergone a reversible, adiabatic expansion. Determine the fraction of steam that has escaped when the steam remaining inside the vessel reaches the saturated vapor line.

8.9 An insulated cylinder fitted with a frictionless piston contains 0.1 kg of superheated vapor steam. The steam expands to ambient pressure, 100 kPa, at which point the temperature of the steam inside the cylinder is 150°C. The steam does 50 kJ of work against the piston during this expansion. What were the initial pressure and temperature?

8.10 A certain elastic balloon supports an internal pressure equal to $P_0 = 100$ kPa until the balloon becomes spherical at a diameter of $D_0 = 0.5$ m, above which

$$P = P_0 + C(D^{*-1} - D^{*-7}), \qquad D^* = D/D_0$$

because of the offsetting effects of balloon curvature and elasticity. This balloon, initially flat and deflated, is connected by a valve to a 130-L insulated, rigid tank containing ammonia at 1 MPa, 50°C. The valve is opened, and ammonia flows from the tank into the balloon, inflating it until the balloon goes through a maximum point in pressure of 300 kPa. During this process it may be assumed that whatever ammonia remains inside the tank has undergone a reversible and adiabatic expansion. And during the expansion the temperature in the uninsulated balloon is always equal to ambient temperature, 20°C. What is the pressure inside the tank when the balloon has reached its maximum pressure of 300 kPa?

8.11 Consider the balloon inflation process of Problem 8.10. Suppose that the valve is left open, and the process continues until the tank and balloon pressures equalize. What is this pressure? What is the temperature inside the tank at this point?

8.12 We wish to cool a given quantity of material rapidly to a temperature of 10°C. The process requires a heat rejection of 2000 kJ. One possibility is to immerse the material in a mixture of ice and water, allowing heat transfer from the material to the ice, which melts the ice. Another possibility is to cool the material by evaporating R-22 at −20°C. The heat transfer to the R-22 changes it from a saturated liquid to a saturated vapor. A third possibility is to evaporate liquid nitrogen at 101.3-kPa pressure.

(a) Calculate the change of entropy of the cooling medium for each of the three cooling techniques.

(b) Discuss the significance of these results.

8.13 A cylinder fitted with a piston contains 3 kg of water at 500 kPa, 600°C. The piston has a cross-sectional area of 0.1 m^2 and is restrained by a linear spring (force proportional to distance moved) with a spring constant of 10 kN/m. The system is allowed to cool until the pressure inside drops to 150 kPa, as heat transfers to the room at 20°C. Calculate the net change of entropy, system plus surroundings, for this process.

8.13E A cylinder fitted with a piston contains 5 lbm of water at 80 lbf/$in.^2$, 1000 F. The piston has a cross-sectional area of 1.0 ft^2 and is restrained by a linear spring (force proportional to distance moved) with a spring constant of 60 lbf/in. The system is allowed to cool until the pressure inside drops to 20 lbf/$in.^2$ as heat transfers to the room at 70 F. Calculate the net change of entropy, system plus surroundings, for this process.

8.14 Calculate the net entropy change for the overall process described in Problems 8.10 and 8.11, assuming that heat transfer is with the ambient.

8.15 An insulated cylinder fitted with a piston has an initial volume of 0.15 m^3 and contains steam at 400 kPa, 200°C. The steam is expanded adiabatically, and during this process the work output is carefully measured and found to be 30 kJ. It is claimed that at the final state the steam is in the two-phase (liquid plus vapor) region. What is your evaluation of this claim?

8.16 Consider the process shown in Fig. 8.18. Tank *A*, which is insulated, has a volume of 600 L and contains steam at 1.4 MPa, 300°C. Tank *B*, which is uninsulated, has a volume of 300 L and contains steam at 200 kPa, 200°C. A valve connecting the two tanks is opened, and steam flows from *A* to *B* until the temperature in *A* reaches 250°C. The valve then is closed. During this process heat is transferred from *B* to

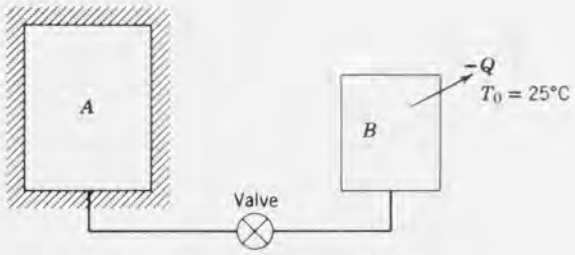


FIGURE 8.18 Sketch for Problem 8.16.

the surroundings at 25°C, such that the temperature inside B remains at 200°C. It may be assumed that the steam remaining inside A has undergone a reversible adiabatic process. Determine

(a) The final pressure in each tank.
(b) The final mass in tank B.
(c) The net entropy change, system plus surroundings, for the process.

8.17 A cylinder fitted with a piston contains saturated vapor R-22 at 10°C; the volume is 10 L. The system is compressed to 2 MPa, 60°C in a reversible (internally) polytropic process. If all heat transfer during the process is with the ambient at 10°C, calculate the net entropy change.

8.18 An insulated cylinder fitted with a piston contains R-12 at 600 kPa, 40°C. Under these conditions the volume is 100 L. The R-12 expands, moving the piston until the pressure in the cylinder has dropped to 100 kPa. It is claimed that the R-12 does 75 kJ of work against the piston during the process. Is this possible?

8.19 A cylinder fitted with a frictionless piston contains water at 200 kPa, 150°C. Under these conditions the volume is 150 L. The piston is moved slowly, compressing the water to a pressure of 700 kPa. During this process

$$PV^{0.9} = \text{constant}$$

Assuming that the room temperature is 20°C, show that this process does not violate the second law.

8.19E A cylinder fitted with a frictionless piston contains water at 20 lbf/in.^{2}, 240 F. Under these conditions the volume is 5 ft^3. The piston is moved slowly, compressing the water to a pressure of 100 lbf/in.^{2}. During this process

$$PV^{0.9} = \text{constant}$$

Assuming that the room temperature is 70 F, show that this process does not violate the second law.

8.20 A vertical cylinder with a frictionless piston contains R-22 at −20°C, 70 percent quality, and the volume is 50 L. This cylinder is brought into a 20°C room, and an electric current of 10 A is passed through a resistor inside the cylinder. The voltage drop across the resistor is 12 V. It is claimed that after 30 minutes the temperature inside the cylinder is 40°C. Is this possible?

8.21 A 10-kg bar of cast iron initially at 400°C is quenched in a 200-L water tank initially at 25°C. Assuming no heat transfer with the surroundings and no boiling away of liquid water, calculate the net entropy change for the process.

8.21E A 10-lbm bar of cast iron initially at 700 F is quenched in a 5-ft^3 water tank initially at 60 F. Assuming no heat transfer with the surroundings and no boiling away of liquid water, calculate the net entropy change for the process.

8.22 A large slab of concrete, 5 × 8 × 0.3 m, is used as a thermal storage mass in a solar-heated house. If the slab temperature cools overnight from 23° to 18°C in an 18°C house, what is the net entropy change associated with this process?

8.23 A 5-kg bar of lead initially at 20°C is heated at constant pressure to 550°C as heat is transferred from a large constant-temperature heat source at 550°C. Calculate the net entropy change for this process. The melting point of lead is 327°C. At this temperature the enthalpy change of melting is 24.6 kJ/kg. The specific heat of the solid is 0.138 kJ/kg K and that of the liquid is 0.155 kJ/kg K.

8.24 A hollow steel sphere with a 0.5-m inside diameter and a 2-mm wall thickness contains water at 2 MPa, 250°C. This system (steel plus water) cools to the ambient temperature, 30°C. Calculate the net entropy change of the system plus surroundings for this process.

8.25 A mass of 1 kg of air contained in a cylinder at 1.5 MPa, 1000 K, expands in a reversible isothermal process to 100 kPa. Calculate

(a) The heat transfer during the process.
(b) The change of entropy of the air.

8.26 A mass of 1 kg of air contained in a cylinder at 1.5 MPa, 1000 K, expands in a reversible adiabatic process to 100 kPa. Calculate the final temperature and the work done during the process, using

(a) Constant specific heat, value from Table A.9.
(b) The ideal-gas air tables, Table A.11.

8.27 We wish to obtain a supply of cold helium gas by applying the following technique. Helium contained in a cylinder at ambient conditions, 100 kPa and 20°C, is compressed in a reversible isothermal process to 600 kPa, after which the gas is expanded back to 100 kPa in a reversible adiabatic process.

(a) Show the processes on a T–s diagram.
(b) Calculate the final temperature and the net work per kilogram of helium.
(c) If a diatomic gas, such as nitrogen or oxygen, is used instead of helium, would the final temperature be higher, lower, or the same?

8.27E We wish to obtain a supply of cold helium gas by applying the following technique. Helium contained in a cylinder at ambient conditions, 14.7 lbf/in.^{2} and 70 F, is compressed in a reversible isothermal process to 90 lbf/in.^{2}, after which the gas is expanded back to 14.7 lbf/in.^{2} in a reversible adiabatic process.

(a) Show the processes on a T–s diagram.
(b) Calculate the final temperature and the net work per pound-mass of helium.
(c) If a diatomic gas, such as nitrogen or oxygen, is used instead of helium, would the final temperature be higher, lower, or the same?

8.28 An insulated cylinder fitted with a frictionless piston contains carbon dioxide gas at 120 kPa, 400 K. The gas is compressed to 2.5 MPa in a reversible adiabatic process. Calculate the final temperature and the work per unit mass, assuming

(a) Variable specific heat, Table A.12.

(b) Constant specific heat, value from Table A.9.
(c) Constant specific heat, value at an intermediate temperature from Table A.10.

8.29 Consider a Carnot-cycle heat pump having 1 kg of nitrogen gas in a cylinder and piston arrangement as the working fluid. This heat pump operates between reservoirs at 300 K and 400 K. At the beginning of the low-temperature heat addition process, the pressure is 1 MPa. During this process the volume triples. Analyze each of the four processes in the cycle, and determine

(a) The pressure, volume, and temperature at each point.
(b) The work and heat transfer for each process.

8.30 A 1-m^3 insulated, rigid tank contains air at 800 kPa, 25°C. A valve on the tank is opened, and the pressure inside quickly drops to 150 kPa, at which point the valve is closed.

(a) Assuming that the air remaining inside the tank has undergone a reversible adiabatic expansion, calculate the mass withdrawn during the process.
(b) Calculate the mass withdrawn by a first-law, control volume analysis. Compare the result with that for part a.
(c) Repeat part b, utilizing a stepwise solution procedure whereby the solution is divided into several parts. Then further develop this approach into a general first-law solution.

8.30E An insulated, rigid 25-ft^3 tank contains air at 110 lbf/$in.^2$, 75 F. A valve on the tank is opened and the pressure inside quickly drops to 15 lbf/$in.^2$, at which point the valve is closed.

(a) Assuming that the air remaining inside the tank has undergone a reversible adiabatic expansion, calculate the mass withdrawn during the process.
(b) Calculate the mass withdrawn by a first-law, control volume analysis. Compare the result with that for part a.
(c) Repeat part b, utilizing a stepwise solution procedure whereby the solution is divided into several parts. Then further develop this approach into a general first-law solution.

8.31 A rigid container with a volume of 200 L is divided into two equal volumes by a partition. Both sides contain nitrogen, one side containing it at 2 MPa, 200°C, and the other at 200 kPa, 100°C. The partition ruptures, and the nitrogen comes to equilibrium at 70°C. Assuming that the temperature of the surroundings is 20°C, determine the work done and the net entropy change for the process.

8.32 Consider the following procedure for measuring the specific heat ratio k of a gas. The gas is initially contained in a rigid vessel at pressure P_1 (slightly higher than ambient pressure P_0) and at the ambient temperature. A valve on the vessel is opened and the gas pressure quickly drops to P_0, at which point the valve is closed. After a long time, the gas remaining inside the vessel returns to thermal equilibrium with the ambient, at which point the pressure inside is P_2. Develop an expression for k in terms of P_0, P_1, and P_2.

8.33 A cylinder fitted with a piston contains carbon dioxide at 1 MPa, 300°C. Under these conditions the volume is 200 L. The total external force acting on the piston is proportional to V^3. This system is allowed to cool to room temperature, 20°C. What is the net entropy change, system plus surroundings, for this process?

8.33E A cylinder fitted with a piston contains carbon dioxide at 150 lbf/in.^{2}, 600 F. Under these conditions the volume is 7 ft^3. The total external force acting on the piston is proportional to V^3. This system is allowed to cool to room temperature, 70 F. What is the net entropy change, system plus surroundings, for this process?

8.34 A cylinder is fitted with an aluminum piston and spring. The device has a total mass of 4 kg. The cylinder has an initial volume of 50 L and contains carbon dioxide gas at 2 MPa. Under these conditions the system (aluminum plus gas) temperature is 200°C. By transferring heat with the surroundings, this system cools to the ambient temperature, 25°C, at which point the pressure is 1.5 MPa. What is the net entropy change of this process?

8.35 A cylinder fitted with a piston contains 1 kg of methane gas at 100 kPa, 20°C. The gas is compressed reversibly to a pressure of 800 kPa. Calculate the work required if the process is

(a) Adiabatic.
(b) Isothermal.
(c) Polytropic, with exponent $n = 1.15$.

8.35E A cylinder fitted with a piston contains 1 lbm of methane gas at 15 lbf/in.^{2}, 70 F. The gas is compressed reversibly to a pressure of 120 lbf/in.^{2}. Calculate the work required if the process is

(a) Adiabatic.
(b) Isothermal.
(c) Polytropic, with exponent $n = 1.15$.

8.36 The power stroke expansion of exhaust gases in an internal combustion engine can be reasonably represented as a polytropic expansion. Consider air contained in a cylinder volume of 0.1 L at 7 MPa, 1800 K. The air expands in a reversible polytropic process, with exponent $n = 1.30$, through a volume ratio of 8:1. Show this process on P–v and T–s coordinates, and calculate the work and heat transfer for the process.

8.37 A mass of 2 kg of ethane gas at 500 kPa, 100°C, undergoes a reversible polytropic expansion with $n = 1.30$ until the final temperature equals that of the ambient, 20°C. Calculate the net entropy change of the system plus surroundings for this process, assuming that heat is transferred with the ambient.

8.38 A cylinder fitted with a piston contains air at ambient conditions, 100 kPa and 20°C. Under these conditions the volume is 0.3 m^3. The air is compressed to 800 kPa in a reversible polytropic process with exponent $n = 1.20$, after which it is expanded back to 100 kPa in a reversible adiabatic process.

(a) Show the two processes on P–v and T–s diagrams.
(b) Determine the final temperature and the net work.
(c) What is the potential refrigeration capacity (in kilojoules) of the air at the final state?

8.38E A cylinder fitted with a piston contains air at ambient conditions, 14.7 lbf/in.^{2} and 70 F. Under these conditions the volume is 10 ft^3. The air is compressed to 100 lbf/in.^{2} in a reversible polytropic process with exponent $n = 1.20$, after which it is expanded back to 14.7 lbf/in.^{2} in a reversible adiabatic process.

(a) Show the two processes on P–v and T–s diagrams.
(b) Determine the final temperature and the net work.
(c) What is the potential refrigeration capacity (in Btu) of the air at the final state?

8.39 An ideal gas having a constant specific heat of

$$\overline{C}_{p0} = 40 \text{ kJ/kmol K}$$

undergoes a reversible polytropic compression in which the polytropic exponent is $n = 1.40$. Will the heat transfer for this process be positive, negative, or zero?

8.40 A cylinder fitted with a frictionless piston contains 500 L of air at 110 kPa, 25°C. The air is compressed in a reversible, polytropic process to a final pressure of 800 kPa, at which point the temperature is 140°C. Assuming that heat transfer is with the ambient at 25°C, determine

(a) The polytropic exponent n.
(b) The final volume of the air.
(c) The work done on the air and the heat transfer for the process.
(d) The net change in entropy for the process.

8.41 A cylinder divided by a frictionless, thermally insulated piston contains air on one side and water on the other, as shown in Fig. 8.19. The cylinder is well insulated, except for the end of the side that contains the water. Each volume is initially 100 L. The air is at 40°C, and the water is at 90°C with a quality of 10 percent. Heat is slowly transferred to the water, until at the final state it exists as saturated vapor. Calculate the final pressure and the amount of heat transferred.

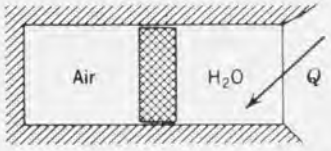


FIGURE 8.19 Sketch for Problem 8.41.

8.42 Consider the system shown in Fig. 8.20. Tank A has a volume of 300 L and initially contains air at 700 kPa, 40°C. Cylinder B is fitted with a frictionless piston resting on the bottom, at which position the spring is fully extended. The piston has a

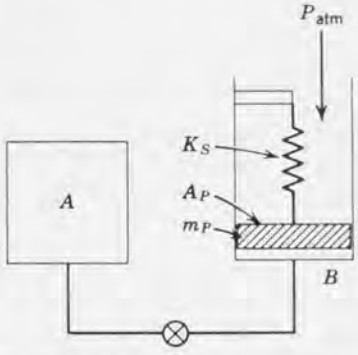


FIGURE 8.20 Sketch for Problem 8.42.

cross-sectional area of 0.065 m^2 and mass of 40 kg, and the spring constant K_s is 17.5 kN/m. The atmospheric pressure is 100 kPa. The valve is opened and air flows into the cylinder until the pressure in A and B become equal, after which the valve is closed. During this process the air remaining in A may be assumed to have undergone a reversible adiabatic process, and the entire process is adiabatic. It may also be assumed that the spring force is proportional to the displacement. Determine the final pressure in the system and the final temperature in cylinder B.

COMPUTER PROBLEMS

8.1C Write a program to solve the following problem. One of the gases listed in Table A.10 undergoes a reversible adiabatic process in a cylinder from P_1, T_1 to P_2. We wish to calculate the final temperature and the work for the process by integrating the specific heat equation; by assuming constant specific heat at temperature T_1; and finally by assuming constant specific heat at an average temperature (by iteration).

8.2C Write a program to solve the following problem. In Problem 5.2C, the enthalpy values in the ideal-gas tables, Table A.12, were used to curve-fit polynomial equations for ideal-gas specific heat as functions of temperature. We wish to use these equations to calculate ideal-gas entropy functions, and to compare the results with the values listed in Table A.12 and with polynomial equations that are curve-fitted directly to the entropy functions as listed in Table A.12. Why are the results different?

8.3C Write a program to follow the path of the ammonia in the tank and balloon for Problems 8.10, 8.11, and 8.14.

8.4C Write a program to solve the general case of Problem 8.13, in which the initial state, spring constant, and final pressure are all variables.

8.5C Write a program to follow the path of the processes in the two tanks of Problem 8.16. The initial states and volumes and the final temperature in tank A are all input variables.

8.6C Write a program to solve the general case of Problem 8.24, in which the sphere dimensions and the initial state of the water are input variables.

8.7C Write a program to solve the general case of Problem 8.41, in which both initial volumes and states are program input variables.

9

SECOND-LAW ANALYSIS FOR A CONTROL VOLUME

In the preceding two chapters we discussed the second law of thermodynamics and the thermodynamic property, entropy. As was done with the first-law analysis, we now consider the more general application of these concepts, the control volume analysis, and a number of cases of special interest. We will also discuss thermodynamic availability and two related thermodynamic properties, the Gibbs and Helmholtz functions.

9.1 THE SECOND LAW OF THERMODYNAMICS FOR A CONTROL VOLUME

The second law of thermodynamics can be applied to a control volume by a procedure similar to that used in Section 6.2 for writing the first law for a control volume. Equation 8.12 states the second law for a system analysis in the form

$$dS = \frac{\delta Q}{T} + \frac{\delta LW}{T}$$

For a change in entropy, $S_2 - S_1$, that occurs during a time interval δt, we can write

$$\frac{S_2 - S_1}{\delta t} = \frac{1}{\delta t}\left(\frac{\delta Q}{T}\right) + \frac{1}{\delta t}\left(\frac{\delta LW}{T}\right) \tag{9.1}$$

Consider the system and control volume shown in Fig. 9.1. During time δt the mass δm_i enters the control volume across the discrete area $\mathscr{A}_i$, the mass δm_e leaves across the discrete area $\mathscr{A}_e$, an amount of heat δQ is transferred to the system across an element of area where the surface temperature is T, and work δW is done by the system. As in the analysis of Section 6.2, we assume that the increment of mass, δm_i, has uniform properties, and similarly that δm_e has uniform properties.

Let

S_t = the entropy in the control volume at time t

$S_{t+\delta t}$ = the entropy in the control volume at time $t + \delta t$

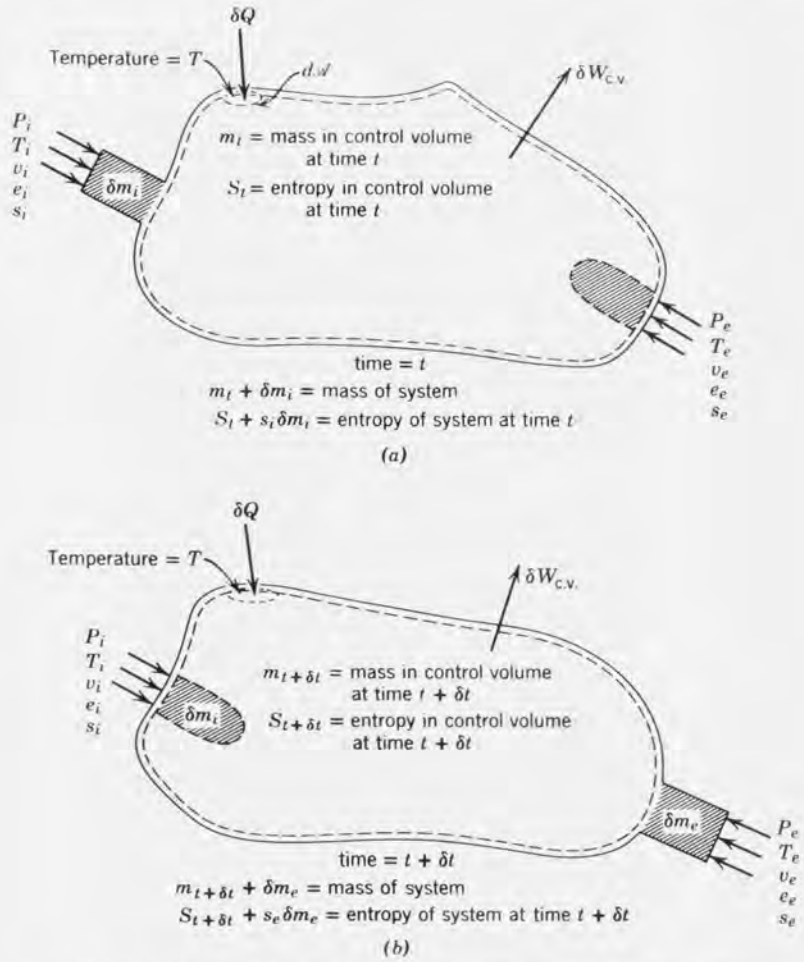


FIGURE 9.1 Schematic diagram for a second law analysis of a control volume.

Then

$$S_1 = S_t + s_i\,\delta m_i = \text{entropy of the system at time } t$$
$$S_2 = S_{t+\delta t} + s_e\,\delta m_e = \text{entropy of the system at time } t + \delta t$$

Therefore,

$$S_2 - S_1 = (S_{t+\delta t} - S_t) + (s_e\,\delta m_e - s_i\,\delta m_i) \tag{9.2}$$

The term $s_e\,\delta m_e - s_i\,\delta m_i$ represents the net flow of entropy out of the control volume during δt as the result of the masses δm_e and δm_i crossing the control surface.

The significance of the remaining terms of Eq. 9.1 must be carefully considered when applied to a control volume. When we write the terms $\delta Q/T$ and $\delta LW/T$ for a system, we normally consider a quantity of mass at uniform temperature at any instant of time. As noted before, for a control volume analysis, we deviate from a

strictly classical concept of thermodynamics and are prepared to consider a variation in temperature throughout the control volume, the assumption of "local" equilibrium.

As a consequence, for the heat-transfer term, we must consider each element of area on the surface across which heat flows and the surface temperature of this local area. Therefore, this term in Eq. 9.1 must be written as the summation of all local $\delta Q/T$ terms over the control surface, or

$$\frac{1}{\delta t}\left(\frac{\delta Q}{T}\right) = \frac{1}{\delta t}\sum_{\text{c.v.}}\left(\frac{\delta Q}{T}\right)_{\text{c.v.}} \tag{9.3}$$

Similarly, for the lost work term, which represents irreversibilities occurring inside the control volume, the result must be written as the summation of all local $\delta LW/T$ terms throughout the interior of the control volume, or

$$\frac{1}{\delta t}\left(\frac{\delta LW}{T}\right) = \frac{1}{\delta t}\sum_{\text{c.v.}}\left(\frac{\delta LW}{T}\right)_{\text{c.v.}} \tag{9.4}$$

Substituting Eqs. 9.2, 9.3, and 9.4 into Eq. 9.1, we have

$$\frac{S_{t+\delta t} - S_t}{\delta t} + \frac{s_e\,\delta m_e}{\delta t} - \frac{s_i\,\delta m_i}{\delta t} = \frac{1}{\delta t}\sum_{\text{c.v.}}\left(\frac{\delta Q}{T}\right)_{\text{c.v.}} + \frac{1}{\delta t}\sum_{\text{c.v.}}\left(\frac{\delta LW}{T}\right)_{\text{c.v.}} \tag{9.5}$$

To reduce this expression to a rate equation, we consider what happens to each of the terms in Eq. 9.5 as δt approaches zero. As in Section 6.2, the two mass quantities become mass flow rates, and the entropy term becomes the time rate of change of entropy in the control volume. The manner is analogous to the energy term in the first-law equation becoming the time rate of change of energy in the control volume. Similarly, the heat-transfer and lost work terms become rate quantities, with each being divided by the appropriate local temperature.

In utilizing these limiting values to express the rate form of the entropy equation for a control volume, we again include summation signs on the flow terms to account for the possibility of additional flow streams entering or leaving the control volume. The resulting expression is

$$\frac{dS_{\text{c.v.}}}{dt} + \sum \dot{m}_e s_e - \sum \dot{m}_i s_i = \sum_{\text{c.v.}} \frac{\dot{Q}_{\text{c.v.}}}{T} + \sum_{\text{c.v.}} \frac{L\dot{W}_{\text{c.v.}}}{T} \tag{9.6}$$

which, for our purposes, is the general expression of the second-law entropy equation. In words, this expression states that the rate of change of entropy inside the control volume plus the net rate of entropy flow out is equal to the sum of two terms, the overall heat-transfer surface term and the positive internal-irreversibility production term. Since this second term is necessarily positive (or zero) and is difficult if not impossible to evaluate quantitatively, Eq. 9.6 is frequently written in the form

$$\frac{dS_{\text{c.v.}}}{dt} + \sum \dot{m}_e s_e - \sum \dot{m}_i s_i \geqslant \sum_{\text{c.v.}} \frac{\dot{Q}_{\text{c.v.}}}{T} \tag{9.7}$$

where the equality applies to internally reversible processes and the inequality to internally irreversible processes.

If there is no mass flow into or out of the control volume and if temperature is considered uniform at any instant of time, Eq. 9.6 reduces to a rate form of the system entropy equation, Eq. 8.12. In this sense, Eq. 9.6 (or 9.7) can be considered a general expression, as was pointed out for the control volume form of the first law.

9.2 THE STEADY-STATE, STEADY-FLOW PROCESS AND THE UNIFORM-STATE, UNIFORM-FLOW PROCESS

We now consider the application of the second-law control volume equation, Eq. 9.6 or 9.7, to the two control volume model processes developed in Chapter 6.

For the steady-state, steady-flow process, which has been defined in Section 6.3, we conclude that there is no change with time of the entropy per unit mass at any point within the control volume, and therefore the first term of Eq. 9.7 equals zero. That is,

$$\frac{dS_{\text{c.v.}}}{dt} = 0 \tag{9.8}$$

so that, for the SSSF process,

$$\sum \dot{m}_e s_e - \sum \dot{m}_i s_i \geq \sum_{\text{c.v.}} \frac{\dot{Q}_{\text{c.v.}}}{T} \tag{9.9}$$

in which the various mass flows, heat transfer rate, and states are all constant with time.

If in a steady-state, steady-flow process there is only one area over which mass enters the control volume at a uniform rate and only one area over which mass leaves the control volume at a uniform rate, we can write

$$\dot{m}(s_e - s_i) \geq \sum_{\text{c.v.}} \frac{\dot{Q}_{\text{c.v.}}}{T} \tag{9.10}$$

For an adiabatic process with these assumptions, it follows that

$$s_e \geq s_i \tag{9.11}$$

where the equality holds for a reversible adiabatic process.

EXAMPLE 9.1

Steam enters a steam turbine at a pressure of 1 MPa, a temperature of 300°C, and a velocity of 50 m/s. The steam leaves the turbine at a pressure of 150 kPa and a velocity of 200 m/s. Determine the work per kilogram of steam flowing through the turbine, assuming the process to be reversible and adiabatic.

Control volume: Turbine.

Sketch: Fig. 9.2.

Inlet state: Fixed (Fig. 9.2).

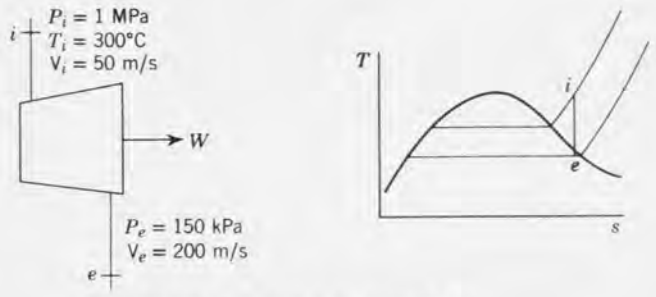


FIGURE 9.2 Sketch for Example 9.1.

Exit state: P_e, $\mathbf{V}_e$ known.
Process: SSSF.
Model: Steam tables.
Analysis:

Continuity equation: $$\dot{m}_e = \dot{m}_i = \dot{m}$$

First law: $$h_i + \frac{\mathbf{V}_i^2}{2} = h_e + \frac{\mathbf{V}_e^2}{2} + w$$

Second law: $$s_e = s_i$$

Solution

From the steam tables,

$$h_i = 3051.2 \text{ kJ/kg}, \qquad s_i = 7.1229 \text{ kJ/kg K}$$

The two properties known in the final state are pressure and entropy.

$$P_e = 0.15 \text{ MPa}, \qquad s_e = s_i = 7.1229 \text{ kJ/kg K}$$

The quality and enthalpy of the steam leaving the turbine can be determined.

$$s_e = 7.1229 = s_f + x_e s_{fg} = 1.4336 + x_e 5.7897$$
$$x_e = 0.9827$$
$$h_e = h_f + x_e h_{fg} = 467.1 + 0.9827(2226.5)$$
$$= 2655.0 \text{ kJ/kg}$$

Therefore, the work per kilogram of steam for this isentropic process may be found using the equation for the first law.

$$w = 3051.2 + \frac{50 \times 50}{2 \times 1000} - 2655.0 - \frac{200 \times 200}{2 \times 1000} = 377.5 \text{ kJ/kg}$$

EXAMPLE 9.2

Consider the reversible adiabatic flow of steam through a nozzle. Steam enters the nozzle at 1 MPa, 300°C, with a velocity of 30 m/s. The pressure of the steam at the nozzle exit is 0.3 MPa. Determine the exit velocity of the steam from the nozzle, assuming a reversible, adiabatic, steady-state, steady-flow process.

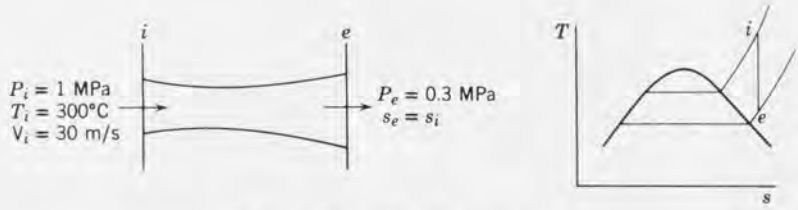


FIGURE 9.3 Sketch for Example 9.2.

Control volume: Nozzle.

Sketch: Fig. 9.3.

Inlet state: Fixed (Fig. 9.3).

Exit state: P_e known.

Process: SSSF.

Model: Steam tables.

Analysis: Because this is a steady-state, steady-flow process in which the work, the heat transfer, and the changes in potential energy are zero, we can write

Continuity equation: $$\dot{m}_e = \dot{m}_i = \dot{m}$$

First law: $$h_i = \frac{\mathbf{V}_i^2}{2} = h_e + \frac{\mathbf{V}_e^2}{2}$$

Second law: $$s_e = s_i$$

Solution

From the steam tables,

$$h_i = 3051.2 \text{ kJ/kg}, \qquad s_i = 7.1229 \text{ kJ/kg K}$$

The two properties that we know in the final state are entropy and pressure.

$$s_e = s_i = 7.1229 \text{ kJ/kg K}, \qquad P_e = 0.3 \text{ MPa}$$

Therefore,

$$T_e = 159.1°\text{C}, \qquad h_e = 2780.2 \text{ kJ/kg}$$

Substituting into the equation for the first law, we have

$$\frac{\mathbf{V}_e^2}{2} = h_i - h_e + \frac{\mathbf{V}_i^2}{2}$$

$$= 3051.2 - 2780.2 + \frac{30 \times 30}{2 \times 1000} = 271.5 \text{ kJ/kg}$$

$$\mathbf{V}_e = 737 \text{ m/s}$$

EXAMPLE 9.3

An inventor reports that she has a refrigeration compressor that receives saturated R-12 vapor at −20°C and delivers the vapor at 1 MPa, 50°C. The compression process is adiabatic. Does the process described violate the second law?

Control volume: Compressor.

Inlet state: Fixed (saturated vapor at T_i).

Exit state: Fixed (P_e, T_e known).

Process: SSSF, adiabatic.

Model: R-12 tables.

Analysis: Because this is a steady-state, steady-flow, adiabatic process, we can write

Second law: $s_e \geq s_i$

Solution

From the R-12 tables,

$$s_e = 0.7026 \text{ kJ/kg K}; \qquad s_i = 0.7087 \text{ kJ/kg K}$$

Therefore, $s_e < s_i$, whereas for this process the second law requires that $s_e \geq s_i$. The process described involves a violation of the second law and thus would be impossible.

EXAMPLE 9.4

Air expands in an air turbine from a pressure of 450 kPa and a temperature of 550 K to an exhaust pressure of 150 kPa. Assume the process to be reversible and adiabatic with negligible changes in kinetic and potential energy. Calculate the work per kilogram of air flowing through the turbine.

Control volume: Turbine.

Inlet state: P_i, T_i known; state fixed.

Exit state: P_e known.

Process: SSSF.

Model: Ideal-gas and air tables, A.11.

Analysis: Because this is a steady-state, steady-flow reversible process, we can write

Continuity equation: $\dot{m}_e = \dot{m}_i = \dot{m}$

First law: $h_i = h_e + w$

Second law: $s_e = s_i$

Solution

From Table A.11,

$$h_i = 555.1 \text{ kJ/kg}, \qquad P_{ri} = 9.538$$

From Eq. 8.28,

$$P_{re} = P_{ri} \frac{P_e}{P_i} = 9.538 \frac{150}{450} = 3.179$$

Therefore,

$$T_e = 404 \text{ K}, \qquad h_e = 405.7$$

and from the first law,

$$w = h_i - h_e = 555.1 - 405.7 = 149.4 \text{ kJ/kg}$$

For the uniform-state, uniform-flow process, which was described in Section 6.5, the second law for a control volume, Eq. 9.7, can be written in the following form.

$$\frac{d}{dt}(ms)_{\text{c.v.}} + \sum \dot{m}_e s_e - \sum \dot{m}_i s_i \geqslant \sum_{\text{c.v.}} \frac{\dot{Q}_{\text{c.v.}}}{T} \tag{9.12}$$

If this is integrated over the time interval t, we have

$$\int_0^t \frac{d}{dt}(ms)_{\text{c.v.}}\, dt = (m_2 s_2 - m_1 s_1)_{\text{c.v.}}$$

$$\int_0^t \left(\sum \dot{m}_e s_e\right) dt = \sum m_e s_e, \qquad \int_0^t \left(\sum \dot{m}_i s_i\right) dt = \sum m_i s_i$$

Therefore, for this period of time t, we can write the second law for the uniform-state, uniform-flow process as

$$(m_2 s_2 - m_1 s_1)_{\text{c.v.}} + \sum m_e s_e - \sum m_i s_i \geqslant \int_0^t \sum_{\text{c.v.}} \frac{\dot{Q}_{\text{c.v.}}}{T}\, dt \tag{9.13}$$

Since in this process the temperature is uniform throughout the control volume at any instant of time, the integral on the right reduces to

$$\int_0^t \sum_{\text{c.v.}} \frac{\dot{Q}_{\text{c.v.}}}{T}\, dt = \int_0^t \frac{1}{T} \sum_{\text{c.v.}} \dot{Q}_{\text{c.v.}}\, dt = \int_0^t \frac{\dot{Q}_{\text{c.v.}}}{T}\, dt$$

and therefore the second law for the uniform-state, uniform-flow process can be written

$$(m_2 s_2 - m_1 s_1)_{\text{c.v.}} + \sum m_e s_e - \sum m_i s_i \geqslant \int_0^t \frac{\dot{Q}_{\text{c.v.}}}{T}\, dt \tag{9.14}$$

By introducing the lost work, we can write this as an equality. In doing so, we note that because the temperature is uniform throughout the control volume at any instant of time,

$$\int_0^t \sum_{\text{c.v.}} \frac{L\dot{W}_{\text{c.v.}}}{T}\, dt = \int_0^t \frac{1}{T} \sum_{\text{c.v.}} L\dot{W}_{\text{c.v.}}\, dt = \int_0^t \frac{L\dot{W}_{\text{c.v.}}}{T}\, dt$$

Therefore,

$$(m_2 s_2 - m_1 s_1)_{\text{c.v.}} + \sum m_e s_e - \sum m_i s_i = \int_0^t \frac{\dot{Q}_{\text{c.v.}} + L\dot{W}_{\text{c.v.}}}{T}\, dt \tag{9.15}$$

9.3 THE REVERSIBLE STEADY-STATE, STEADY-FLOW PROCESS

An expression can be derived for the work in a reversible adiabatic, steady-state, steady-flow process that is of great help in understanding its significant variables. We have noted that when a steady-state, steady-flow process involves a single flow of fluid into and out of the control volume, the first law, Eq. 6.17, can be written,

$$q + h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i = h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e + w$$

and the second law, Eq. 9.10, is

$$\dot{m}(s_e - s_i) \geqslant \sum_{\text{c.v.}} \frac{\dot{Q}_{\text{c.v.}}}{T}$$

Let us now consider two types of flow, a reversible adiabatic process and a reversible isothermal process.

If the process is reversible and adiabatic, the second-law equation reduces to

$$s_e = s_i$$

It follows from the property relation

$$T\,ds = dh - v\,dP$$

that

$$h_e - h_i = \int_i^e v\,dP \tag{9.16}$$

Substituting these relations into Eq. 6.17 and noting that $q = 0$, we have for the reversible, adiabatic process

$$\begin{aligned} w &= (h_i - h_e) + \frac{\mathbf{V}_i^2 - \mathbf{V}_e^2}{2} + g(Z_i - Z_e) \\ &= -\int_i^e v\,dP + \frac{\mathbf{V}_i^2 - \mathbf{V}_e^2}{2} + g(Z_i - Z_e) \end{aligned} \tag{9.17}$$

If, instead, the process is reversible and isothermal, the second law reduces to

$$\dot{m}(s_e - s_i) = \frac{1}{T}\sum_{\text{c.v.}} \dot{Q}_{\text{c.v.}} = \frac{\dot{Q}_{\text{c.v.}}}{T}$$

or (9.18)

$$T(s_e - s_i) = \frac{\dot{Q}_{\text{c.v.}}}{\dot{m}} = q$$

and the property relation can be integrated to give

$$T(s_e - s_i) = (h_e - h_i) - \int_i^e v\,dP \tag{9.19}$$

Substituting Eqs. 9.18 and 9.19 into the first law, Eq. 6.17, gives us the same expression as for the reversible adiabatic process, Eq. 9.17. We further note that any other reversible process can be constructed, in the limit, from a series of alternate

adiabatic and isothermal processes. Thus, we may conclude that Eq. 9.17 is valid for any reversible, steady-state, steady-flow process without the restriction that it be either adiabatic or isothermal.

This expression has a wide range of application. If we consider a reversible steady-state, steady-flow process in which the work is zero (such as flow through a nozzle) and the fluid is incompressible (v = constant), Eq. 9.17 can be integrated to give

$$v(P_e - P_i) + \frac{\mathbf{V}_e^2 - \mathbf{V}_i^2}{2} + g(Z_e - Z_i) = 0 \tag{9.20}$$

Known as the Bernoulli equation (after Daniel Bernoulli), this is a very important equation in fluid mechanics.

Equation 9.17 is also frequently applied to the large class of flow processes involving work (such as turbines and compressors) in which changes in kinetic and potential energies of the working fluid are small. The model process for these machines is then a reversible, SSSF process with no change in kinetic or potential energy (and commonly, although not necessarily, adiabatic as well). For this process Eq. 9.17 reduces to the form

$$w = -\int_i^e v\, dP \tag{9.21}$$

From this result, we conclude that the shaft work associated with this type of process is closely related to the specific volume of the fluid during the process. To amplify this point further, consider the simple steam power plant shown in Fig. 9.4. Suppose this is an ideal power plant with no pressure drop in the piping, the boiler, or the condenser. Thus, the pressure increase in the pump is equal to the pressure decrease in the turbine. Neglecting kinetic and potential energy changes, the work done in each of these processes is given by Eq. 9.21. Since the pump handles liquid, which has a very small specific volume compared to that of the vapor that flows through the turbine, the power input to the pump is much less than the power output of the turbine. The difference is the net power output of the power plant.

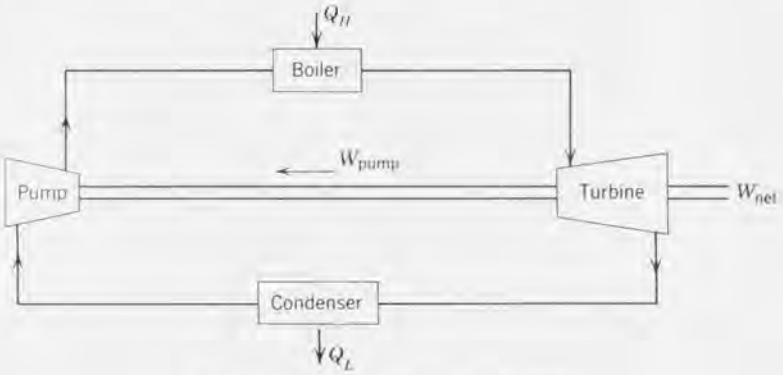


FIGURE 9.4 Simple steam power plant.

This same line of reasoning can be qualitatively applied to actual devices that involve steady-state, steady-flow processes, even though the processes are not exactly reversible and adiabatic.

EXAMPLE 9.5

Calculate the work per kilogram to pump water isentropically from 100 kPa, 30°C, to 5 MPa.

Control volume: Pump.

Inlet state: P_i, T_i known; state fixed.

Exit state: P_e known.

Process: SSSF.

Model: Steam tables.

Analysis: Since the process is SSSF, reversible, and adiabatic, and changes in kinetic and potential energies can be neglected,

First law: $h_i = h_e + w$

Second law: $s_e - s_i = 0$

Solution

Since P_e and s_e are known, state e is fixed and, therefore h_e is known and w can be found from the first law. However, the process is reversible, SSSF, with negligible changes in kinetic and potential energies, so that Eq. 9.21 is also valid. Furthermore, since a liquid is being pumped, the specific volume will change very little during the process.

From the steam tables, $v_i = 0.001\ 004\ \text{m}^3/\text{kg}$. Assuming that the specific volume remains constant and using Eq. 9.21, we have

$$-w = \int_1^2 v\,dP = v(P_2 - P_1) = 0.001\ 004(5000 - 100) = 4.92\ \text{kJ/kg}$$

As a final application of Eq. 9.17, we recall the reversible polytropic process for an ideal gas, discussed in Section 8.11 for a system process. For the SSSF process with no change in kinetic and potential energies, from the relations,

$$w = -\int_i^e v\,dP \qquad \text{and} \qquad Pv^n = \text{constant} = C^n$$

$$w = -\int_i^e v\,dP = -C\int_i^e \frac{dP}{P^{1/n}} \tag{9.22}$$

$$= -\frac{n}{n-1}(P_e v_e - P_i v_i) = -\frac{nR}{n-1}(T_e - T_i)$$

If the process is isothermal, then $n = 1$ and the integral becomes

$$w = -\int_i^e v\,dP = -\text{constant}\int_i^e \frac{dP}{P} = -P_i v_i \ln\frac{P_e}{P_i} \tag{9.23}$$

These evaluations of the integral

$$\int_i^e v\, dP$$

may also be used in conjunction with Eq. 9.17 for instances in which kinetic and potential energy changes are not negligibly small.

9.4 PRINCIPLE OF THE INCREASE OF ENTROPY

The principle of the increase of entropy for a system analysis was discussed in Section 8.8. The same general conclusion is reached for a control volume analysis. To demonstrate this, consider a control volume, Fig. 9.5, that exchanges both mass and heat with its surroundings. At the point in the surroundings where the heat transfer occurs, the temperature is T_0. From Eq. 9.7 the second law for this process is

$$\frac{dS_{\text{c.v.}}}{dt} + \sum \dot{m}_e s_e - \sum \dot{m}_i s_i \geqslant \sum_{\text{c.v.}} \frac{\dot{Q}_{\text{c.v.}}}{T}$$

We recall that the first term represents the rate of change of entropy within the control volume, and the next terms the net entropy flow out of the control volume resulting from the mass flow. Therefore, for the surroundings, we can write

$$\frac{dS_{\text{surr}}}{dt} = \sum \dot{m}_e s_e - \sum \dot{m}_i s_i - \frac{\dot{Q}_{\text{c.v.}}}{T_0} \tag{9.24}$$

Adding Eqs. 9.7 and 9.24, we have

$$\frac{dS_{\text{net}}}{dt} = \frac{dS_{\text{c.v.}}}{dt} + \frac{dS_{\text{surr}}}{dt} \geqslant \sum_{\text{c.v.}} \frac{\dot{Q}_{\text{c.v.}}}{T} - \frac{\dot{Q}_{\text{c.v.}}}{T_0} \tag{9.25}$$

Because $\dot{Q}_{\text{c.v.}} > 0$ when $T_0 > T$ and $\dot{Q}_{\text{c.v.}} < 0$ when $T_0 < T$, it follows that

$$\frac{dS_{\text{net}}}{dt} = \frac{dS_{\text{c.v.}}}{dt} + \frac{dS_{\text{surr}}}{dt} \geqslant 0 \tag{9.26}$$

which can be termed the general statement of the principle of the increase of entropy.

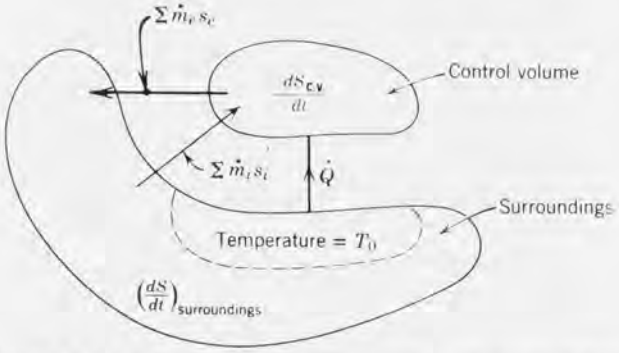


FIGURE 9.5 Entropy change for a control volume plus surroundings.

When we use Eq. 9.26 to check any particular process for a possible violation of the second law, it will be in connection with one of our model processes. For example, in a steady-state, steady-flow process, as we consider the two terms in Eq. 9.26, we realize that, in accordance with Eq. 9.8, the first term is zero. As a result, all the entropy change that is due to irreversibilities in this type of process is observed in the surroundings. This term may then be evaluated using Eq. 9.24. On the other hand, for the uniform-state, uniform-flow process, there are both control volume and surroundings terms to evaluate. Each term is integrated over the time t of the process, as was done in Section 9.2. Thus, Eq. 9.26 is integrated to

$$\Delta S_{\text{net}} = \Delta S_{\text{c.v.}} + \Delta S_{\text{surr}} \tag{9.27}$$

in which the control volume term is

$$\Delta S_{\text{c.v.}} = (m_2 s_2 - m_1 s_1)_{\text{c.v.}} \tag{9.28}$$

The term for the surroundings is, after applying Eq. 9.15 to the surroundings and integrating,

$$\Delta S_{\text{surr}} = \frac{-Q_{\text{c.v.}}}{T_0} + \sum m_e s_e - \sum m_i s_i \tag{9.29}$$

9.5 EFFICIENCY

In Chapter 7 we noted that the second law of thermodynamics led to the concept of thermal efficiency for a heat engine cycle, namely

$$\eta_{\text{th}} = \frac{W_{\text{net}}}{Q_H}$$

where W_{net} is the net work of the cycle and Q_H is the heat transfer from the high-temperature body.

In this chapter we have extended our consideration of the second law to control volume processes, which leads us now to consider the efficiency of a process. For example, we might be interested in the efficiency of a turbine in a steam power plant or the compressor in a gas turbine engine.

In general, we can say that to determine the efficiency of a machine in which a process takes place, we compare the actual performance of the machine under given conditions and the performance that would have been achieved in an ideal process. It is in the definition of this ideal process that the second law becomes a major consideration. For example, a steam turbine is intended to be an adiabatic machine. The only heat transfer is the unavoidable heat transfer that takes place between the given turbine and the surroundings. We also note that for a given steam turbine operating in a steady-state, steady-flow manner, the state of the steam entering the turbine and the exhaust pressure are fixed. Therefore, the ideal process is a reversible adiabatic process, which is an isentropic process, between the inlet state and the turbine exhaust pressure. If we denote the actual work done per unit mass of steam flow through the turbine as w_a and the work that would have been done in a reversible adiabatic process between the inlet state and the

turbine exhaust pressure as w_s, the efficiency of the turbine is defined as

$$\eta_{\text{turbine}} = \frac{w_a}{w_s} \tag{9.30}$$

The same relation holds for a gas turbine.

A few other examples may help to clarify this point. For a nozzle, the objective is to have the maximum kinetic energy leaving the nozzle for the given inlet conditions and exhaust pressure. The nozzle is also an adiabatic device, and therefore the ideal process is a reversible adiabatic or isentropic process. The efficiency of a nozzle is the ratio of the actual kinetic energy leaving the nozzle, $\mathbf{V}_a^2/2$, to the kinetic energy for an isentropic process between the same inlet conditions and exhaust pressure—$\mathbf{V}_s^2/2$. Thus we have

$$\eta_{\text{nozzle}} = \frac{\mathbf{V}_a^2/2}{\mathbf{V}_s^2/2} \tag{9.31}$$

For compressors of air or other gases, there are two ideal processes to which their actual performance can be compared. If no effort is made to cool the gas during compression (that is, when the process is adiabatic), the ideal process is a reversible adiabatic or isentropic process between the given inlet state and exhaust pressure. If we denote the work per unit mass of gas flow through the compressor for this isentropic process as w_s and the actual work as w_a (the actual work input will be greater than the work input for an isentropic process), the efficiency is defined by the relation

$$\eta_{\text{adiabatic compressor}} = \frac{w_s}{w_a} \tag{9.32}$$

If an attempt is made to cool the air during compression by using a water jacket or fins, the ideal process is considered a reversible isothermal process. If w_t is the work for the reversible isothermal process between the given inlet state and exhaust pressure, and w_a the actual work, the efficiency is defined by the relation

$$\eta_{\text{cooled compressor}} = \frac{w_t}{w_a} \tag{9.33}$$

Thus, to determine the efficiency of a device that carries out a process (rather than a cycle), we compare the actual performance to what would be achieved in a related, but well-defined ideal process.

EXAMPLE 9.6

A steam turbine receives steam at a pressure of 1 MPa, 300°C. The steam leaves the turbine at a pressure of 15 kPa. The work output of the turbine is measured and is found to be 600 kJ/kg of steam flowing through the turbine. Determine the efficiency of the turbine.

Control volume: Turbine.

Inlet state: P_i, T_i known; state fixed.

Exit state: P_e known.

Process: SSSF.

Model: Steam tables.

Analysis: The efficiency of the turbine is given by Eq. 9.30.

$$\eta_{\text{turbine}} = \frac{w_a}{w_s}$$

Thus, to determine the turbine efficiency, we calculate the work that would be done in an isentropic process between the given inlet state and final pressure. For this isentropic process,

Continuity equation: $\dot{m}_i = \dot{m}_e = \dot{m}$

First law: $h_i = h_{es} + w_s$

Second law: $s_i = s_{es}$

Solution

From the steam tables,

$$h_i = 3051.2 \text{ kJ/kg}, \qquad s_i = 7.1229 \text{ kJ/kg K}$$

Therefore, at $P_e = 15$ kPa,

$$s_{es} = s_i = 7.1229 = 0.7549 + x_{es}7.2536$$
$$x_{es} = 0.8779$$
$$h_{es} = 225.9 + 0.8779(2373.1) = 2309.3 \text{ kJ/kg}$$

From the first law for the isentropic process,

$$w_s = h_i - h_{es} = 3051.2 - 2309.3 = 741.9 \text{ kJ/kg}$$

But, since

$$w_a = 600 \text{ kJ/kg}$$

we find that

$$\eta_{\text{turbine}} = \frac{w_a}{w_s} = \frac{600}{741.9} = 0.809 = 80.9 \text{ percent}$$

In connection with this example, it should be noted that to find the actual state e of the steam exiting the turbine, we need to analyze the real process taking place. For the real process

$$\dot{m}_i = \dot{m}_e = \dot{m}$$
$$h_i = h_e + w_a$$
$$s_e > s_i$$

Therefore, from the first law for the real process, we have

$$h_e = 3051.2 - 600 = 2451.2 \text{ kJ/kg}$$
$$2451.2 = 225.9 + x_e 2373.1$$
$$x_e = 0.9377$$

9.6 AVAILABLE ENERGY, REVERSIBLE WORK, AND IRREVERSIBILITY

From the concept of the efficiency of a device, such as a turbine, nozzle, or compressor (perhaps more correctly termed a first-law efficiency, since it is given as the ratio of two energy terms), we proceed now to develop concepts that include more meaningful second-law analysis. Our ultimate goal is to use this analysis to manage our natural resources and environment better.

We first focus our attention on the potential for producing useful work from some source or supply of energy. Consider the simple situation shown in Fig. 9.6*a*, in which there is an energy source Q in the form of heat transfer from a very large and, therefore, constant-temperature reservoir at temperature T. What is the ultimate potential for producing work?

To answer this question, we imagine that a cyclic heat engine is available, as shown in Fig. 9.6*b*. To convert the maximum fraction of Q to work requires that the engine be completely reversible, that is, a Carnot cycle, and that the lower-temperature reservoir be at the lowest temperature possible, often, but not necessarily, at the ambient temperature. From the first and second laws for the Carnot cycle and the usual consideration of all the Q's as positive quantities, we find

$$W_{\text{rev H.E.}} = Q - Q_0$$

$$\frac{Q}{T} = \frac{Q_0}{T_0}$$

so that

$$W_{\text{rev H.E.}} = Q\left(1 - \frac{T_0}{T}\right) \tag{9.34}$$

We might say that the fraction of Q given by the right side of Eq. 9.34 is the available portion of the total energy quantity Q. To carry this thought one step farther, consider the situation shown on the T–S diagram in Fig. 9.7. The total shaded area is Q. The portion of Q that is below T_0, the environment temperature,

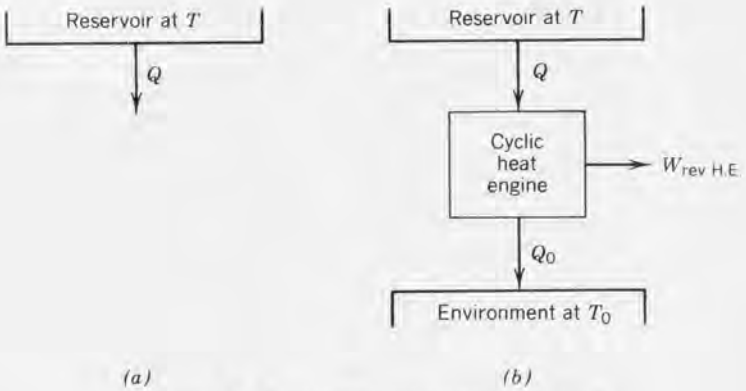


FIGURE 9.6 Constant-temperature energy source.

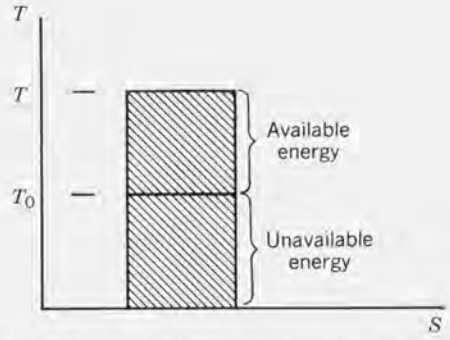


FIGURE 9.7 *T–S diagram for constant-temperature energy source.*

cannot be converted into work by the heat engine and must instead be thrown away. This portion is therefore the unavailable portion of total energy Q, and the portion lying between the two temperatures T and T_0 is the available energy.

Let us next consider the same situation, except that the heat transfer Q is available from a constant-pressure source, for example, a simple heat exchanger as shown in Fig. 9.8*a*. The Carnot cycle must now be replaced by a sequence of such engines, with the result shown in Fig. 9.8*b*. The only difference between the first and second laws is that the second law includes an integral, which corresponds to ΔS.

$$\Delta S = \int \frac{\delta Q_{\text{rev}}}{T} = \frac{Q_0}{T_0}$$

Substituting into the first law, we have

$$W_{\text{rev H.E.}} = Q - T_0 \, \Delta S \tag{9.35}$$

Note that this ΔS quantity does not include the standard sign convention. It corresponds to the amount of change of entropy shown in Fig. 9.8*b*. Equation 9.35 specifies the available portion of the quantity Q. The portion unavailable for producing work in this circumstance lies below T_0 in Fig. 9.8*b*.

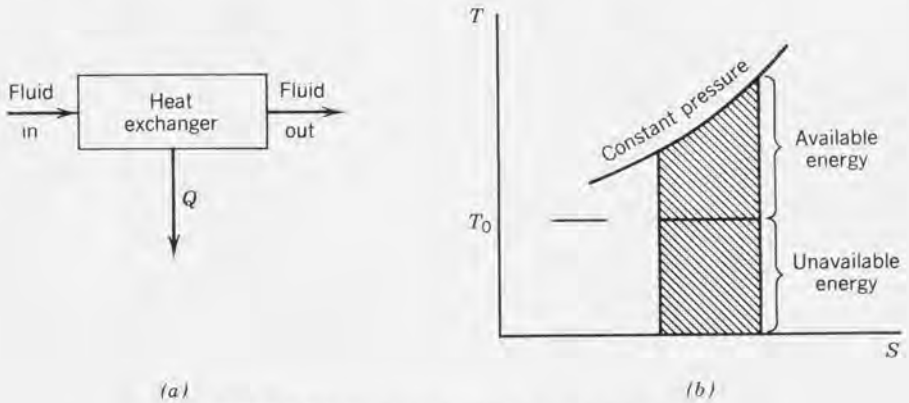


FIGURE 9.8 Changing-temperature energy source.

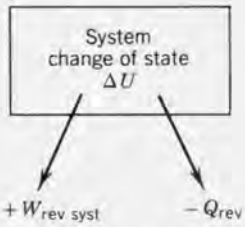


FIGURE 9.9 *System undergoing a change of state ΔU.*

We now proceed along a similar but slightly different line. Consider the thermodynamic system, shown in Fig. 9.9, which undergoes a change of state represented by ΔU, with a corresponding change ΔS. The question now is what maximum work can theoretically be produced through this change of state? The process would have to be internally reversible, with the associated work and heat-transfer quantities, as shown in Fig. 9.9. We also recognize that the heat transfer could itself be the source of a second work output, for example, work done by hypothetical Carnot engines while expanding the energy source to the temperature level of the accessible environment, T_0. In other words, the process is also externally reversible, for, there is no heat transfer through a finite temperature difference. The system work is given by the first law, and the heat engine work is given by Eq. 9.35. The total work for this idealized situation is, accounting for proper signs of the ΔU and ΔS as relating to changes in the system,

$$\begin{aligned} W_{\text{rev}} &= (-Q_{\text{rev}} - \Delta U) + (Q_{\text{rev}} + T_0\,\Delta S) \\ &= -\Delta U + T_0\,\Delta S \end{aligned} \tag{9.36}$$

This quantity is termed the reversible work corresponding to the specified change of state for a system interacting with the environment T_0. We recognize that a real process undergoing this same change of state would not produce this amount of work, since the real process is not internally reversible. In addition, whatever heat is transferred in the real process does not interact with the environment through reversible heat engines. Instead, the quantity W_{rev} establishes a theoretical upper limit for what might be accomplished in a totally idealized situation; the quantity may therefore be useful to us in evaluating real processes.

It is a straightforward matter to generalize this procedure for any type of process, including other energy terms. For a system undergoing a change of state from initial state 1 to final state 2, using the first law, Eq. 5.11, and the second law, Eq. 8.3, we have

$$w_{\text{rev}} = \left(\frac{W_{\text{rev}}}{m}\right)_2 = \left(u_1 - T_0 s_1 + \frac{\mathbf{V}_1^2}{2} + gZ_1\right) - \left(u_2 - T_0 s_2 + \frac{\mathbf{V}_2^2}{2} + gZ_2\right) \tag{9.37}$$

For a steady-state, steady-flow process with one flow stream in and one out, from Eqs. 6.17 and 9.10 we have

$$w_{\text{rev}} = \frac{\dot{W}_{\text{rev}}}{\dot{m}} = \left(h_i - T_0 s_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) - \left(h_e - T_0 s_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right) \tag{9.38}$$

For a uniform-state, uniform-flow process (ignoring kinetic and potential energy terms for convenience), from Eqs. 6.21 and 9.13 we have

$$W_{rev} = m_i(h_i - T_0 s_i) - m_e(h_e - T_0 s_e) - [m_2(u_2 - T_0 s_2) - m_1(u_1 - T_0 s_1)]_{c.v.} \tag{9.39}$$

As mentioned earlier, the reversible work for a given change of state (as can be calculated for a given type of process by one of the expressions 9.37 through 9.39) represents a theoretical upper limit for what might have been achieved had this change of state occurred in a completely (that is, both internally and externally) reversible process while interacting with the system's accessible environment. A real process taking place between these same end states will in general, be both internally and externally irreversible, with a correspondingly smaller amount of work done. Let us define the difference between these two quantities to be the irreversibility of the actual process,

$$I = W_{rev} - W_{act} \tag{9.40}$$

Irreversibility is plainly a measure of the "inefficiency" of an actual process, since the less the actual work done for a given change of state, the greater the irreversibility. The irreversibility would be zero for a completely reversible process, and otherwise is always greater than zero.

If we follow the procedures applied in developing the principle of increase of entropy in Sections 8.8 and 9.4, and use the first-law and second-law expressions in connection with Eq. 9.40, it is a straightforward matter to show that, for any process, the irreversibility is the product of the temperature of the surroundings and the net entropy change associated with the process, which on a rate basis is

$$\dot{I} = T_0 \frac{dS_{net}}{dt} \tag{9.41}$$

This equation can be written in an integrated form for system analysis and for the USUF process. From Eq. 9.41 we conclude that the concept of irreversibility can be interpreted as a general statement of the second law of thermodynamics (the principle of increase of entropy) in energy terms.

The concepts of reversible work and irreversibility are illustrated in the following example. Unless otherwise stated, we will use 25°C for the temperature of the surroundings. This temperature has been selected because thermochemical data are frequently given relative to this base and because it is a reasonable temperature to assume for the surroundings.

EXAMPLE 9.7

Referring to Example 9.6, determine the reversible work and the irreversibility for the actual change of state that takes place as the steam flows through the turbine (using 25°C as the temperature of the surroundings).

Solution

It will be helpful to refer to the temperature–entropy diagram shown in Fig. 9.10.

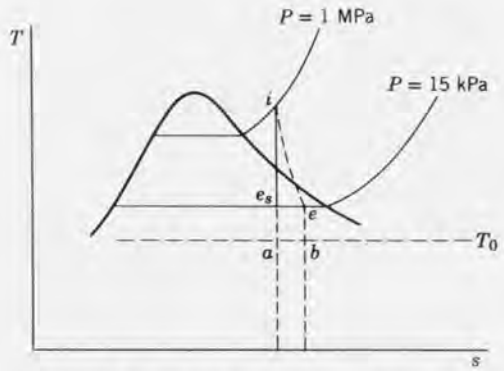


FIGURE 9.10 Sketch for Examples 9.6 and 9.7.

In Example 9.6 we determined the actual state exiting the turbine to be a quality of 0.9377 at a pressure of 15 kPa. Therefore,

$$s_e = 0.7549 + 0.9377(7.2536) = 7.5566 \text{ kJ/kg K}$$

We calculate the reversible work using Eq. 9.38 with no changes in kinetic or potential energy:

$$\begin{aligned}\frac{\dot{W}_{rev}}{\dot{m}} &= (h_i - T_0 s_i) - (h_e - T_0 s_e) \\ &= (3051.2 - 2451.2) - 298.15(7.1229 - 7.5566) \\ &= 729.3 \text{ kJ/kg}\end{aligned}$$

The irreversibility can be found using Equation 9.40:

$$\begin{aligned}\frac{\dot{I}}{\dot{m}} &= \frac{\dot{W}_{rev}}{\dot{m}} - \frac{\dot{W}_{c.v.}}{\dot{m}} \\ &= 729.3 - 600 = 129.3 \text{ kJ/kg}\end{aligned}$$

It may help in understanding these concepts if we conceive of a device that could achieve this amount of reversible work. Consider the device shown in Fig. 9.11, in which the steam expands in a reversible adiabatic process until the pressure reaches 15 kPa, followed by a heat-transfer process in which heat is transferred to the steam in a constant-pressure process. The heat is transferred from the surroundings, which requires a heat pump, with a work input, W_c.

We have already found from Example 9.6 that the work for the reversible adiabatic process is 741.9 kJ/kg. The work required for the heat pump is area $e_s abee_s$ on Fig. 9.10.

$$\begin{aligned}W_c &= (T_e - T_0)(s_e - s_i) \\ &= (327.12 - 298.15)(7.5566 - 7.1229) = 12.6 \text{ kJ/kg} \\ W_{rev} &= 741.9 - 12.6 = 729.3 \text{ kJ/kg}\end{aligned}$$

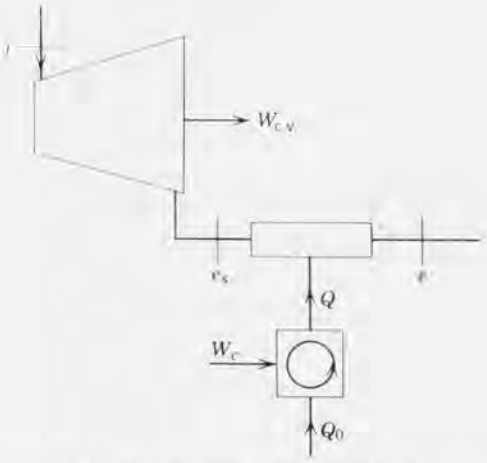


FIGURE 9.11 Sketch for Example 9.7.

9.7 AVAILABILITY AND SECOND-LAW EFFICIENCY

What is the maximum reversible work that can be done by a system in a given state? In Section 9.6 we developed an expression for the reversible work for a given change of state of a system. But the question posed is what final state will give the maximum reversible work?

The answer to this question is that when a system is in equilibrium with the environment, no spontaneous change of state will occur and the system will be incapable of doing any work. Therefore, if a system in a given state undergoes a completely reversible process until it reaches a state in which it is in equilibrium with the environment, the maximum reversible work will have been done by the system.

If a system is in equilibrium with the surroundings, it must certainly be in pressure and temperature equilibrium with the surroundings, that is, at pressure P_0 and temperature T_0. It must also be in chemical equilibrium with the surroundings, which implies that no further chemical reaction will take place. Equilibrium with the surroundings also requires that the system have zero velocity and minimum potential energy. Similar requirements could be set forth regarding magnetic, electrical, and surface effects if these are relevant to a given problem.

The same general remarks can be made about a quantity of mass that undergoes a steady-state, steady-flow process. With a given state for the mass entering the control volume, the reversible work will be a maximum when this mass leaves the control volume in equilibrium with the surroundings. This means that as the mass leaves the control volume, it must be at the pressure and temperature of the surroundings, in chemical equilibrium with the surroundings, and have minimum potential energy and zero velocity. (The mass leaving the control volume must of necessity have some velocity but it can be made to approach zero.)

Let us first consider the availability associated with a steady-state, steady-flow process. In Eq. 9.38 we noted that when we consider a single flow,

$$w_{rev} = \left(h_i - T_0 s_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) - \left(h_e - T_0 s_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right)$$

This reversible work will be maximum when the mass leaving the control volume is in equilibrium with the surroundings. If we designate this state in which the fluid is in equilibrium with the surroundings with subscript 0, the reversible work will be a maximum when $h_e = h_0$, $s_e = s_0$, $\mathbf{V}_e = 0$, and $Z_e = Z_0$. Designating this maximum reversible work per unit mass flow as the availability per unit mass flow and assigning this the symbol ψ, we have

$$\psi = \left(h - T_0 s + \frac{\mathbf{V}^2}{2} + gZ\right) - (h_0 - T_0 s_0 + gZ_0) \tag{9.42}$$

The initial state is written without a subscript to indicate that this is the availability associated with a substance in any state as it enters a control volume in a steady-state, steady-flow process. It also follows that the reversible work per unit mass flow between any two states is equal to the decrease in availability between these two states.

$$w_{rev} = \psi_i - \psi_e \tag{9.43}$$

If we have more than one flow into and out of the control volume in a steady-state, steady-flow process, we can write

$$\dot{W}_{rev} = \sum \dot{m}_i \psi_i - \sum \dot{m}_e \psi_e \tag{9.44}$$

The availability associated with a system is developed in a similar way, except for one factor. When the volume of a system increases, some work is done by the system against the surroundings, and this is not available for doing useful work.

To simplify this analysis, let us also assume that the change in kinetic and potential energy of the system is negligible. Therefore, w_{rev}, as given by Eq. 9.37 is

$${}_1(w_{rev})_2 = (u_1 - T_0 s_1) - (u_2 - T_0 s_2)$$

If the final state is in equilibrium with the surroundings, then $u_2 = u_0$ and $s_2 = s_0$. Therefore, the reversible work is a maximum. If we designate this maximum reversible work as $(w_{rev})_{max}$, and write it without a subscript to indicate a general state, we have

$$(w_{rev})_{max} = (u - T_0 s) - (u_0 - T_0 s_0) \tag{9.45}$$

The availability per unit mass for a system is equal to this maximum reversible work minus the work done against the surroundings. This work done against the surroundings, W_{surr}, is

$$W_{surr} = P_0(V_0 - V) = -mP_0(v - v_0) \tag{9.46}$$

The availability per unit mass for a system in the absence of kinetic and potential energy changes is designated ϕ.

$$\begin{aligned}\phi &= (w_{rev})_{max} - w_{surr}\\ \phi &= (u - T_0 s) - (u_0 - T_0 s_0) + P_0(v - v_0)\\ \phi &= (u + P_0 v - T_0 s) - (u_0 + P_0 v_0 - T_0 s_0)\\ \phi &= (u - u_0) + P_0(v - v_0) - T_0(s - s_0)\end{aligned} \tag{9.47}$$

It follows that

$${}_1(w_{rev})_2 = \phi_1 - \phi_2 - P_0(v_1 - v_2) + \frac{\mathbf{V}_1^2 - \mathbf{V}_2^2}{2} + g(Z_1 - Z_2) \tag{9.48}$$

The use of availability and irreversibility in an actual thermodynamic problem is shown in Fig. 9.12. A theoretical analysis was made of a reciprocating internal-combustion automotive engine to see what happened to the availability of the air–fuel mixture that entered the engine and where the irreversibility occurred during the process. The abscissa on Fig. 9.12 is the crank angle, the left side representing bottom dead center when the cylinder is assumed to be filled with an air–fuel mixture having the availability indicated on the ordinate. As the compression process takes place, this mixture becomes more available through the work done in compressing the mixture. When the piston passes top dead center, the expansion process takes place. The beginning and end of combustion are also indicated on the diagram. During the combustion and expansion process irreversibilities occur. Those associated with the combustion process itself and those associated with heat transfer to the cooling water or surroundings are both indicated. The work done

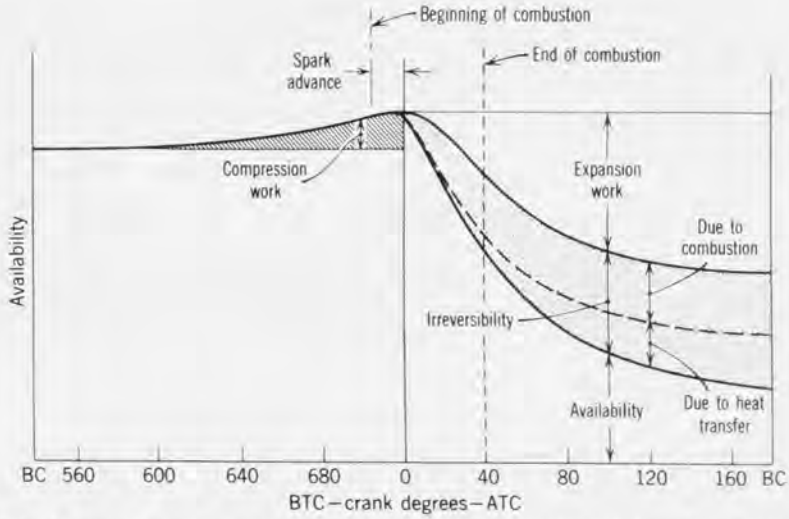


FIGURE 9.12 Availability versus crank angle of the charge in a spark-ignited internal-combustion engine. (From D. J. Patterson and G. J. Van Wylen, "A Digital Computer Simulation for Spark Ignited Engine Cycles," *SAE Progress in Technology Series*, 7, p. 88. Published by SAE Inc., New York, 1964.)

during the expansion process and the availability at the end of the expansion are indicated on the right ordinate. The availability that remains in the cylinder at the end of the expansion stroke is exhausted to the atmosphere.

The less the irreversibility associated with a given change of state, the greater the amount of work that will be done (or the smaller the amount of work that will be required). This relation is significant in at least two regards. The first is that availability is one of our natural resources. This availability is found in such forms as oil reserves, coal reserves, and uranium reserves. Suppose we wish to accomplish a given objective that requires a certain amount of work. If this work is produced reversibly while drawing on one of the availability reserves, the decrease in availability is exactly equal to the reversible work. However, since there are irreversibilities in producing this required amount of work, the actual work will be less than the reversible work, and the decrease in availability will be greater (by the amount of the irreversibility) than if this work had been produced reversibly. Thus the more irreversibilities we have in all our processes, the greater will be the decrease in our availability reserves.[1] The conservation and effective use of these availability reserves is an important responsibility for all of us.

The second reason that it is desirable to accomplish a given objective with the smallest irreversibility is an economic one. Work costs money, and in many cases a given objective can be accomplished at less cost when the irreversibility is less. It should be noted, however, that many factors enter into the total cost of accomplishing a given objective, and an optimization process that considers many factors is often necessary to arrive at the most economical design. For example, in a heat-transfer process, the smaller the temperature difference across which the heat is transferred, the less the irreversibility. However, for a given rate of heat transfer, a smaller temperature difference will require a larger (and therefore more expensive) heat exchanger. These various factors must all be considered in developing the optimum and most economical design.

In many engineering decisions other factors, such as the impact on the environment (for example, air pollution and water pollution) and the impact on society must be considered in developing the optimum design.

Along with the increased use of availability analysis in recent years, a term called the "second-law efficiency" has come into more common use. This term refers to comparison of the desired output of a process with the cost, or input, in terms of the thermodynamic availability. Thus, the isentropic turbine efficiency defined by Eq. 9.30 as the actual work output divided by the work for a hypothetical isentropic expansion from the same inlet state to the same exit pressure might well be called a "first-law efficiency," in that it is a comparison of two energy quantities. The "second-law efficiency," as just described, would be the actual work output of the turbine divided by the decrease in availability from the same inlet state to the same exit state. In this sense, this concept provides a rating or measure of the real process in terms of the actual change of state, and is simply another convenient way of utilizing the concept of thermodynamic availability.

[1] In many popular talks reference is made to our energy reserves. From a thermodynamic point of view, availability reserves would be a much more acceptable term. There is much energy in the atmosphere and the ocean, but relatively little availability.

EXAMPLE 9.8

A steam turbine, Fig. 9.13, receives 30 kg of steam per second at 3 MPa, 350°C. At the point in the turbine where the pressure is 0.5 MPa, steam is bled off for processing equipment at the rate of 5 kg/s. The temperature of this steam is 200°C. The balance of the steam leaves the turbine at 15 kPa, 90 percent quality. The heat transfer to the surroundings is 150 kW. Determine the availability per kilogram of the steam entering and at both points at which steam leaves the turbine, the reversible work for the given change of state and the second-law efficiency for this process.

Control volume: Turbine.

Inlet state: P_1, T_1 known; state fixed.

Exit states: P_2, T_2 known; P_3, x_3 known; both states fixed.

Process: SSSF.

Model: Steam tables.

Analysis: The availability at any point for the steam entering or leaving the turbine is given by Eq. 9.42.

$$\psi = (h - h_0) - T_0(s - s_0) + \frac{\mathbf{V}^2}{2} + g(Z - Z_0)$$

Since there are no changes in kinetic and potential energy in this problem, this equation reduces to

$$\psi = (h - h_0) - T_0(s - s_0)$$

The reversible work can then be found from Eq. 9.44.

$$\dot{W}_{rev} = \dot{m}_1\psi_1 - \dot{m}_2\psi_2 - \dot{m}_3\psi_3$$

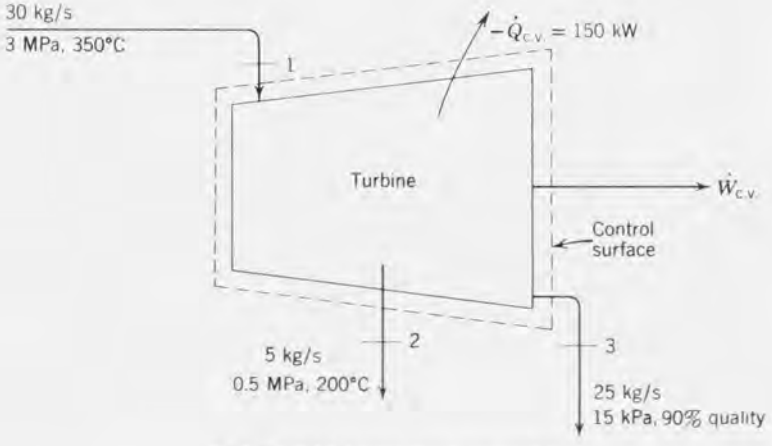


FIGURE 9.13 Sketch for Example 9.8.

Solution

At the pressure and temperature of the surroundings, 0.1 MPa, 25°C, the water is a slightly compressed liquid, and the properties of the water are essentially equal to those for saturated liquid at 25°C.

$$h_0 = 104.9 \text{ kJ/kg}, \qquad s_0 = 0.3674 \text{ kJ/kg K}$$

From Eq. 9.42

$$\psi_1 = (3115.3 - 104.9) - 298.15(6.7428 - 0.3674) = 1109.6 \text{ kJ/kg}$$
$$\psi_2 = (2855.4 - 104.9) - 298.15(7.0592 - 0.3674) = 755.3 \text{ kJ/kg}$$
$$\psi_3 = (2361.8 - 104.9) - 298.15(7.2831 - 0.3674) = 195.0 \text{ kJ/kg}$$

From Eq. 9.44,

$$\dot{W}_{\text{rev}} = 30(1109.6) - 5(755.3) - 25(195.0) = 24\,637 \text{ kW}$$

The actual turbine output is, from Eq. 6.14,

$$\dot{W} = -150 + 30(3115.3) - 5(2855.4) - 25(2361.8) = 19\,987 \text{ kW}$$

so that the second-law efficiency is

$$\eta_{\text{2nd law}} = \frac{19\,987}{24\,637} = 0.811$$

EXAMPLE 9.9

A lead storage battery of the type used in an automobile is able to deliver 5.2 MJ of electrical energy. This energy is available for starting the car.

Suppose we wish to use compressed air for doing an equivalent amount of work in starting the car. The compressed air is to be stored at 7 MPa, 25°C. What volume of tank is required for the compressed air to have an availability of 5.2 MJ?

System: Compressed air tank.

State: P, T known; state fixed.

Model: Ideal gas.

Solution

Let us first find the availability of air at 7 MPa, 25°C. From Eq. 9.47,

$$\phi = (u - u_0) - T_0(s - s_0) + P_0(v - v_0)$$

$$v = \frac{RT}{P} = \frac{0.287 \times 298.15}{7000} = 0.012\,22 \text{ m}^3/\text{kg}$$

$$v_0 = \frac{RT_0}{P_0} = \frac{0.287 \times 298.15}{100} = 0.8557 \text{ m}^3/\text{kg}$$

$$\phi = 0 - 298.15\left(0 - 0.287 \ln \frac{7000}{100}\right) + 100(0.012\,22 - 0.8557)$$
$$= 0 + 363.5 - 84.3 = 279.2 \text{ kJ/kg}$$

To have an availability of 5.2 MJ, the mass of air is

$$m = \frac{5200}{279.2} = 18.625 \text{ kg}$$

$$V = mv = 18.625(0.012\,22) = 0.2276 \text{ m}^3$$

9.8 PROCESSES INVOLVING CHEMICAL REACTIONS

Although chemical reactions will not be considered in detail until Chapter 13, some preliminary remarks regarding availability in such processes can be made here. We observe that the reactants are often in pressure and temperature equilibrium with the surroundings before the reaction takes place, and the same is true of the products after the reaction. An automobile engine is an example of such a process if we visualize the products being cooled to atmospheric temperature before they are discharged from the engine.

Let us first consider the implications of temperature equilibrium with the surroundings during a chemical reaction in a system. The temperature of the system T is equal to T_0, the temperature of the surroundings. Therefore, from Eq. 9.40, we can write (noting that $T_0 = T$)

$$_1(w_{rev})_2 = \left(u_1 - T_1 s_1 + \frac{\mathbf{V}_1^2}{2} + gZ_1\right) - \left(u_2 - T_2 s_2 + \frac{\mathbf{V}_2^2}{2} + gZ_2\right)$$

The quantity $U - TS$ is a thermodynamic property of a substance and is called the Helmholtz function. It is an extensive property and we designate it by the symbol A. Thus,

$$\begin{aligned} A &= U - TS \\ a &= u - Ts \end{aligned} \tag{9.49}$$

Therefore, when a system undergoes a change of state while in temperature equilibrium with the surroundings, the reversible work is given by the relation

$$_1(w_{rev})_2 = \left(a_1 + \frac{\mathbf{V}_1^2}{2} + gZ_1\right) - \left(a_2 + \frac{\mathbf{V}_2^2}{2} + gZ_2\right)$$

In cases in which the kinetic and potential energy changes are not significant, this reduces to

$$_1(W_{rev})_2 = A_1 - A_2 = m(a_1 - a_2) \tag{9.50}$$

Let us now consider a system that undergoes a chemical reaction while in both pressure and temperature equilibrium with the surroundings. The availability function ϕ for a system has been defined as

$$\phi = (u + P_0 v - T_0 s) - (u_0 + P_0 v_0 - T_0 s_0)$$

If $P = P_0$ and $T = T_0$, then

$$\begin{aligned} \phi &= (u + Pv - Ts) - (u_0 + P_0 v_0 - T_0 s_0) \\ &= (h - Ts) - (h_0 - T_0 s_0) \end{aligned} \tag{9.51}$$

The quantity $h - Ts$ is a thermodynamic property and is termed the Gibbs function. It is designated by the symbol G.

$$\begin{aligned} G &= H - TS \\ g &= h - Ts \end{aligned} \tag{9.52}$$

Introducing the Gibbs function into Eq. 9.51, we have, when a system is in pressure and temperature equilibrium with the surroundings,

$$\phi = g - g_0$$

From Eq. 9.48 it follows that under these same conditions,

$$_1(w_{rev})_2 = (g_1 - g_2) - P_0(v_1 - v_2) + \frac{\mathbf{V}_1^2 - \mathbf{V}_2^2}{2} + g(Z_1 - Z_2) \tag{9.53}$$

The Gibbs function is also significant in a steady-state, steady-flow process that takes place in temperature equilibrium with the surroundings. Because $T_i = T_e = T_0$, Eq. 9.38 reduces to

$$\dot{W}_{rev} = \dot{m}_i\left(h_i - T_i s_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) - \dot{m}_e\left(h_e - T_e s_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right)$$

Introducing the Gibbs function, we have

$$\dot{W}_{rev} = \dot{m}_i\left(g_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) - \dot{m}_e\left(g_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right) \tag{9.54}$$

Thus, we have introduced two new properties, the Helmholtz function, A, and the Gibbs function, G. Both these functions are very important in the thermodynamics of chemical reactions and will be used extensively in later chapters of this book.

9.9 SOME GENERAL COMMENTS REGARDING ENTROPY

It is quite possible at this point that a student may have a good grasp of the material that has been covered, but only a vague understanding of the significance of entropy. In fact, the question "What is entropy?" is frequently raised by students with the implication that no one really knows! This section has been included in an attempt to give insight into the qualitative and philosophical aspects of the concept of entropy, and to illustrate the broad application of entropy to many different disciplines.

The concept of energy arises from the first law of thermodynamics and the concept of entropy from the second law of thermodynamics. Actually it is just as difficult to answer the question "What is energy?" as it is to answer the question "What is entropy?" Because we regularly use the term energy and are able to relate this term to phenomena that we observe every day, the word energy has a definite meaning and thus serves as an effective vehicle for thought and communication. The word entropy could serve in the same capacity. If when we observed a highly irreversible process (such as cooling coffee by placing an ice cube in it), we said,

"That surely increases the entropy," we would soon be as familiar with the word *entropy* as we are with the word *energy*. In many cases when we speak about a higher efficiency we are actually speaking about accomplishing a given objective with a smaller total increase in entropy.

A second point to be made regarding entropy is that, in statistical thermodynamics, the property entropy is defined in terms of probability. Although this topic will be examined in detail in Chapter 17, a few brief remarks regarding entropy and probability may prove helpful here. From this point of view the net increase in entropy that occurs during an irreversible process can be associated with a change of state from a less probable state to a more probable state. For instance, to use an earlier example, we are more likely to find gas on both sides of the ruptured membrane of Fig. 7.11 than to find a gas on one side and a vacuum on the other. Thus, when the membrane ruptures, the direction of the process is from a less probable state to a more probable state, and associated with this process is an increase in entropy. Similarly, the more probable state is that a cup of coffee will be at the same temperature as its surroundings than at a higher (or lower) temperature. Therefore, as the coffee cools because heat is transferred to the surroundings, there is a change from a less probable to a more probable state, and associated with this is an increase in entropy.

The final point to be made is that the second law of thermodynamics and the principle of the increase of entropy have philosophical implications. Does the second law of thermodynamics apply to the universe as a whole? Are there processes unknown to us occurring somewhere in the universe, such as "continual creation," that have a decrease in entropy associated with them, and thus offset the continual increase in entropy that is associated with the natural processes that are known to us? If the second law is valid for the universe (we of course do not know whether the universe can be considered as an isolated system), how did it get in the state of low entropy? On the other end of the scale, if all processes known to us have an increase in entropy associated with them, what is the future of the natural world as we know it?

Quite obviously it is impossible to give conclusive answers to these questions on the basis of the second law of thermodynamics alone. Nevertheless, we see the second law of thermodynamics as a description of the prior and continuing work of a Creator, who also holds the answer to our future destiny and that of the universe.

PROBLEMS

9.1 In a heat pump that uses R-22 as the working fluid, the R-22 enters the compressor as saturated vapor at 0°C and at a steady rate of 0.1 kg/s. In the compressor the R-22 is compressed to a pressure so that when it is subsequently cooled at constant pressure in the condenser condensation will occur at 40°C. Calculate the power input required in the compressor, assuming the process to be reversible and adiabatic.

9.2 Consider the design of a nozzle in which nitrogen gas flowing in a pipe at 500 kPa, 200°C, and at a velocity of 10 m/s, is to be expanded to produce a velocity of 300 m/s. Determine the exit pressure and cross-sectional area of the nozzle if the mass flow rate is 0.15 kg/s, and the nozzle expansion is reversible and adiabatic.

9.3 Steam enters a turbine at 2.0 MPa, 400°C, expands in a reversible adiabatic process, and exhausts at 10 kPa. Changes in kinetic and potential energies between the inlet and exit conditions of the turbine are small. The power output of this turbine is 800 kW. What is the mass flow rate of steam through the turbine?

9.3E Steam enters a turbine at 300 lbf/in.^{2}, 800 F, expands in a reversible adiabatic process, and exhausts at 2 lbf/in.^{2}. Changes in kinetic and potential energies between the inlet and exit conditions of the turbine are small. The power output of this turbine is 1000 hp. What is the mass flow rate of steam through the turbine?

9.4 A diffuser is a steady-state, steady-flow device in which a fluid flowing at high velocity is decelerated in such a way that the pressure increases during the process. Consider a diffuser in which air enters at 120 kPa, 30°C, with a velocity of 200 m/s, and exits with a velocity of 20 m/s. Assuming that the process is reversible and adiabatic, what are the exit pressure and the temperature of the air?

9.4E A diffuser is a steady-state, steady-flow device in which a fluid flowing at high velocity is decelerated in such a way that the pressure increases during the process. Consider a diffuser in which air enters at 18 lbf/in.^{2}, 90 F, with a velocity of 600 ft/s, and exits with a velocity of 60 ft/s. Assuming that the process is reversible and adiabatic, what are the exit pressure and the temperature of the air?

9.5 A certain industrial process requires a steady supply of saturated-vapor steam at 200 kPa, at the rate of 0.5 kg/s. Also required is a steady supply of compressed air at 500 kPa, at the rate of 0.1 kg/s. Both are to be supplied by the process shown in Fig. 9.14. Steam is expanded in a turbine to supply the power needed to drive the air compressor, and the exhaust steam exits the turbine at the desired state. Air inlet to the compressor is at ambient conditions, 100 kPa and 20°C. What are the required steam turbine inlet pressure and temperature, assuming that both the turbine and compressor are reversible and adiabatic?

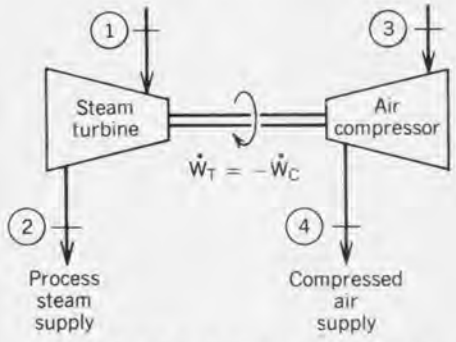


FIGURE 9.14 Sketch for Problem 9.5.

9.6 Air enters a turbine at 800 kPa, 1200 K, and expands in a reversible adiabatic process to 100 kPa. Calculate the exit temperature and the work output per kilogram of air, using

(a) The ideal-gas air tables, Table A.9.
(b) Constant specific heat, value at 300 K from Table A.9.
(c) Constant specific heat, value at an intermediate temperature from Fig. 5.10.

Discuss why the method of part b gives a poor value for the exit temperature and yet a relatively good value for the work output.

9.7 Consider a geothermal supply of hot water available as saturated liquid at $P_1 = 1.5$ MPa. This liquid is to be flashed (throttled) to some lower pressure P_2. The saturated liquid and saturated vapor at this pressure are separated, and the vapor is expanded through a reversible adiabatic turbine to the exhaust pressure $P_3 = 10$ kPa. Study the turbine power output per unit initial mass m_1 as a function of the value of pressure P_2.

9.8 One technique for operating a steam turbine at part-load power output is to throttle the steam to a lower pressure before it enters the turbine, as shown in Fig. 9.15. The steamline conditions are 2 MPa, 400 °C, and the turbine exhaust pressure is fixed at 10 kPa. Assuming the expansion inside the turbine to be reversible and adiabatic, determine

(a) The full-load work output of the turbine per kilogram of steam.

(b) The pressure to which the steam must be throttled to produce 80 percent of the full-load output. Show both processes on a T–s diagram.

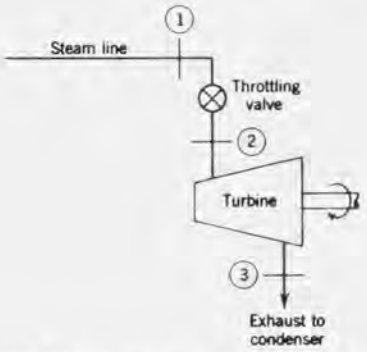


FIGURE 9.15 Sketch for Problems 9.8 and 9.8E

9.8E One technique for operating a steam turbine at part-load power output is to throttle the steam to a lower pressure before it enters the turbine, as shown in Fig. 9.15. The steamline conditions are 200 lbf/in.^{2}, 600 F, and the turbine exhaust pressure is fixed at 1 lbf/in.^{2}. Assuming the expansion inside the turbine to be reversible and adiabatic, determine

(a) The full-load work output of the turbine per pound-mass of steam.

(b) The pressure to which the steam must be throttled to produce 80 percent of the full-load output. Show both processes on a T–s diagram.

9.9 Liquid water at ambient conditions, 100 kPa and 25 °C, enters a pump at the rate of 0.5 kg/s. Power input to the pump is 3 kW. Assuming the pump process to be reversible, determine the pump exit pressure and temperature.

9.9E Liquid water at ambient conditions, 14.7 lbf/in.^{2} and 75 F, enters a pump at the rate of 1 lbm/s. Power input to the pump is 4 hp. Assuming the pump process to be reversible, determine the pump exit pressure and temperature.

9.10 A large storage tank contains liquefied natural gas (LNG), which may be assumed to be pure methane. The tank contains saturated liquid at ambient pressure, 100 kPa; it is to be pumped to 500 kPa and fed to a pipeline at the rate of 0.5 kg/s. How much power input is required for the pump, assuming it to be reversible?

9.11 Consider a steam turbine power plant operating at supercritical pressure, as shown in Fig. 9.16. As a first approximation, it may be assumed that both the turbine and the pump processes are reversible and adiabatic. Neglecting any changes in kinetic and potential energies, calculate

(a) The turbine work output, and the state at the exit from the turbine.

(b) The pump work input, and the enthalpy of the liquid at the exit from the pump.

(c) The thermal efficiency of the cycle.

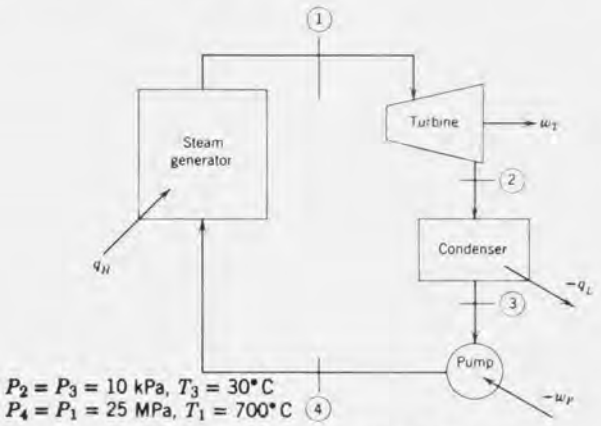


FIGURE 9.16 Sketch for Problem 9.11.

9.12 Helium gas enters a steady-flow expander at 800 kPa, 300°C, and exits at 120 kPa. The mass flow rate is 0.2 kg/s, and the expansion process can be considered reversible and polytropic, with a polytropic exponent $n = 1.30$. Calculate the power output of the expander.

9.12E Helium gas enters a steady-flow expander at 120 lbf/in.^{2}, 500 F, and exits at 18 lbf/in.^{2}. The mass flow rate is 0.4 lbm/s, and the expansion process can be considered reversible and polytropic, with a polytropic exponent $n = 1.30$. Calculate the power output of the expander.

9.13 Ammonia enters a nozzle at 800 kPa, 50°C, at a velocity of 10 m/s and at the rate of 0.1 kg/s. The nozzle expansion is assumed to be a reversible, polytropic SSSF process. Ammonia exits the nozzle at 200 kPa; the rate of heat transfer to the nozzle is 8.2 kW. What is the velocity of the ammonia exiting the nozzle?

9.14 One type of feedwater heater for preheating the water before entering a boiler operates on the principle of mixing the water with steam that has been bled from

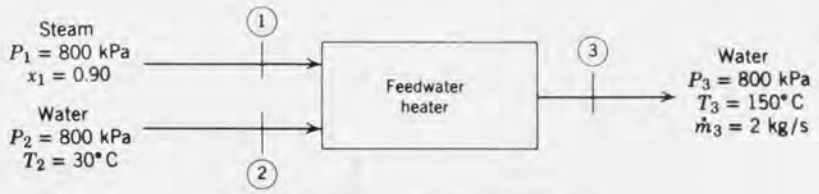


FIGURE 9.17 Sketch for Problem 9.14.

the turbine. For the states as shown in Fig. 9.17, calculate the rate of net entropy increase for this process, assuming the process to be steady-flow and adiabatic.

9.15 Consider the scheme shown in Fig. 9.18 for producing fresh water from salt water. The conditions are as shown in the figure. Assume that the properties of salt water are the same as for pure water, and that the pump is reversible and adiabatic.

(a) Determine the ratio (m_7/m_1), that is, the fraction of salt water purified by the process.

(b) Determine the input quantities, w_P and q_H.

(c) Make a second-law analysis of the overall system.

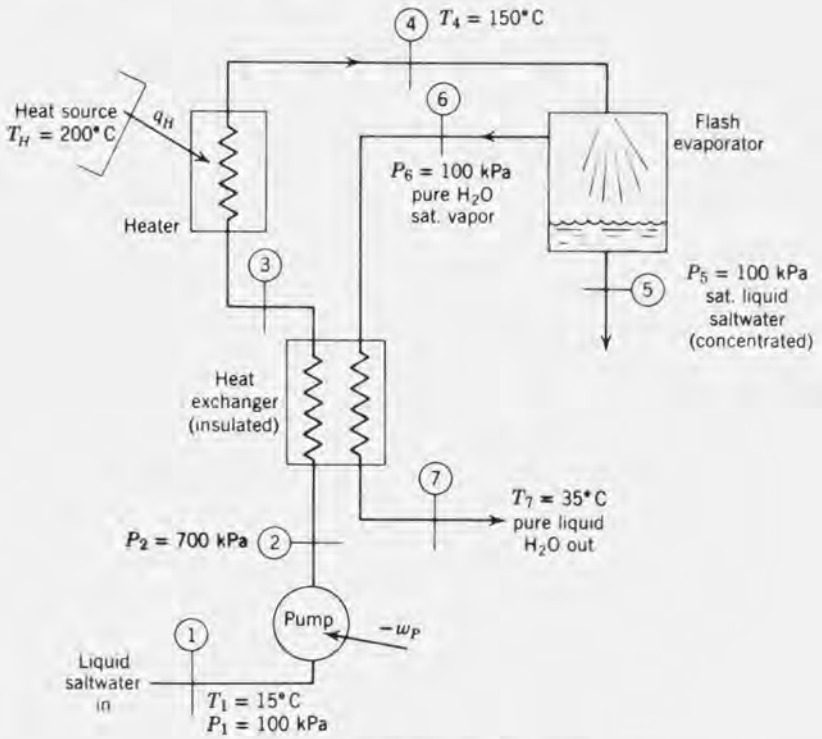


FIGURE 9.18 Sketch for Problem 9.15.

9.16 Air from a line at 12 MPa, 15°C, flows into a 500-L rigid tank that initially contained air at ambient conditions, 100 kPa and 15°C. This process occurs rapidly and is essentially adiabatic. The valve is closed when the pressure inside reaches some value P_2. The tank eventually cools to room temperature, at which time the pressure inside is 5 MPa. What is the pressure P_2? What is the net entropy change for the overall process?

9.16E Air from a line at 1800 lbf/in.^{2}, 60 F, flows into a 20-ft^3 rigid tank that initially contained air at ambient conditions, 14.7 lbf/in.^{2} and 60 F. This process occurs rapidly and is essentially adiabatic. The valve is closed when the pressure inside reaches some value P_2. The tank eventually cools to room temperature, at which time the pressure inside is 750 lbf/in.^{2}. What is the pressure P_2? What is the net entropy change for the overall process?

9.17 A 1-m^3 rigid tank contains 100 kg of R-22 at ambient temperature, 15°C. A valve on top of the tank is opened, and saturated vapor is throttled to ambient pressure, 100 kPa, and discharged. During this process the temperature inside the tank remains at 15°C. The valve is closed when no liquid remains inside. Calculate

(a) The heat transfer to the tank.
(b) The net entropy change for the process.

9.18 A cylinder with a piston restrained by an external force contains R-12 at 50°C, 90 percent quality. Under these conditions the volume is 100 L. The cylinder is attached to a line flowing R-12 at 3 MPa, 150°C. The valve is opened, and mass flows into the cylinder until the pressure inside reaches 3 MPa, at which point the temperature inside is 100°C. It is claimed that during the process the R-12 does 150 kJ of work by movement at the boundary against the external restraining force. It is also claimed that any heat transfer is with the ambient at 20°C. Does this process violate the second law?

9.19 A stream of ammonia enters a steady-flow device at 100 kPa, 50°C, at the rate of 1 kg/s. Two streams exit the device at equal mass flow rates: one at 200 kPa, 50°C, and the other as saturated liquid at 10°C. It is claimed that this device operates in a 25°C room on an electrical power input of 250 kW. Is this possible?

9.20 A spherical aluminum tank having an inside diameter of 1 m and a wall thickness of 5 mm contains water at 2 MPa, 300°C. A valve on the tank is opened, allowing steam to flow out until the tank and steam remaining inside both reach 150°C, at which point the valve is closed. The steam inside now has a quality of 90 percent.

(a) How much steam was lost from the tank?
(b) Taking a control volume that includes the tank and its contents, calculate the entropy change of the control volume and that of its surroundings for this process.

9.20E A spherical aluminum tank having an inside diameter of 3 ft and a wall thickness of 0.2 in. contains water at 300 lbf/$in.^2$, 550 F. A valve on the tank is opened, allowing steam to flow out until the tank and steam remaining inside both reach 300 F, at which point the valve is closed. The steam inside now has a quality of 90 percent.

(a) How much steam was lost from the tank?
(b) Taking a control volume that includes the tank and its contents, calculate the entropy change of the control volume and that of its surroundings for this process.

9.21 Liquid water enters a pump at 25°C, 100 kPa, and exits at a pressure of 5 MPa. If the isentropic efficiency of the pump is 75 percent, determine the enthalpy (steam tables reference) of the water at the pump exit.

9.21E Liquid water enters a pump at 70 F, 14.7 lbf/$in.^2$, and exits at a pressure of 1000 lbf/$in.^2$. If the isentropic efficiency of the pump is 75 percent, determine the enthalpy (steam tables reference) of the water at the pump exit.

9.22 Repeat Problem 9.5, assuming that the steam turbine and the air compressor each have an isentropic efficiency of 80 percent.

9.23 Repeat Problem 9.11 assuming that the turbine and pump each have an isentropic efficiency of 85 percent.

9.24 In one type of heat-powered refrigeration system, part of the working fluid is expanded through a turbine to drive the compressor of the refrigeration cycle. Consider the turbine–compressor unit of such a refrigeration cycle, as shown in Fig. 9.19. The turbine produces just enough power to drive the compressor, and both exit streams then mix together. Specifying any assumptions, find the ratio of mass flow rates $\dot{m}_3/\dot{m}_1$ and T_5 (x_5 if in the two-phase region) if

(a) The turbine and compressor are reversible and adiabatic.
(b) The turbine and compressor each have an isentropic efficiency of 70 percent.

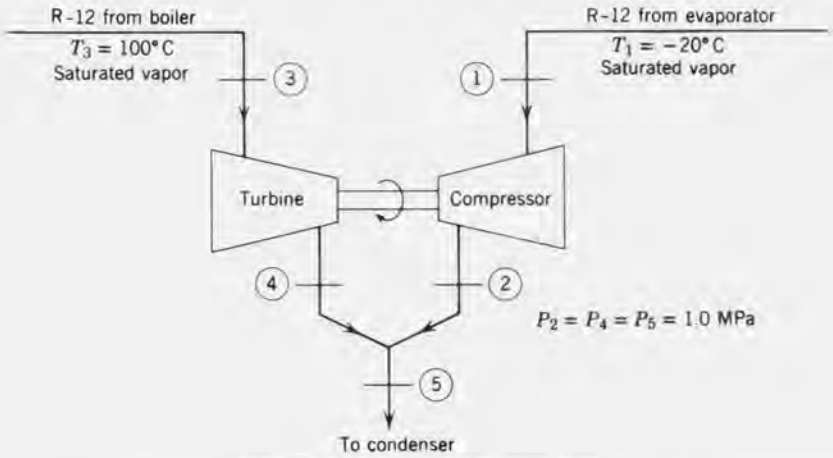


FIGURE 9.19 Sketch for Problem 9.24.

9.25 Air enters an insulated compressor at ambient conditions, 100 kPa and 20°C, at the rate of 0.1 kg/s and exits at 200°C. The isentropic efficiency of the compressor is 70 percent. What is the exit pressure? How much power input is required to drive the compressor?

9.25E Air enters an insulated compressor at ambient conditions, 14.7 lbf/in.^{2} and 70 F, at the rate of 0.1 lbm/s and exits at 400 F. The isentropic efficiency of the compressor is 70 percent. What is the exit pressure? How much power input is required to drive the compressor?

9.26 Steam enters a turbine at 300°C and exhausts at 20 kPa. It is estimated that the isentropic efficiency of the turbine is 70 percent. What is the maximum turbine inlet pressure if the exhaust is not to be in the two-phase region?

9.26E Steam enters a turbine at 500 F and exhausts at 2 lbf/in.^{2}. It is estimated that the isentropic efficiency of the turbine is 70 percent. What is the maximum turbine inlet pressure if the exhaust is not to be in the two-phase region?

9.27 A nozzle is required to produce a stream of air at 200 m/s at a condition of 20°C, 100 kPa. It is estimated that the nozzle has an isentropic efficiency of 92 percent. What nozzle inlet pressure and temperature are required?

9.28 A centrifugal compressor takes in ambient air at 100 kPa, 15°C, and discharges it at 450 kPa. What is your best estimate of the discharge temperature?

9.29 A jet-ejector pump, shown schematically in Fig. 9.20, is a device in which a low-pressure (secondary) fluid is compressed by entrainment in a high-velocity (primary)

fluid stream. The compression results from deceleration in a diffuser. For purposes of analysis, an ideal jet pump can be considered as equivalent to the ideal (reversible and adiabatic) turbine–compressor unit shown in Fig. 9.19. States 1, 3, and 5 correspond to those in Fig. 9.20. Now consider a steam jet pump in which state 1 is saturated vapor at 35 kPa; state 3 is 300 kPa, 150°C; and the discharge pressure P_5 is 100 kPa.

(a) Calculate the ideal mass flow ratio $\dot{m}_1/\dot{m}_3$.
(b) The efficiency of a jet pump is defined as

$$\eta_{\text{jet pump}} = \frac{(\dot{m}_1/\dot{m}_3)\ \text{actual}}{(\dot{m}_1/\dot{m}_3)\ \text{ideal}}$$

for the same inlet conditions and discharge pressure. Determine the discharge temperature of the jet pump if its efficiency is 10 percent.

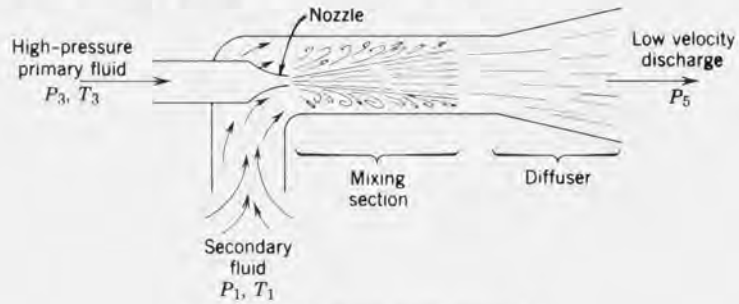


FIGURE 9.20 Sketch for Problem 9.29.

9.30 A geothermal supply of hot water at 500 kPa, 150°C, is fed to an insulated flash evaporator at the rate of 1.5 kg/s. A stream of saturated liquid at 200 kPa is drained from the bottom of the flash evaporator, and a stream of saturated vapor at 200 kPa is drawn from the top and fed to a turbine. The turbine has an isentropic efficiency of 70 percent and an exit pressure of 15 kPa. Evaluate the second law for this process for a control volume that includes the flash evaporator and turbine.

9.30E A geothermal supply of hot water at 80 lbf/in.^{2}, 300 F, is fed to an insulated flash evaporator at the rate of 10 000 lbm/h. A stream of saturated liquid at 30 lbf/in.^{2} is drained from the bottom of the flash evaporator, and a stream of saturated vapor at 30 lbf/in.^{2} is drawn from the top and fed to a turbine. The turbine has an isentropic efficiency of 70 percent and an exit pressure of 2 lbf/in.^{2}. Evaluate the second law for this process for a control volume that includes the flash evaporator and turbine.

9.31 A turbocharger is to be used to boost the inlet air pressure to an automobile engine. This device consists of an exhaust gas-driven turbine directly connected to an air compressor, as shown in Fig. 9.21. At a certain engine load, the conditions are as shown in the figure. If it is assumed that the turbine and compressor are both reversible and adiabatic, calculate

(a) The turbine exit temperature and power output.
(b) The compressor exit pressure and temperature.
(c) Repeat parts a and b, but assume that the turbine has an isentropic efficiency of 85 percent and the compressor an isentropic efficiency of 80 percent.

9.32 A nozzle is required to produce a steady stream of R-12 at 280 m/s. The R-12 is to be at ambient conditions, 100 kPa and 20°C. The isentropic nozzle efficiency may

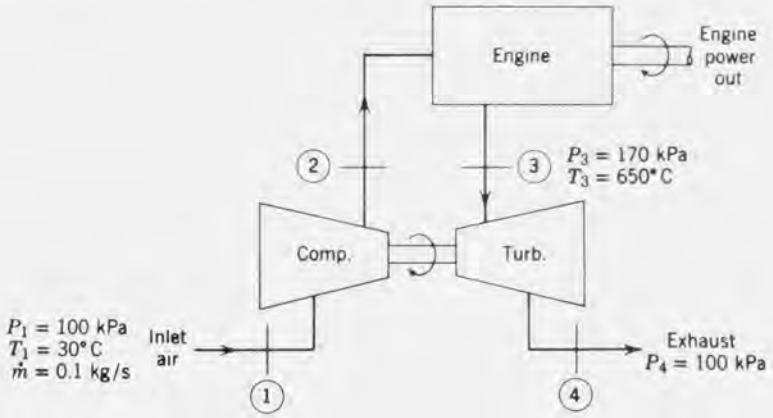


FIGURE 9.21 Sketch for Problem 9.31.

be assumed to be 90 percent. What pressure and temperature are required in the line upstream of the nozzle?

9.33 A certain industrial process requires a steady stream of saturated-vapor steam at 200 kPa at the rate of 2 kg/s. There are two alternatives for supplying this steam from ambient liquid water at 20°C, 100 kPa.

1. Pump the water to 200 kPa and feed to a steam generator.
2. Pump the water to 5 MPa, feed to a steam generator, and then expand through a turbine, from which the steam exhausts at the desired state.

(a) Compare these two alternatives, making reasonable assumptions about the various processes.

(b) What is the rate of net entropy increase for each of the alternatives?

9.34 A cylinder fitted with a piston and containing 2 kg of ammonia at −10°C, 90 percent quality is brought into a 20°C room and attached to a line flowing ammonia at 800 kPa, 40°C. The total restraining force on the piston is proportional to the cylinder volume squared. The valve is opened, and ammonia flows into the cylinder until the mass inside is twice the initial mass, at which point the valve is closed. An electrical current of 15 A is now passed through a 2-ohm resistor inside the cylinder for 20 minutes. It is claimed that the final pressure in the cylinder is 600 kPa. Is this possible?

9.35 tank pressure drops to that value of pressure, at which point the nitrogen flow stops 300 K. The tank is connected by an adjustable pressure regulator to an insulated turbine that exhausts to atmospheric pressure, 100 kPa. The regulator maintains a fixed turbine–inlet pressure by throttling gas from the storage tank until the storage tank pressure drops to that value of pressure, at which point the nitrogen flow stops and the process ends. During the process enough heat is transferred to the storage tank that the temperature inside remains constant at 300 K. We wish to obtain the maximum total work output of the turbine. Assuming a reasonable value for turbine isentropic efficiency, determine

(a) The optimum regulator pressure setting.
(b) The total work output.
(c) The net entropy change for the process.

9.36 A commercial laundry requires a hot-water supply of 2.5 kg/s at 85°C. This supply is to be produced in a steady-flow process by mixing the 10°C water supply with steam coming from a boiler as saturated vapor at 100 kPa pressure. Determine the rate of irreversibility of the mixing process.

9.37 Calculate the irreversibility for the process described in Problem 6.38.

9.38 What is the minimum work required to change one kilogram of methane gas from 500 kPa, 300 K, to saturated liquid at 100 kPa? Sketch an apparatus that would be used in such a process, and show the process on a temperature–entropy diagram.

9.39 Air enters the turbocharger compressor of an automotive engine at 100 kPa, 30°C, and exits at 170 kPa. The air is cooled by 50 degrees in an intercooler before entering the engine. If the isentropic compressor efficiency is 75 percent, determine the temperature of the air entering the engine and the irreversibility of the compression–cooling process.

9.39E Air enters the turbocharger compressor of an automotive engine at 14.7 lbf/in.^{2}, 90 F, and exits at 25 lbf/in.^{2}. The air is cooled by 90 degrees in an intercooler before entering the engine. If the isentropic compressor efficiency is 75 percent, determine the temperature of the air entering the engine and the irreversibility of the compression–cooling process.

9.40 A 10-kg copper vessel contains 100 L of R-22 at −20°C, 40 percent quality. This vessel is brought indoors and eventually comes to room temperature, 20°C. What is the irreversibility of this process?

9.41 A solid aluminum sphere 0.1 m in diameter and initially at 200°C is allowed to cool to ambient temperature, 25°C. What is the irreversibility of this process?

9.42 A steady stream of liquid R-22 at ambient temperature, 10°C, and at 750 kPa enters a solar collector. The stream exits at 80°C, 700 kPa. Calculate the change in availability of the R-22 between these two states.

9.42E A steady stream of liquid R-22 at ambient temperature, 50 F, and at 110 lbf/in.^{2} enters a solar collector. The stream exits at 180 F, 100 lbf/in.^{2}. Calculate the change in availability of the R-22 between these two states.

9.43 Consider the following device proposed as an outdoor portable power supply for winter use. A 100-L rigid tank contains 90 percent liquid water and 10 percent nitrogen gas, by volume, at 200 kPa, 0°C. The tank is left outdoors overnight, and the water freezes, compressing the nitrogen. A regulating valve is opened, allowing nitrogen at 200 kPa, 0°C, to flow to an expansion engine to produce power, as desired. This device will operate until the tank pressure drops back to 200 kPa. What is the availability of the nitrogen? Would it be better to fill the tank with different proportions of water and nitrogen?

9.44 Consider a geothermal supply of hot water at 200°C, 3 MPa. What is the availability of this energy resource with respect to an ambient temperature of 25°C?

9.44E Consider a geothermal supply of hot water at 300 F, 500 lbf/in.^{2}. What is the availability of this energy resource with respect to an ambient temperature of 77 F?

9.45 At a certain location in the ocean, the local water temperature a short distance beneath the surface is 15°C, compared with an ambient air temperature of 10°C. What is the thermodynamic availability of the water?

9.46 Air enters a compressor at ambient conditions, 100 kPa and 300 K, and exits at 800 kPa. If the isentropic compressor efficiency is 85 percent, what is the second-law efficiency of the compression process?

9.47 Consider two metal blocks. Block A is aluminum with a mass of 20 kg and is initially at 300 K; block B is copper with a mass of 10 kg and is initially at 1000 K. The two blocks are brought to a common final temperature.

(a) If the process is reversible, find the final temperature and the work done during the process.

(b) If the process is accomplished by simply bringing the blocks into thermal communication, find the final temperature and the irreversibility of the process.

9.47E Consider two metal blocks. Block A is aluminum with a mass of 40 lbm and is initially at 80 F; block B is copper with a mass of 20 lbm and is initially at 1200 F. The two blocks are brought to a common final temperature.

(a) If the process is reversible, find the final temperature and the work done during the process.

(b) If the process is accomplished by simply bringing the blocks into thermal communication, find the final temperature and the irreversibility of the process.

9.48 A steady combustion of natural gas yields 0.15 kg/s of products (having approximately the same properties as air) at 1100°C, 100 kPa. The products are passed through a heat exchanger and exit at 550°C. What is the maximum theoretical power output from a cyclic heat engine operating on the heat rejected from the combustion products, assuming that the ambient temperature is 20°C?

9.49 One kmol of carbon dust is burned with 1 kmol of oxygen to form 1 kmol of carbon dioxide in a steady-flow process. The temperature of the carbon and oxygen before combustion is 25°C, and the temperature of the carbon dioxide after combustion is also 25°C. The heat transferred during the process is −393 522 kJ, and the entropy of the carbon dioxide after combustion is 2.908 kJ/kmol K higher than the entropy of carbon and oxygen before combustion. Calculate the reversible work and the irreversibility for this process.

COMPUTER PROBLEMS

9.1C Write a program to solve the following problem. An ideal gas with constant specific heat enters a nozzle at a known inlet state P_1, T_1 with velocity $\mathbf{V}_1$ and area A_1, and expands in a reversible adiabatic process. We wish to map out the nozzle contour in terms of cross-sectional area A as a function of the local pressure P, where P is any value less than the inlet pressure. This problem should be studied over a range of conditions for given values of the constants R and k.

9.2C Write a program to solve the general case of Problems 9.5 and 9.22, in which the states, flow rates, and isentropic efficiencies of both the steam turbine and air compressor are to be input variables.

9.3C Write a program to solve Problem 9.8, in which the supply line pressure and temperature and the percent of full-load power output are variables. Also include turbine isentropic efficiency as a variable in this study.

9.4C Write a program to solve the general case of the power plant described in Problems 9.11 and 9.23. The states given in Problem 9.11 and the isentropic efficiencies are to be program input variables.

9.5C Write a program to solve the general storage tank–turbine expansion optimization described in Problem 9.35, using real ammonia as the working fluid. The storage tank initial state and the turbine efficiency are to be input variables.

9.6C Write a program to solve the general case of Problem 9.40, using ammonia as the working fluid. The initial state is to be the program input.

10

SOME POWER AND REFRIGERATION CYCLES

Some power plants, such as the simple steam power plant, which we have considered several times, operate in a cycle. That is, the working fluid undergoes a series of processes and finally returns to the initial state. In other power plants, such as the internal-combustion engine and the gas turbine, the working fluid does not go through a thermodynamic cycle, even though the engine itself may operate in a mechanical cycle. In this instance the working fluid has a different composition or is in a different state at the conclusion of the process than it had or was at the beginning. Such equipment is sometimes said to operate on the open cycle (the word cycle is really a misnomer), whereas the steam power plant operates on a closed cycle. The same distinction between open and closed cycles can be made regarding refrigeration devices. For both the open- and closed-cycle apparatus, however, it is advantageous to analyze the performance of an idealized closed cycle similar to the actual cycle. Such a procedure is particularly advantageous for determining the influence of certain variables on performance. For example, the spark-ignition internal-combustion engine is usually approximated by the Otto cycle. From an analysis of the Otto cycle we conclude that increasing the compression ratio increases the efficiency. This is also true for the actual engine, even though the Otto-cycle efficiencies may deviate significantly from the actual efficiencies.

This chapter is concerned with these idealized cycles for both power and refrigeration apparatuses. Both vapors and ideal gases are considered as working fluids. An attempt will be made to point out how the processes in actual apparatuses deviate from the ideal. Consideration is also given to certain modifications of the basic cycles that are intended to improve performance. These modifications include the use of devices such as regenerators, multistage compressors and expanders, and intercoolers. The cycles will be considered in the following order: (1) vapor power cycles, (2) vapor refrigeration cycles, (3) air-standard power cycles, and (4) air-standard refrigeration cycles. Various combinations of these types of cycles and also special applications, such as topping cycles, bottoming cycles, and cogeneration of electrical power and energy, can then be studied; these special topics are examined in the chapter problems.

VAPOR POWER CYCLES

10.1 THE RANKINE CYCLE

The ideal cycle for a simple steam power plant is the Rankine cycle, shown in Fig. 10.1. The processes that comprise the cycle are

1–2: Reversible adiabatic pumping process in the pump.
2–3: Constant-pressure transfer of heat in the boiler.
3–4: Reversible adiabatic expansion in the turbine (or other prime mover such as a steam engine).
4–1: Constant-pressure transfer of heat in the condenser.

The Rankine cycle also includes the possibility of superheating the vapor, as cycle 1–2–3′–4′–1.

If changes of kinetic and potential energy are neglected, heat transfer and work may be represented by various areas on the T–s diagram. The heat transferred to the working fluid is represented by area a–2–2′–3–b–a, and the heat transferred from the working fluid by area a–1–4–b–a. From the first law we conclude that the area representing the work is the difference between these two areas—area 1–2–2′–3–4–1. The thermal efficiency is defined by the relation

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_H} = \frac{\text{area } 1\text{–}2\text{–}2'\text{–}3\text{–}4\text{–}1}{\text{area } a\text{–}2\text{–}2'\text{–}3\text{–}b\text{–}a} \tag{10.1}$$

For analyzing the Rankine cycle, it is helpful to think of efficiency as depending on the average temperature at which heat is supplied and the average temperature at which heat is rejected. Any changes that increase the average temperature at which heat is supplied or decrease the average temperature at which heat is rejected will increase the Rankine-cycle efficiency.

It should be stated that in analyzing the ideal cycles in this chapter, the changes in kinetic and potential energies from one point in the cycle to another are neglected. In general, this is a reasonable assumption for the actual cycles.

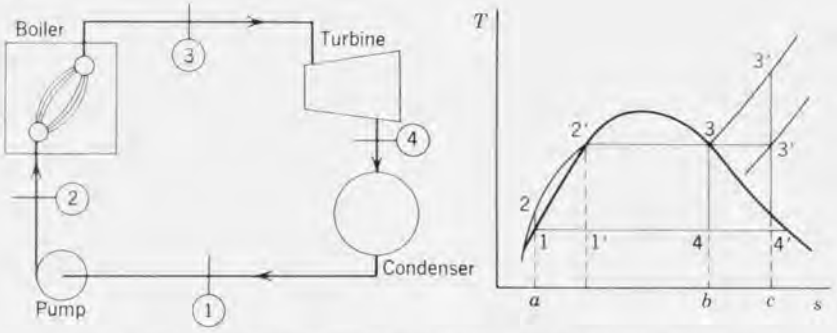


FIGURE 10.1 Simple steam power plant which operates on the Rankine cycle.

It is readily evident that the Rankine cycle has a lower efficiency than a Carnot cycle with the same maximum and minimum temperatures as a Rankine cycle, because the average temperature between 2 and 2′ is less than the temperature during evaporation. We might well ask, why choose the Rankine cycle as the ideal cycle? Why not select the Carnot cycle 1′–2′–3–4–1′? At least two reasons can be given. The first reason concerns the pumping process. State 1′ is a mixture of liquid and vapor. Great difficulties are encountered in building a pump that will handle the mixture of liquid and vapor at 1′ and deliver saturated liquid at 2′. It is much easier to condense the vapor completely and handle only liquid in the pump; the Rankine cycle is based on this fact. The second reason concerns superheating the vapor. In the Rankine cycle the vapor is superheated at constant pressure, process 3–3′. In the Carnot cycle all the heat transfer is at constant temperature, and therefore the vapor is superheated in process 3–3″. Note, however, that during this process the pressure is dropping, which means that the heat must be transferred to the vapor as it undergoes an expansion process in which work is done. This heat transfer is also very difficult to achieve in practice. Thus, the Rankine cycle is the ideal cycle that can be approximated in practice. In the following sections we will consider some variations on the Rankine cycle that enable it to approach more closely the efficiency of the Carnot cycle.

Before we discuss the influence of certain variables on the performance of the Rankine cycle, an example is given.

EXAMPLE 10.1

Determine the efficiency of a Rankine cycle using steam as the working fluid in which the condenser pressure is 10 kPa. The boiler pressure is 2 MPa. The steam leaves the boiler as saturated vapor.

In solving Rankine-cycle problems, we will let w_p denote the work into the pump per kilogram of fluid flowing, and q_L the heat rejected from the working fluid per kilogram of fluid flowing.

To solve this problem we consider, in succession, a control surface around the pump, the boiler, the turbine, and the condenser. For each the thermodynamic model is the steam tables, and the process is SSSF with negligible changes in kinetic and potential energies. Now, in turn,

Control volume: Pump.

Inlet state: P_1 known, saturated liquid; state fixed.

Exit state: P_2 known.

Analysis:

First law: $$w_p = h_2 - h_1$$

Second law: $$s_2 = s_1$$

Because

$$s_2 = s_1, \qquad h_2 - h_1 = \int_1^2 v\, dP$$

Solution

Assuming the liquid to be incompressible, we have

$$w_p = v(P_2 - P_1) = (0.001\,01)(2000 - 10) = 2.0 \text{ kJ/kg}$$
$$h_2 = h_1 + w_p = 191.8 + 2.0 = 193.8$$

Control volume: Boiler.
Inlet state: P_2, h_2 known; state fixed.
Exit state: P_3 known, saturated vapor; state fixed.
Analysis:

First law: $q_H = h_3 - h_2$

Solution

$$q_H = h_3 - h_2 = 2799.5 - 193.8 = 2605.7 \text{ kJ/kg}$$

Control volume: Turbine.
Inlet state: State 3 known (above).
Exit state: P_4 known.
Analysis:

First law: $w_t = h_3 - h_4$

Second law: $s_3 = s_4$

Solution

We can determine the quality at state 4 as follows:

$$s_3 = s_4 = 6.3409 = 0.6493 + x_4 7.5009, \qquad x_4 = 0.7588$$
$$h_4 = 191.8 + 0.7588(2392.8) = 2007.5$$
$$w_t = 2799.5 - 2007.5 = 792.0 \text{ kJ/kg}$$

Control volume: Condenser.
Inlet state: State 4 known (as given).
Exit state: State 1 known (as given).
Analysis:

First law: $q_L = h_4 - h_1$

Solution

$$q_L = h_4 - h_1 = 2007.5 - 191.8 = 1815.7 \text{ kJ/kg}$$

We can now calculate the thermal efficiency:

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_H} = \frac{q_H - q_L}{q_H} = \frac{w_t - w_p}{q_H} = \frac{792.0 - 2.0}{2605.7} = 30.3 \text{ percent}$$

We could also write an expression for thermal efficiency in terms of properties at various points in the cycle.

$$\eta_{th} = \frac{(h_3 - h_2) - (h_4 - h_1)}{h_3 - h_2} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2}$$
$$= \frac{2605.7 - 1815.7}{2605.7} = \frac{792.0 - 2.0}{2605.7} = 30.3 \text{ percent}$$

10.2 EFFECT OF PRESSURE AND TEMPERATURE ON THE RANKINE CYCLE

Let us first consider the effect of exhaust pressure and temperature on the Rankine cycle. This effect is shown on the T–s diagram of Fig. 10.2.

Let the exhaust pressure drop from P_4 to P_4', with the corresponding decrease in temperature at which heat is rejected. The net work is increased by area 1–4–4′–1′–2′–2–1 (shown by the cross-hatching). The heat transferred to the steam is increased by area a'–2′–2–a–a'. Since these two areas are approximately equal, the net result is an increase in cycle efficiency. This is also evident from the fact that the average temperature at which heat is rejected is decreased. Note, however, that lowering the back pressure causes the moisture content of the steam leaving the turbine to increase. This is a significant factor because if the moisture in the low-pressure stages of the turbine exceeds about 10 percent, not only is there a decrease in turbine efficiency, but erosion of the turbine blades may also be a very serious problem.

Next, consider the effect of superheating the steam in the boiler, as shown in Fig. 10.3. It is readily evident that the work is increased by area 3–3′–4′–4–3, and the heat transferred in the boiler is increased by area 3–3′–b'–b–3. Since the ratio of these two areas is greater than the ratio of net work to heat supplied for the rest of the cycle, it is evident that for given pressures, superheating the steam

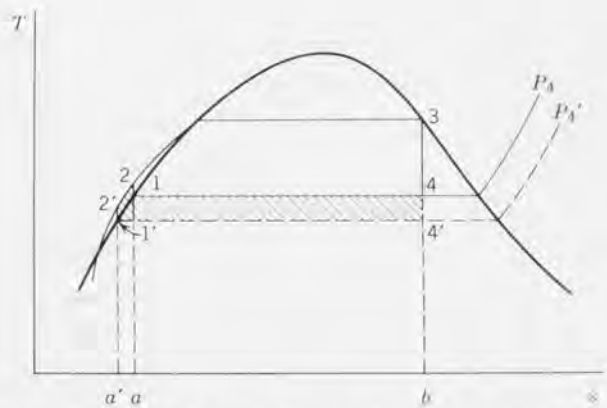


FIGURE 10.2 Effect of exhaust pressure on Rankine-cycle efficiency.

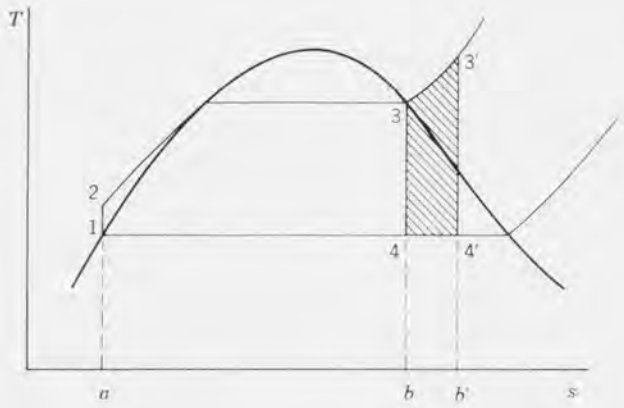


FIGURE 10.3 Effect of superheating on Rankine-cycle efficiency.

increases the Rankine-cycle efficiency. This increase in efficiency would also follow from the fact that the average temperature at which heat is transferred to the steam is increased. Note also that when the steam is superheated, the quality of the steam leaving the turbine increases.

Finally, the influence of the maximum pressure of the steam must be considered, and this is shown in Fig. 10.4. In this analysis the maximum temperature of the steam, as well as the exhaust pressure, is held constant. The heat rejected decreases by area b'–4'–4–b–b'. The net work increases by the amount of the single cross-hatching and decreases by the amount of the double cross-hatching. Therefore, the net work tends to remain the same, but the heat rejected decreases, and hence the Rankine-cycle efficiency increases with an increase in maximum pressure. Note that in this instance too the average temperature at which heat is supplied increases

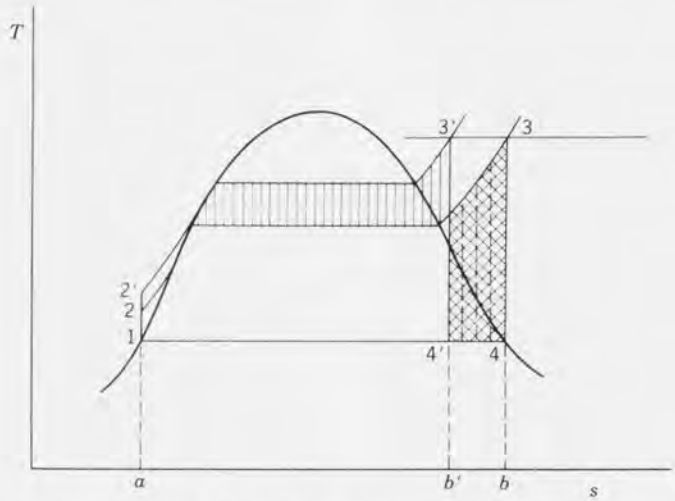


FIGURE 10.4 Effect of boiler pressure on Rankine-cycle efficiency.

with an increase in pressure. The quality of the steam leaving the turbine decreases as the maximum pressure increases.

To summarize this section, we can say that the efficiency of the Rankine cycle can be increased by lowering the exhaust pressure, by increasing the pressure during heat addition, and by superheating the steam. The quality of the steam leaving the turbine is increased by superheating the steam and decreased by lowering the exhaust pressure and by increasing the pressure during heat addition.

EXAMPLE 10.2

In a Rankine cycle steam leaves the boiler and enters the turbine at 4 MPa, 400°C. The condenser pressure is 10 kPa. Determine the cycle efficiency.

To determine the cycle efficiency, we must calculate the turbine work, the pump work, and the heat transfer to the steam in the boiler. We do this by considering a control surface around each of these components in turn. In each case the thermodynamic model is the steam tables, and the process is SSSF with negligible changes in kinetic and potential energies.

Control volume: Pump.

Inlet state: P_1 known, saturated liquid; state fixed.

Exit state: P_2 known.

Analysis:

First law: $w_p = h_2 - h_1$

Second law: $s_2 = s_1$

Since $s_2 = s_1$,

$$h_2 - h_1 = \int_1^2 v\, dP = v(P_2 - P_1)$$

Solution

$$w_p = v(P_2 - P_1) = (0.001\,01)(4000 - 10) = 4.0 \text{ kJ/kg}$$
$$h_1 = 191.8$$
$$h_2 = 191.8 + 4.0 = 195.8$$

Control volume: Turbine.

Inlet state: P_3, T_3 known; state fixed.

Exit state: P_4 known.

Analysis:

First law: $w_t = h_3 - h_4$

Second law: $s_4 = s_3$

Solution

$$h_3 = 3213.6, \qquad s_3 = 6.7690$$
$$s_3 = s_4 = 6.7690 = 0.6493 + x_4 7.5009, \qquad x_4 = 0.8159$$
$$h_4 = 191.8 + 0.8159(2392.8) = 2144.1$$

$$w_t = h_3 - h_4 = 3213.6 - 2144.1 = 1069.5 \text{ kJ/kg}$$
$$w_{net} = w_t - w_p = 1069.5 - 4.0 = 1065.5 \text{ kJ/kg}$$

Control volume: Boiler.
Inlet state: P_2, h_2 known; state fixed.
Exit state: State 3 fixed (as given).
Analysis:

First law: $$q_H = h_3 - h_2$$

Solution

$$q_H = h_3 - h_2 = 3213.6 - 195.8 = 3017.8 \text{ kJ/kg}$$
$$\eta_{th} = \frac{w_{net}}{q_H} = \frac{1065.5}{3017.8} = 35.3 \text{ percent}$$

The net work could also be determined by calculating the heat rejected in the condenser, q_L, and noting, from the first law, that the net work for the cycle is equal to the net transfer. Considering a control surface around the condenser, we have

$$q_L = h_4 - h_1 = 2144.1 - 191.8 = 1952.3 \text{ kJ/kg}$$

Therefore,

$$w_{net} = q_H - q_L = 3017.8 - 1952.3 = 1065.5 \text{ kJ/kg}$$

10.3 THE REHEAT CYCLE

In the last section we noted that the efficiency of the Rankine cycle could be increased by increasing the pressure during the addition of heat. However, the increase in pressure also increases the moisture content of the steam in the low-pressure end of the turbine. The reheat cycle has been developed to take advantage of the increased efficiency with higher pressures, and yet avoid excessive moisture in the low-pressure stages of the turbine. This cycle is shown schematically and on a T–s diagram in Fig. 10.5. The unique feature of this cycle is that the steam is expanded to some intermediate pressure in the turbine and is then reheated in the boiler, after which it expands in the turbine to the exhaust pressure. It is evident from the T–s diagram that there is very little gain in efficiency from reheating the steam, because the average temperature at which heat is supplied is not greatly changed. The chief advantage is in decreasing to a safe value the moisture content in the low-pressure stages of the turbine. If metals could be found that would enable us to superheat the steam to 3′, the simple Rankine cycle would be more efficient than the reheat cycle, and there would be no need for the reheat cycle.

EXAMPLE 10.3

Consider a reheat cycle utilizing steam. Steam leaves the boiler and enters the turbine at 4 MPa, 400°C. After expansion in the turbine to 400 kPa, the steam is

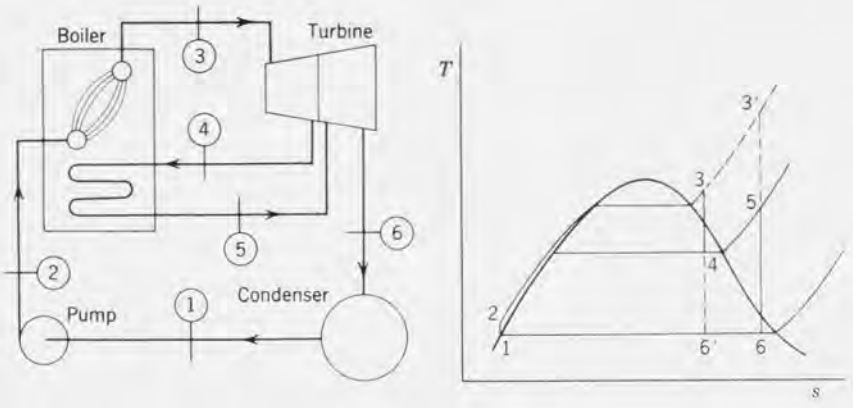


FIGURE 10.5 The ideal reheat cycle.

reheated to 400°C and then expanded in the low-pressure turbine to 10 kPa. Determine the cycle efficiency.

For each control volume analyzed, the thermodynamic model is the steam tables, the process is SSSF, and changes in kinetic and potential energies are negligible.

Control volume: High-pressure turbine.
Inlet state: P_3, T_3 known; state fixed.
Exit state: P_4 known.
Analysis:

First law: $$w_{h\text{-}p} = h_3 - h_4$$

Second law: $$s_3 = s_4$$

Solution

$$h_3 = 3213.6, \qquad s_3 = 6.7690$$
$$s_4 = s_3 = 6.7690 = 1.7766 + x_4 5.1193, \qquad x_4 = 0.9752$$
$$h_4 = 604.7 + 0.9752(2133.8) = 2685.6$$

Control volume: Low-pressure turbine.
Inlet state: P_5, T_5 known; state fixed.
Exit state: P_6 known.
Analysis:

First law: $$w_{l\text{-}p} = h_5 - h_6$$

Second law: $$s_5 = s_6$$

Solution

$$h_5 = 3273.4, \qquad s_5 = 7.8985$$
$$s_6 = s_5 = 7.8985 = 0.6493 + x_6 7.5009, \qquad x_6 = 0.9664$$
$$h_6 = 191.8 + 0.9664(2392.8) = 2504.3$$

For the overall turbine, the total work output w_t is the sum of $w_{h\text{-}p}$ and $w_{l\text{-}p}$, so that

$$\begin{aligned} w_t &= (h_3 - h_4) + (h_5 - h_6) \\ &= (3213.6 - 2685.6) + (3273.4 - 2504.3) \\ &= 1297.1 \text{ kJ/kg} \end{aligned}$$

Control volume: Pump.
Inlet state: P_1 known, saturated liquid; state fixed.
Exit state: P_2 known.
Analysis:

First law: $w_p = h_2 - h_1$

Second law: $s_2 = s_1$

Since $s_2 = s_1$,

$$h_2 - h_1 = \int_1^2 v\, dP = v(P_2 - P_1)$$

Solution

$$\begin{aligned} w_p &= v(P_2 - P_1) = (0.001\,01)(4000 - 10) = 4.0 \text{ kJ/kg} \\ h_2 &= 191.8 + 4.0 = 195.8 \end{aligned}$$

Control volume: Boiler.
Inlet state: States 3 and 5 both known (above).
Exit states: States 2 and 4 both known (as given).
Analysis:

First law: $q_H = (h_3 - h_2) + (h_5 - h_4)$

Solution

$$\begin{aligned} q_H &= (h_3 - h_2) + (h_5 - h_4) \\ &= (3213.6 - 195.8) + (3273.4 - 2685.6) = 3605.6 \text{ kJ/kg} \end{aligned}$$

Therefore,

$$w_{\text{net}} = w_t - w_p = 1297.1 - 4.0 = 1293.1 \text{ kJ/kg}$$

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_H} = \frac{1293.1}{3605.6} = 35.9 \text{ percent}$$

By comparing this example with Example 10.2, we find that through reheating the gain in efficiency is relatively small, but the moisture content of the vapor leaving the turbine is decreased from 18.4 to 3.4 percent.

10.4 THE REGENERATIVE CYCLE

Another important variation from the Rankine cycle is the regenerative cycle, which uses feedwater heaters. The basic concepts of this cycle can be demonstrated by

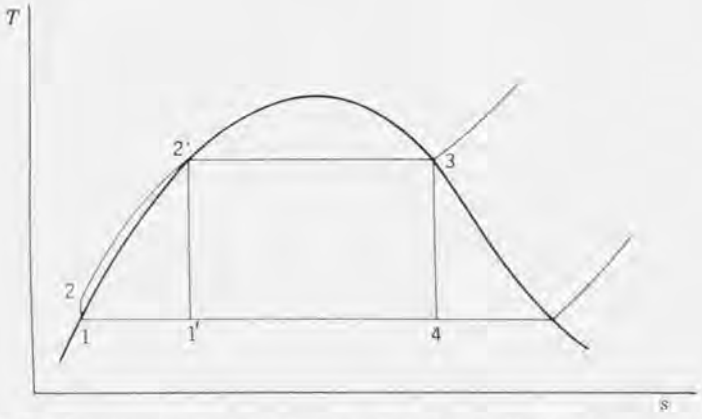


FIGURE 10.6 Temperature-entropy diagram showing the relationship between Carnot-cycle efficiency and Rankine-cycle efficiency.

considering the Rankine cycle without superheat as shown in Fig. 10.6. During the process between states 2 and 2′, the working fluid is heated while in the liquid phase, and the average temperature of the working fluid is much lower than during the vaporization process 2′–3. The process between states 2 and 2′ causes the average temperature at which heat is supplied in the Rankine cycle to be lower than in the Carnot cycle 1′–2′–3–4–1′. Consequently, the efficiency of the Rankine cycle is lower than that of the corresponding Carnot cycle. In the regenerative cycle the working fluid enters the boiler at some state between 2 and 2′, and consequently the average temperature at which heat is supplied is higher.

Consider first an idealized regenerative cycle, as shown in Fig. 10.7. The unique feature of this cycle compared to the Rankine cycle is that after leaving the pump, the liquid circulates around the turbine casing, counterflow to the direction of vapor flow in the turbine. Thus, it is possible to transfer to the liquid flowing around the turbine the heat from the vapor as it flows through the turbine. Let us assume for the moment that this is a reversible heat transfer; that is, at each point the temperature of the vapor is only infinitesimally higher than the temperature of the liquid. In this instance line 4–5 on the T–s diagram of Fig. 10.7, which represents the states of the vapor flowing through the turbine, is exactly parallel to line 1–2–3, which represents the pumping process (1–2) and the states of the liquid flowing around the turbine. Consequently, areas 2–3–b–a–2 and 5–4–d–c–5 are not only equal but congruous, and these areas, respectively, represent the heat transferred to the liquid and from the vapor. Heat is also transferred to the working fluid at constant temperature in process 3–4, and area 3–4–d–b–3 represents this heat transfer. Heat is transferred from the working fluid in process 5–1, and area 1–5–c–a–1 represents this heat transfer. This area is exactly equal to area 1′–5′–d–b–1′, which is the heat rejected in the related Carnot cycle 1′–3–4–5′–1′. Thus, the efficiency of this idealized regenerative cycle is exactly equal to the efficiency of the Carnot cycle with the same heat supply and heat rejection temperatures.

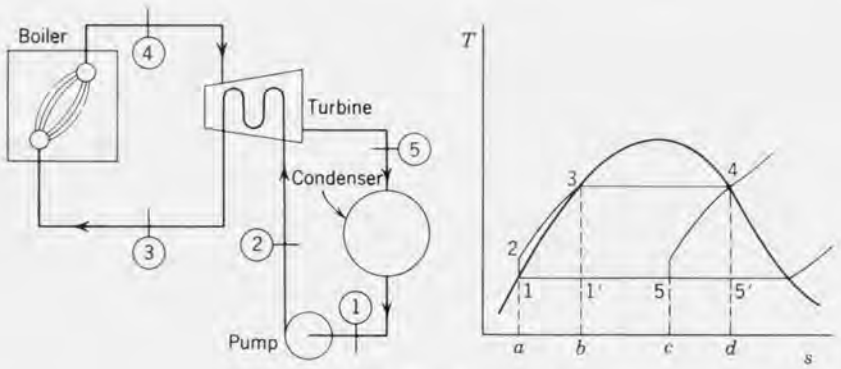


FIGURE 10.7 The ideal regenerative cycle.

Quite obviously this idealized regenerative cycle is impractical. First, it would be impossible to effect the necessary heat transfer from the vapor in the turbine to the liquid feedwater. Furthermore, the moisture content of the vapor leaving the turbine increases considerably as a result of the heat transfer. The disadvantage of this has been noted previously. The practical regenerative cycle extracts some of the vapor after it has partially expanded in the turbine and uses feedwater heaters, as shown in Fig. 10.8.

Steam enters the turbine at state 5. After expansion to state 6, some of the steam is extracted and enters the feedwater heater. The steam that is not extracted is expanded in the turbine to state 7 and is then condensed in the condenser. This condensate is pumped into the feedwater heater where it mixes with the steam extracted from the turbine. The proportion of steam extracted is just sufficient to cause the liquid leaving the feedwater heater to be saturated at state 3. Note that the liquid has not been pumped to the boiler pressure, but only to the intermediate pressure corresponding to state 6. Another pump is required to pump the liquid leaving the feedwater heater to boiler pressure. The significant point is that the average temperature at which heat is supplied has been increased.

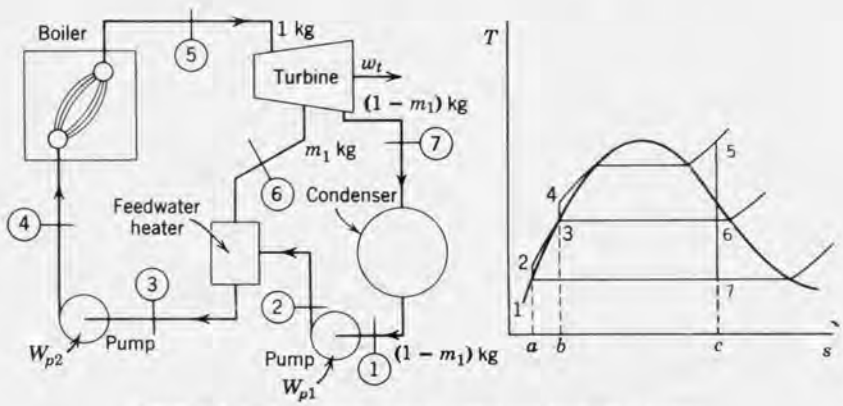


FIGURE 10.8 Regenerative cycle with open feedwater heater.

This cycle is somewhat difficult to show on a T–s diagram because the masses of steam flowing through the various components vary. The T–s diagram of Fig. 10.8 simply shows the state of the fluid at the various points.

Area 4–5–c–b–4 in Fig. 10.8 represents the heat transferred per kilogram of working fluid. Process 7–1 is the heat rejection process, but since not all the steam passes through the condenser, area 1–7–c–a–1 represents the heat transfer per kilogram flowing through the condenser, which does not represent the heat transfer per kilogram of working fluid entering the turbine. Between states 6 and 7 only part of the steam is flowing through the turbine. The example that follows illustrates the calculations for the regenerative cycle.

EXAMPLE 10.4

Consider a regenerative cycle using steam as the working fluid. Steam leaves the boiler and enters the turbine at 4 MPa, 400°C. After expansion to 400 kPa, some of the steam is extracted from the turbine for the purpose of heating the feedwater in an open feedwater heater. The pressure in the feedwater heater is 400 kPa and the water leaving it is saturated liquid at 400 kPa. The steam not extracted expands to 10 kPa. Determine the cycle efficiency.

The line diagram and T–s diagram for this cycle are shown in Fig. 10.8.

As in previous examples, the model for each control volume is the steam tables, the process is SSSF, and kinetic and potential energy changes are negligible.

From Examples 10.2 and 10.3 we have the following properties:

$$h_5 = 3213.6 \qquad h_6 = 2685.6$$
$$h_7 = 2144.1 \qquad h_1 = 191.8$$

Control volume: Low-pressure pump.

Inlet state: P_1 known, saturated liquid; state fixed.

Exit state: P_2 known.

Analysis:

First law: $$w_{p1} = h_2 - h_1$$

Second law: $$s_2 = s_1$$

Therefore,

$$h_2 - h_1 = \int_1^2 v\, dP = v(P_2 - P_1)$$

Solution

$$w_{p1} = v(P_2 - P_1) = (0.001\,01)(400 - 10) = 0.4 \text{ kJ/kg}$$
$$h_2 = h_1 + w_p = 191.8 + 0.4 = 192.2$$

Control volume: Turbine.

Inlet state: P_5, T_5 known; state fixed.

Exit state: P_6 known; P_7 known.

Analysis:

First law: $w_t = (h_5 - h_6) + (1 - m_1)(h_6 - h_7)$

Second law: $s_5 = s_6 = s_7$

Solution

From the second law, the values for h_6 and h_7 given previously were calculated in Examples 10.2 and 10.3.

Control volume: Feedwater heater.
Inlet states: States 2 and 6 both known (as given).
Exit state: P_3 known, saturated liquid; state fixed.
Analysis:

First law: $m_1(h_6) + (1 - m_1)h_2 = h_3$

Solution

$$m_1(2685.6) + (1 - m_1)(192.2) = 604.7$$
$$m_1 = 0.1654$$

We can now calculate the turbine work.

$$\begin{aligned} w_t &= (h_5 - h_6) + (1 - m_1)(h_6 - h_7) \\ &= (3213.6 - 2685.6) + (1 - 0.1654)(2685.6 - 2144.1) \\ &= 979.9 \text{ kJ/kg} \end{aligned}$$

Control volume: High-pressure pump.
Inlet state: State 3 known (as given).
Exit state: P_4 known.
Analysis:

First law: $w_{p2} = h_4 - h_3$

Second law: $s_4 = s_3$

Solution

$$w_{p2} = v(P_4 - P_3) = (0.001\,084)(4000 - 400) = 3.9 \text{ kJ/kg}$$
$$h_4 = h_3 + w_{p2} = 604.7 + 3.9 = 608.6$$

Therefore,

$$\begin{aligned} w_{\text{net}} &= w_t - (1 - m_1)w_{p1} - w_{p2} \\ &= 979.9 - (1 - 0.1654)(0.4) - 3.9 = 975.7 \text{ kJ/kg} \end{aligned}$$

Control volume: Boiler.
Inlet state: P_4, h_4 known (as given); state fixed.
Exit state: State 5 known (as given).

Analysis:

First law: $q_H = h_5 - h_4$

Solution

$$q_H = h_5 - h_4 = 3213.6 - 608.6 = 2605.0 \text{ kJ/kg}$$

$$\eta_{th} = \frac{w_{net}}{q_H} = \frac{975.7}{2605.0} = 37.5 \text{ percent}$$

Note the increase in efficiency over the efficiency of the Rankine cycle of Example 10.2.

Up to this point the discussion and examples have tacitly assumed that the extraction steam and feedwater are mixed in the feedwater heater. Another much-used type of feedwater heater, known as a closed heater, is one in which the steam and feedwater do not mix; rather heat is transferred from the extracted steam as it condenses on the outside of tubes while the feedwater flows through the tubes. In a closed heater, a schematic sketch of which is shown in Fig. 10.9, the steam and feedwater may be at considerably different pressures. The condensate may be pumped into the feedwater line, or it may be removed through a trap to a lower-pressure heater or to the condenser. (A trap is a device that permits liquid but not vapor to flow to a region of lower pressure.)

Open feedwater heaters have the advantage of being less expensive and having better heat-transfer characteristics compared to closed feedwater heaters. They have the disadvantage of requiring a pump to handle the feedwater between each heater.

In many power plants a number of stages of extraction are used, though only rarely more than five. The number is, of course, determined by economics. It is evident that using a very large number of extraction stages and feedwater heaters allows the cycle efficiency to approach that of the idealized regenerative cycle of Fig. 10.7, where the feedwater enters the boiler as saturated liquid at the maximum pressure. In practice, however, this could not be economically justified because the

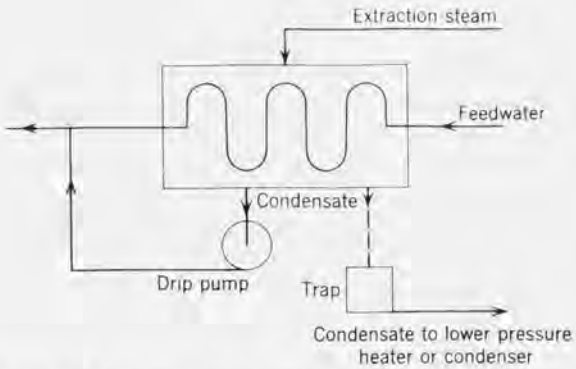


FIGURE 10.9 Schematic arrangement for a closed feedwater heater.

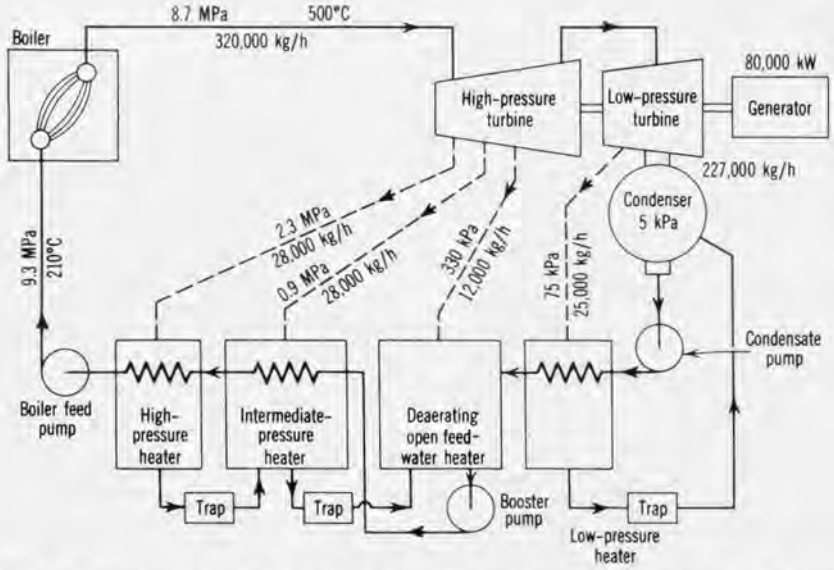


FIGURE 10.10 *Arrangement of heaters in an actual power plant utilizing regenerative feedwater heaters.*

savings effected by the increase in efficiency would be more than offset by the cost of additional equipment (feedwater heaters, piping, and so forth).

A typical arrangement of the main components in an actual power plant is shown in Fig. 10.10. Note that one open feedwater heater is a deaerating feedwater heater; this heater has the dual purpose of heating and removing the air from the feedwater. Unless the air is removed, excessive corrosion occurs in the boiler. Note also that the condensate from the high-pressure heater drains (through a trap) to the intermediate heater, and the intermediate heater drains to the deaerating feedwater heater. The low-pressure heater drains to the condenser.

Many actual power plants combine one reheat stage with a number of extraction stages. The principles already considered are readily applied to such a cycle.

10.5 DEVIATION OF ACTUAL CYCLES FROM IDEAL CYCLES

Before we leave the matter of vapor power cycles, a few comments are in order regarding the ways in which an actual cycle deviates from an ideal cycle. The losses associated with the combustion process are considered in a later chapter. The most important of these losses are the following.

PIPING LOSSES

Pressure drops caused by frictional effects and heat transfer to the surroundings are the most important piping losses. Consider, for example, the pipe connecting the turbine to the boiler. If only frictional effects occur, states *a* and *b* in Fig. 10.11

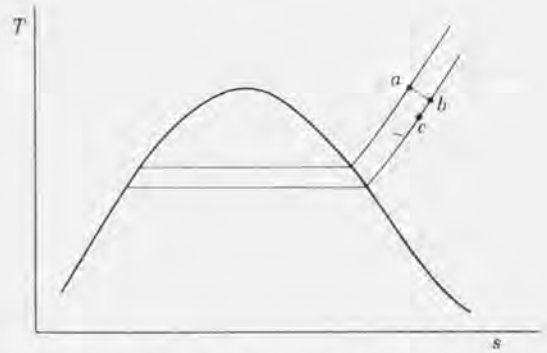


FIGURE 10.11 Temperature-entropy diagram showing effect of losses between boiler and turbine.

would represent the states of the steam leaving the boiler and entering the turbine, respectively. Note that the frictional effects cause an increase in entropy. Heat transferred to the surroundings at constant pressure can be represented by process *bc*. This effect decreases entropy. Both the pressure drop and heat transfer decrease the availability of the steam entering the turbine. The irreversibility of this process can be calculated by the methods outlined in Chapter 9.

A similar loss is the pressure drop in the boiler. Because of this pressure drop, the water entering the boiler must be pumped to a much higher pressure than the desired steam pressure leaving the boiler, and this requires additional pump work.

TURBINE LOSSES

The losses in the turbine are primarily those associated with the flow of the working fluid through the turbine. Heat transfer to the surroundings also represents a loss, but this is usually of secondary importance. The effects of these two losses are the same as those outlined for piping losses. The process might be represented as shown in Fig. 10.12, where 4_s represents the state after an isentropic expansion and state 4 represents the actual state leaving the turbine. The governing procedures may

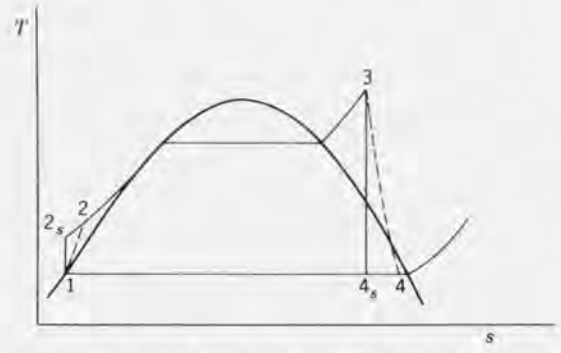


FIGURE 10.12 Temperature-entropy diagram showing effect of turbine and pump inefficiencies on cycle performance.

also cause a loss in the turbine, particularly if a throttling process is used to govern the turbine.

The efficiency of the turbine was defined in Chapter 9 as

$$\eta_t = \frac{w_t}{h_3 - h_{4s}}$$

where the states are as designated in Fig. 10.12.

PUMP LOSSES

The losses in the pump are similar to those of the turbine and are primarily due to the irreversibilities associated with the fluid flow. Heat transfer is usually a minor loss.

The pump efficiency is defined as

$$\eta_p = \frac{h_{2s} - h_1}{w_p}$$

where the states are as shown in Fig. 10.12, and w_p is the actual work input per kilogram of fluid.

CONDENSER LOSSES

The losses in the condenser are relatively small. One of these minor losses is the cooling below the saturation temperature of the liquid leaving the condenser. This represents a loss because additional heat transfer is necessary to bring the water to its saturation temperature.

The influence of these losses on the cycle is illustrated in the following example, which should be compared to Example 10.2.

EXAMPLE 10.5

A steam power plant operates on a cycle with pressures and temperatures as designated in Fig. 10.13. The efficiency of the turbine is 86 percent and the efficiency of the pump is 80 percent. Determine the thermal efficiency of this cycle.

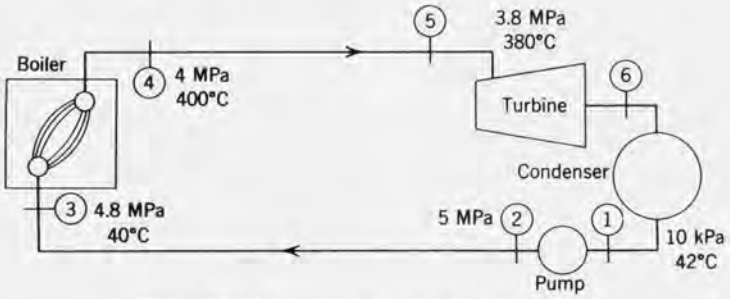


FIGURE 10.13 Schematic diagram for Example 10.5.

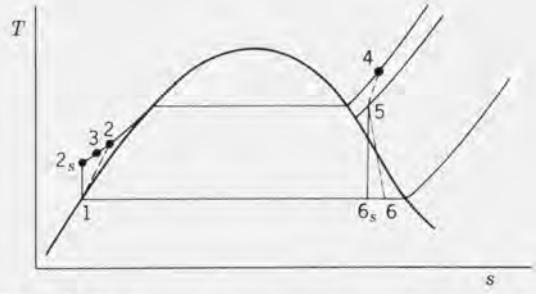


FIGURE 10.14 Temperature-entropy diagram for Example 10.5.

As in previous examples, for each control volume the model used is the steam tables, and each process is SSSF with no changes in kinetic or potential energy. This cycle is shown on the T–s diagram of Fig. 10.14.

Control volume: Turbine.
Inlet state: P_5, T_5 known; state fixed.
Exit state: P_6 known.
Analysis:

First law: $$w_t = h_5 - h_6$$

Second law: $$s_{6s} = s_5$$

$$\eta_t = \frac{w_t}{h_5 - h_{6s}} = \frac{h_5 - h_6}{h_5 - h_{6s}}$$

Solution

From the steam tables,

$$h_5 = 3169.1, \qquad s_5 = 6.7235$$

$$s_{6s} = s_5 = 6.7235 = 0.6493 + x_{6s}7.5009, \qquad x_{6s} = 0.8098$$

$$h_{6s} = 191.8 + 0.8098(2392.8) = 2129.5$$

$$w_t = \eta_t(h_5 - h_{6s}) = 0.86(3169.1 - 2129.5) = 894.1 \text{ kJ/kg}$$

Control volume: Pump.
Inlet state: P_1, T_1 known; state fixed.
Exit state: P_2 known.
Analysis:

First law: $$w_p = h_2 - h_1$$

Second law: $$s_{2s} = s_1$$

$$\eta_p = \frac{h_{2s} - h_1}{w_p} = \frac{h_{2s} - h_1}{h_2 - h_1}$$

Since $s_{2s} = s_1$,

$$h_{2s} - h_1 = v(P_2 - P_1)$$

Therefore,

$$w_p = \frac{h_{2s} - h_1}{\eta_p} = \frac{v(P_2 - P_1)}{\eta_p}$$

Solution

$$w_p = \frac{v(P_2 - P_1)}{\eta_p} = \frac{(0.001\,009)(5000 - 10)}{0.80} = 6.3 \text{ kJ/kg}$$

Therefore,

$$w_{\text{net}} = w_t - w_p = 894.1 - 6.3 = 887.8 \text{ kJ/kg}$$

Control volume: Boiler.
Inlet state: P_3, T_3 known; state fixed.
Exit state: P_4, T_4 known; state fixed.
Analysis:

First law: $$q_H = h_4 - h_3$$

Solution

$$q_H = h_4 - h_3 = 3213.6 - 171.8 = 3041.8 \text{ kJ/kg}$$

$$\eta_{\text{th}} = \frac{887.8}{3041.8} = 29.2 \text{ percent}$$

This result compares to the Rankine efficiency of 35.3 percent for the similar cycle of Example 10.2.

VAPOR REFRIGERATION CYCLES

10.6 VAPOR-COMPRESSION REFRIGERATION CYCLES

The ideal cycle for vapor-compression refrigeration is shown in Fig. 10.15 as cycle 1–2–3–4–1. Saturated vapor at low pressure enters the compressor and undergoes

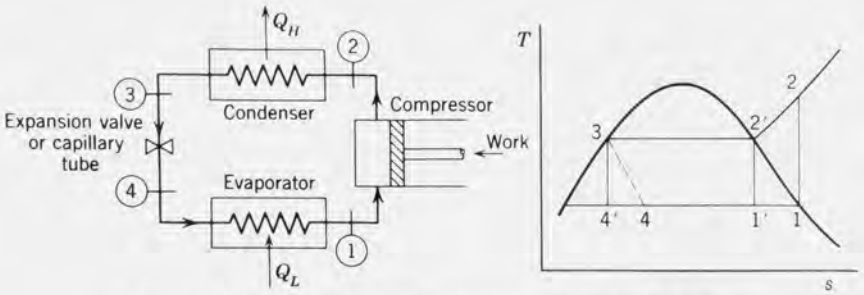


FIGURE 10.15 The ideal vapor-compression refrigeration cycle.

a reversible adiabatic compression, process 1–2. Heat is then rejected at constant pressure in process 2–3, and the working fluid leaves the condenser as saturated liquid. An adiabatic throttling process follows, process 3–4, and the working fluid is then evaporated at constant pressure, process 4–1, to complete the cycle.

The similarity between this cycle and the Rankine cycle is evident, for it is essentially the same cycle in reverse, except that an expansion valve replaces the pump. This throttling process is irreversible, whereas the pumping process of the Rankine cycle is reversible. The deviation of this ideal cycle from the Carnot cycle $1'$–$2'$–3–$4'$–$1'$ is evident from the T–s diagram. The reason for the deviation is that it is much more expedient to have a compressor handle only vapor than a mixture of liquid and vapor, as would be required in process $1'$–$2'$ of the Carnot cycle. It is virtually impossible to compress (at a reasonable rate) a mixture such as that represented by state $1'$ and still maintain equilibrium between the liquid and vapor. There must instead be a heat and mass transfer across the phase boundary. It is also much simpler to have the expansion process take place irreversibly through an expansion valve than to have an expansion device that receives saturated liquid and discharges a mixture of liquid and vapor, as would be required in process 3–$4'$. For these reasons the ideal cycle for vapor-compression refrigeration is as shown in Fig. 10.15 by cycle 1–2–3–4–1.

As we saw in Chapter 7, the performance of a refrigeration cycle is given in terms of the coefficient of performance, β, which is defined for a refrigeration cycle as

$$\beta = \frac{q_L}{w_c} \tag{10.2}$$

If the cycle is to be used as a heat pump, the desired energy quantity is q_H instead of q_L, and this quantity is used in the numerator of the expression for coefficient of performance. It is important to note whether any given coefficient of performance refers to the use of the machine as a refrigerator or as a heat pump.

EXAMPLE 10.6

Consider an ideal refrigeration cycle which uses R-12 as the working fluid. The temperature of the refrigerant in the evaporator is $-20°C$ and in the condenser it is 40°C. The refrigerant is circulated at the rate of 0.03 kg/s. Determine the coefficient of performance and the capacity of the plant in rate of refrigeration.

The diagram for this example is as shown in Fig. 10.15. For each control volume analyzed, the thermodynamic model is the R-12 tables. Each process is SSSF with no changes in kinetic or potential energy.

Control volume: Compressor.

Inlet state: T_1 known, saturated vapor; state fixed.

Exit state: P_2 known (saturation pressure at T_3).

Analysis:

First law: $w_c = h_2 - h_1$

Second law: $s_2 = s_1$

Solution

At $T_3 = 40°C$,

$$P_g = P_2 = 0.9607 \text{ MPa}$$

From the R-12 tables,

$$h_1 = 178.61, \qquad s_1 = 0.7082$$

Therefore,

$$s_2 = s_1 = 0.7082$$

so that

$$T_2 = 50.8°C \qquad \text{and} \qquad h_2 = 211.38$$
$$w_c = h_2 - h_1 = 211.38 - 178.61 = 32.77 \text{ kJ/kg}$$

Control volume: Expansion valve.
Inlet state: T_3 known, saturated liquid; state fixed.
Exit state: T_4 known.
Analysis:

First law: $$h_3 = h_4$$

Solution

$$h_4 = h_3 = 74.53$$

Control volume: Evaporator.
Inlet state: State 4 known (as given).
Exit state: State 1 known (as given).
Analysis:

First law: $$q_L = h_1 - h_4$$

Solution

$$q_L = h_1 - h_4 = 178.61 - 74.53 = 104.08 \text{ kJ/kg}$$

Therefore,

$$\beta = \frac{q_L}{w_c} = \frac{104.08}{32.77} = 3.18$$
$$\text{Capacity} = 104.08 \times 0.03 = 3.12 \text{ kW}$$

10.7 WORKING FLUIDS FOR VAPOR-COMPRESSION REFRIGERATION SYSTEMS

A much larger number of different working fluids (refrigerants) are utilized in vapor-compression refrigeration systems than in vapor power cycles. Ammonia and sulfur

dioxide were important in the early days of vapor-compression refrigeration, but both are highly toxic and therefore dangerous substances. For many years now, the principal refrigerants have been the halogenated hydrocarbons, which are marketed under the trade names of Freon and Genatron. For example, dichlorodifluoromethane (CCl_2F_2) is known as Freon-12 and Genatron-12, and therefore as refrigerant-12 or R-12. This group of substances, known commonly as chorofluorocarbons or CFCs, are chemically very stable at ambient temperature, especially those lacking any hydrogen atoms. This characteristic is necessary for a refrigerant working fluid. This same characteristic, however, has devastating consequences if the gas, having leaked from an appliance into the atmosphere, spends many years slowly diffusing upward into the stratosphere. There it is broken down, releasing chlorine, which destroys the protective ozone layer of the stratosphere. It is therefore of overwhelming importance to us all to eliminate completely the widely used but life-threatening CFCs, particularly R-11 and R-12, and to develop suitable and acceptable replacements. The CFCs containing hydrogen (often termed HCFCs), such as R-22, have shorter atmospheric lifetimes, and therefore are not as likely to reach the stratosphere before being broken up and rendered harmless. The most desirable fluids, called HFCs, contain no chlorine atoms at all.

There are two important considerations when selecting refrigerant working fluids: the temperature at which refrigeration is needed and the type of equipment to be used.

As the refrigerant undergoes a change of phase during the heat transfer process, the pressure of the refrigerant will be the saturation pressure during the heat supply and heat rejection processes. Low pressures mean large specific volumes and correspondingly large equipment. High pressures mean smaller equipment, but it must be designed to withstand higher pressure. In particular, the pressures should be well below the critical pressure. For extremely low temperature applications a binary fluid system may be used by cascading two separate systems.

The type of compressor used has a particular bearing on the refrigerant. Reciprocating compressors are best adapted to low specific volumes, which means higher pressures, whereas centrifugal compressors are most suitable for low pressures and high specific volumes.

It is also important that the refrigerants used in domestic applicances be nontoxic. Other beneficial characteristics, in addition to being environmentally acceptable, are miscibility with compressor oil, dielectric strength, stability, and low cost. Refrigerants, however, have an unfortunate tendency to cause corrosion. For given temperatures during evaporation and condensation, not all refrigerants have the same coefficient of performance for the ideal cycle. It is, of course, desirable to use the refrigerant with the highest coefficient of performance, other factors permitting.

10.8 DEVIATION OF THE ACTUAL VAPOR-COMPRESSION REFRIGERATION CYCLE FROM THE IDEAL CYCLE

The actual refrigeration cycle deviates from the ideal cycle primarily because of pressure drops associated with fluid flow and heat transfer to or from the surroundings. The actual cycle might approach the one shown in Fig. 10.16.

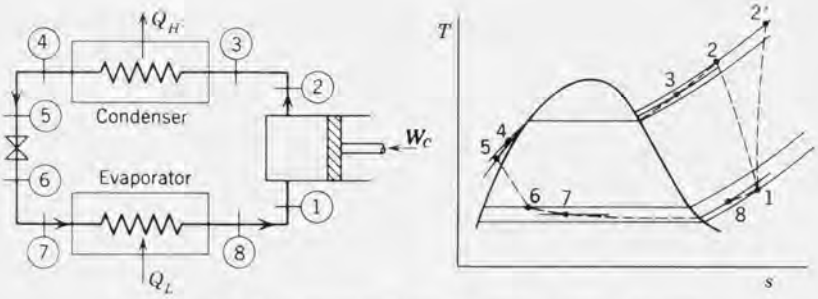


FIGURE 10.16 The actual vapor-compression refrigeration cycle.

The vapor entering the compressor will probably be superheated. During the compression process there are irreversibilities and heat transfer either to or from the surroundings, depending on the temperature of the refrigerant and the surroundings. Therefore, the entropy might increase or decrease during this process, for the irreversibility and the heat transferred to the refrigerant cause an increase in entropy, and the heat transferred from the refrigerant causes a decrease in entropy. These possibilities are represented by the two dashed lines 1–2 and 1–2′. The pressure of the liquid leaving the condenser will be less than the pressure of the vapor entering, and the temperature of the refrigerant in the condenser will be somewhat higher than that of the surroundings to which heat is being transferred. Usually the temperature of the liquid leaving the condenser is lower than the saturation temperature. It might drop somewhat more in the piping between the condenser and expansion valve. This represents a gain, however, because as a result of this heat transfer the refrigerant enters the evaporator with a lower enthalpy, which permits more heat to be transferred to the refrigerant in the evaporator.

There is some drop in pressure as the refrigerant flows through the evaporator. It may be slightly superheated as it leaves the evaporator, and through heat transferred from the surroundings its temperature will increase in the piping between the evaporator and the compressor. This heat transfer represents a loss, because it increases the work of the compressor, since the fluid entering it has an increased specific volume.

EXAMPLE 10.7

A refrigeration cycle utilizes R-12 as the working fluid. Following are the properties at various points of the cycle designated in Fig. 10.16.

$P_1 = 125$ kPa	$T_1 = -10°C$
$P_2 = 1.2$ MPa	$T_2 = 100°C$
$P_3 = 1.19$ MPa	$T_3 = 80°C$
$P_4 = 1.16$ MPa	$T_4 = 45°C$
$P_5 = 1.15$ MPa	$T_5 = 40°C$
$P_6 = P_7 = 140$ kPa	$x_6 = x_7$
$P_8 = 130$ kPa	$T_8 = -20°C$

The heat transfer from R-12 during the compression process is 4 kJ/kg. Determine the coefficient of performance of this cycle.

For each control volume, the model is the R-12 tables. Each process is SSSF with no changes in kinetic or potential energy.

Control volume: Compressor.
Inlet state: P_1, T_1 known; state fixed.
Exit state: P_2, T_2 known; state fixed.
Analysis:

First law: $$q + h_1 = h_2 + w$$
$$w_c = -w = h_2 - h_1 - q$$

Solution

From the R-12 tables,

$$h_1 = 185.16, \qquad h_2 = 245.52$$

Therefore,

$$w_c = 245.52 - 185.16 - (-4) = 64.36 \text{ kJ/kg}$$

Control volume: Throttling valve plus line.
Inlet state: P_5, T_5 known; state fixed.
Exit state: $P_7 = P_6$ known, $x_7 = x_6$.
Analysis:

First law: $$h_5 = h_6$$

Since $x_7 = x_6$, it follows that $h_7 = h_6$.

Solution

$$h_5 = h_6 = h_7 = 74.53$$

Control volume: Evaporator.
Inlet state: P_7, h_7 known (above).
Exit state: P_8, T_8 known; state fixed.
Analysis:

First law: $$q_L = h_8 - h_7$$

Solution

$$q_L = h_8 - h_7 = 179.12 - 74.53 = 104.59 \text{ kJ/kg}$$

Therefore,

$$\beta = \frac{q_L}{w_c} = \frac{104.59}{64.36} = 1.625$$

10.9 THE AMMONIA ABSORPTION REFRIGERATION CYCLE

The ammonia absorption refrigeration cycle differs from the vapor-compression cycle in the manner in which compression is achieved. In the absorption cycle the low-pressure ammonia vapor is absorbed in water and the liquid solution is pumped to a high pressure by a liquid pump. Figure 10.17 shows a schematic arrangement of the essential elements of such a system.

The low-pressure ammonia vapor leaving the evaporator enters the absorber where it is absorbed in the weak ammonia solution. This process takes place at a temperature slightly higher than that of the surroundings. Heat must be transferred to the surroundings during this process. The strong ammonia solution is then pumped through a heat exchanger to the generator where a higher pressure and temperature are maintained. Under these conditions ammonia vapor is driven from the solution as heat is transferred from a high-temperature source. The ammonia vapor goes to the condenser where it is condensed, as in a vapor-compression system, and then to the expansion valve and evaporator. The weak ammonia solution is returned to the absorber through the heat exchanger.

The distinctive feature of the absorption system is that very little work input is required because the pumping process involves a liquid. This follows from the fact that for a reversible steady-flow process with negligible changes in kinetic and potential energy, the work is equal to $-\int v\,dP$ and the specific volume of the liquid is much less than the specific volume of the vapor. On the other hand, a relatively high-temperature source of heat must be available (100° to 200°C). There is more equipment in an absorption system than in a vapor-compression system, and it can usually be economically justified only when a suitable source of heat is available

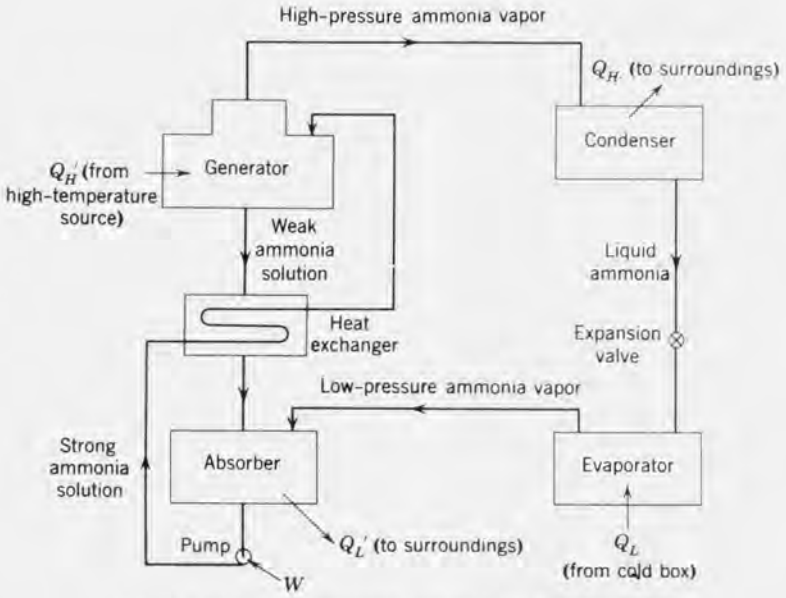


FIGURE 10.17 The ammonia-absorption refrigeration cycle

that would otherwise be wasted. In recent years, the absorption cycle has been given increased attention in connection with alternate energy sources, for example, solar energy or supplies of geothermal energy.

This cycle brings out the important principle that since the work in a reversible steady-flow process with negligible changes in kinetic and potential energy is $-\int v\,dP$, a compression process should take place with the smallest possible specific volume.

AIR-STANDARD POWER CYCLES

10.10 AIR-STANDARD CYCLES

Many work-producing devices (engines) utilize a working fluid that is always a gas. The spark-ignition automotive engine is a familiar example, and so are the Diesel engine and the conventional gas turbine. In all these engines there is a change in the composition of the working fluid, because during combustion it changes from air and fuel to combustion products. For this reason these engines are called internal-combustion engines. In contrast, the steam power plant may be called an external-combustion engine, because heat is transferred from the products of combustion to the working fluid. External-combustion engines using a gaseous working fluid (usually air) have been built. To date they have had very limited application, but the use of the gas-turbine cycle in conjunction with a nuclear reactor has been investigated extensively. Other external-combustion engines are currently receiving serious attention in an effort to combat air pollution.

Because the working fluid does not go through a complete thermodynamic cycle in the engine (even though the engine operates in a mechanical cycle) the internal-combustion engine operates on the so-called open cycle. However, for analyzing internal-combustion engines, it is advantageous to devise closed cycles that closely approximate the open cycles. One such approach is the air-standard cycle, which is based on the following assumptions.

1. A fixed mass of air is the working fluid throughout the entire cycle, and the air is always an ideal gas. Thus, there is no inlet process or exhaust process.
2. The combustion process is replaced by a process transferring heat from an external source.
3. The cycle is completed by heat transfer to the surroundings (in contrast to the exhaust and intake process of an actual engine).
4. All processes are internally reversible.
5. An additional assumption is usually made, that air has a constant specific heat.

The principal value of the air-standard cycle is to enable us to examine qualitatively the influence of a number of variables on performance. The results obtained from the air-standard cycle, such as efficiency and mean effective pressure, will differ a great deal from those of the actual engine. Our emphasis, therefore, in our consideration of the air-standard cycle, will be primarily on the qualitative aspects.

The term "mean effective pressure" (mep), which is used in conjunction with reciprocating engines, is defined as the pressure that, if it acted on the piston during the entire power stroke, would do an amount of work equal to that actually done on the piston. The work for one cycle is found by multiplying this mean effective pressure by the area of the piston (minus the area of the rod on the crank end of a double-acting engine) and by the stroke.

10.11 THE AIR-STANDARD CARNOT CYCLE

The air-standard Carnot cycle is shown on the P–v and T–s diagrams of Fig. 10.18. Such a cycle could be achieved in either a reciprocating or a steady-flow device, as shown in the same figure.

In Chapter 7 it was noted that the efficiency of a Carnot cycle depends only on the temperatures at which heat is supplied and rejected, and is given by the relation

$$\eta_{\text{th}} = 1 - \frac{T_L}{T_H} = 1 - \frac{T_4}{T_1} = 1 - \frac{T_3}{T_2}$$

where the subscripts refer to Fig. 10.18. The efficiency may also be expressed by the pressure ratio or compression ratio during the isentropic processes. This follows from the fact that

$$\text{Isentropic pressure ratio} = r_{\text{ps}} = \frac{P_1}{P_4} = \frac{P_2}{P_3} = \left(\frac{T_3}{T_2}\right)^{k/(1-k)}$$

$$\text{Isentropic compression ratio} = r_{\text{vs}} = \frac{V_4}{V_1} = \frac{V_3}{V_2} = \left(\frac{T_3}{T_2}\right)^{1/(1-k)}$$

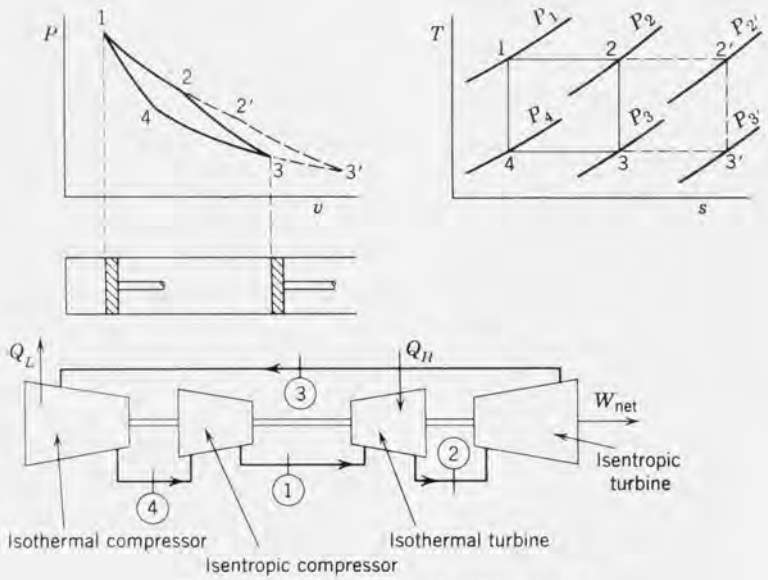


FIGURE 10.18 The air-standard Carnot cycle.

Therefore,

$$\eta_{th} = 1 - r_{ps}^{(1-k)/k} = 1 - r_{vs}^{1-k} \tag{10.3}$$

One other important variable in the air-standard Carnot cycle is the amount of heat transferred to the working fluid per cycle. It is evident from Fig. 10.18 that increasing the heat transfer per cycle at a given T_H causes a larger change in volume during the cycle, and this causes a lower mean effective pressure in a reciprocating engine. In fact, for air-standard Carnot cycles having a minimum pressure between 0.1 and 1 MPa and a reasonable heat transfer per cycle, the mean effective pressure is so low that it would scarcely overcome friction forces.

Another practical difficulty of the Carnot cycle, which applies to both the reciprocating and the steady-flow types of cycle, is the difficulty of transferring heat during the isothermal expansion and compression processes. It is virtually impossible even to approach this in an actual machine operating at a reasonable rate of speed. Thus, the air-standard Carnot cycle is impractical. Nonetheless, it is of value as a standard for comparison with other cycles. In a later section we will consider the ideal-gas turbine cycle with intercooling and reheating and note how its efficiency approaches that of the corresponding Carnot cycle.

EXAMPLE 10.8

In an air-standard Carnot cycle heat is transferred to the working fluid at 1200 K and heat is rejected at 300 K. The heat transferred to the working fluid at 1200 K is 100 kJ/kg. The minimum pressure in the cycle is 0.1 MPa. Assuming constant specific heat of air, determine the cycle efficiency and the mean effective pressure.

System: Carnot heat engine.

Diagram: Figure 10.18.

State information:

$$T_H = T_1 = T_2 = 1200 \text{ K}$$
$$T_L = T_3 = T_4 = 300 \text{ K}$$
$$P_3 = 0.1 \text{ MPa}$$

Process information: Four processes known (Fig. 10.18). Also,

$$q_H = {}_1q_2 = 100 \text{ kJ/kg}$$

Model: Ideal gas, constant specific heat, value at 300 K.

Analysis: For a Carnot cycle,

$$\eta_{th} = 1 - \frac{T_L}{T_H}$$

Second law and property relation for process 1–2:

$${}_1q_2 = T_1(s_2 - s_1) = RT_1 \ln \frac{V_2}{V_1} = RT_1 \ln \frac{P_1}{P_2}$$

Second law for process 2–3:

$$s_2 = s_3$$

so that

$$\frac{T_2}{T_3} = \left(\frac{P_2}{P_3}\right)^{(k-1)/k}$$

In addition,

$$\text{mep}(v_3 - v_1) = w_{\text{net}} = \eta_{\text{th}} \times {}_1q_2$$

Solution

$$\frac{T_2}{T_3} = \left(\frac{P_2}{P_3}\right)^{(k-1)/k} = 4$$

$$\frac{P_2}{P_3} = 128$$

$$P_2 = 0.1(128) = 12.8 \text{ MPa}$$

$${}_1q_2 = RT_1 \ln \frac{V_2}{V_1} = RT_1 \ln \frac{P_1}{P_2} = 0.287 \times 1200 \ln \frac{P_1}{P_2} = 100$$

Therefore,

$$\frac{P_1}{P_2} = 1.337, \qquad P_1 = 17.11 \text{ MPa}$$

$$\text{mep}(v_3 - v_1) = w_{\text{net}} = \eta_{\text{th}} \times {}_1q_2 = 0.75(100) = 75.0 \text{ kJ/kg}$$

$$v_3 = \frac{RT_3}{P_3} = \frac{0.287 \times 300}{100} = 0.861 \text{ m}^3/\text{kg}$$

$$v_1 = \frac{RT_1}{P_1} = \frac{0.287 \times 1200}{17\,110} = 0.0201 \text{ m}^3/\text{kg}$$

$$\text{mep} = \frac{75.0}{0.861 - 0.0201} = 89.2 \text{ kPa}$$

This is a much lower mean effective pressure than can be effectively utilized in a reciprocating engine.

10.12 THE AIR-STANDARD OTTO CYCLE

The air-standard Otto cycle is an ideal cycle that approximates a spark-ignition internal-combustion engine. This cycle is shown on the P–v and T–s diagrams of Fig. 10.19. Process 1–2 is an isentropic compression of the air as the piston moves from crank-end dead center to head-end dead center. Heat is then added at constant volume while the piston is momentarily at rest at head-end dead center. (This process corresponds to the ignition of the fuel–air mixture by the spark and the subsequent burning in the actual engine.) Process 3–4 is an isentropic expansion,

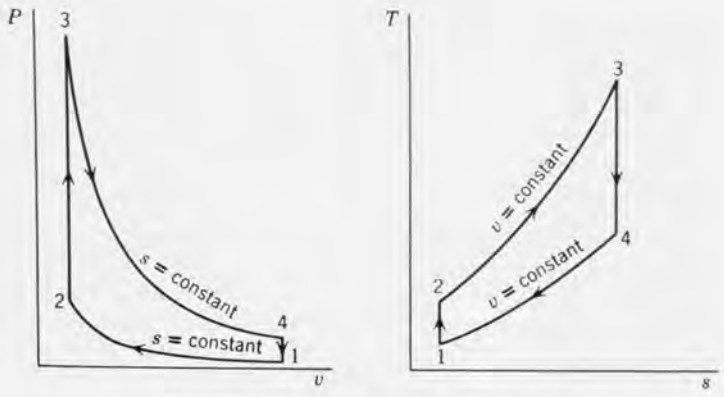


FIGURE 10.19 The air-standard Otto cycle.

and process 4–1 is the rejection of heat from the air while the piston is at crank-end dead center.

The thermal efficiency of this cycle is found as follows, assuming constant specific heat of air.

$$\eta_{\text{th}} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{mC_v(T_4 - T_1)}{mC_v(T_3 - T_2)}$$
$$= 1 - \frac{T_1}{T_2}\frac{(T_4/T_1 - 1)}{(T_3/T_2 - 1)}$$

We note further that

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1} = \left(\frac{V_4}{V_3}\right)^{k-1} = \frac{T_3}{T_4}$$

Therefore,

$$\frac{T_3}{T_2} = \frac{T_4}{T_1}$$

and

$$\eta_{\text{th}} = 1 - \frac{T_1}{T_2} = 1 - (r_v)^{1-k} = 1 - \frac{1}{r_v^{k-1}} \tag{10.4}$$

where

$$r_v = \text{compression ratio} = \frac{V_1}{V_2} = \frac{V_4}{V_3}$$

The important thing to note is that the efficiency of the air-standard Otto cycle is a function only of the compression ratio, and that the efficiency is increased by increasing the compression ratio. Figure 10.20 is a plot of the air-standard cycle thermal efficiency versus compression ratio. It is also true of an actual spark-ignition engine that the efficiency can be increased by increasing the compression ratio. The trend toward higher compression ratios is prompted by the effort to

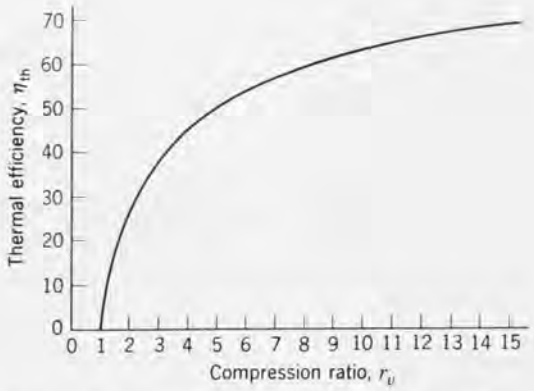


FIGURE 10.20 *Thermal efficiency of the Otto cycle as a function of compression ratio.*

obtain higher thermal efficiency. In the actual engine there is an increased tendency for the fuel to detonate as the compression ratio is increased. After detonation the fuel burns rapidly, and strong pressure waves present in the engine cylinder give rise to the so-called spark knock. Therefore, the maximum compression ratio that can be used is fixed by the fact that detonation must be avoided. The advance in compression ratios over the years in the actual engine was originally made possible by developing fuels with better antiknock characteristics, primarily through the addition of tetraethyl lead. More recently, however, nonleaded gasolines with good antiknock characteristics have been developed in an effort to reduce atmospheric contamination.

Some of the most important ways in which the actual open-cycle spark-ignition engine deviates from the air-standard cycle are as follows.

1. The specific heats of the actual gases increase with an increase in temperature.
2. The combustion process replaces the heat-transfer process at high temperature, and combustion may be incomplete.
3. Each mechanical cycle of the engine involves an inlet and an exhaust process and, because of the pressure drop through the valves, a certain amount of work is required to charge the cylinder with air and exhaust the products of combustion.
4. There will be considerable heat transfer between the gases in the cylinder and the cylinder walls.
5. There will be irreversibilities associated with pressure and temperature gradients.

EXAMPLE 10.9

The compression ratio in an air-standard Otto cycle is 8. At the beginning of the compression stroke the pressure is 0.1 MPa and the temperature is 15°C. The heat transfer to the air per cycle is 1800 kJ/kg air. Determine

1. The pressure and temperature at the end of each process of the cycle.

2. The thermal efficiency.
3. The mean effective pressure.

System: Air inside cylinder.

Diagram: Figure 10.19.

State information: $P_1 = 0.1$ MPa, $T_1 = 288.2$ K.

Process information: Four processes known (Fig. 10.19). Also $r_v = 8$ and $q_H = 1800$ kJ/kg.

Model: Ideal gas, constant specific heat, value at 300 K.

Analysis:

Second law for compression process 1–2:

$$s_2 = s_1$$

so that

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{k}$$

First law for heat addition process 2–3:

$$q_H = {}_2q_3 = u_3 - u_2 = C_v(T_3 - T_2)$$

Second law for expansion process 3–4:

$$s_4 = s_3$$

so that

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{k-1}$$

$$\frac{P_3}{P_4} = \left(\frac{V_4}{V_3}\right)^{k}$$

In addition,

$$\eta_{\text{th}} = 1 - \frac{1}{r_v^{k-1}}, \qquad \text{mep} = \frac{w_{\text{net}}}{v_1 - v_2}$$

Solution

$$v_1 = \frac{0.287 \times 288.2}{100} = 0.827 \text{ m}^3/\text{kg}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1} = 8^{0.4} = 2.3, \qquad T_2 = 662 \text{ K}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{k} = 8^{1.4} = 18.38, \qquad P_2 = 1.838 \text{ MPa}$$

$$v_2 = \frac{0.827}{8} = 0.1034 \text{ m}^3/\text{kg}$$

$${}_2q_3 = C_v(T_3 - T_2) = 1800 \text{ kJ/kg}$$

$$T_3 - T_2 = \frac{1800}{0.7165} = 2512, \qquad T_3 = 3174 \text{ K}$$

$$\frac{T_3}{T_2} = \frac{P_3}{P_2} = \frac{3174}{662} = 4.795, \qquad P_3 = 8.813 \text{ MPa}$$

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{k-1} = 8^{0.4} = 2.3, \qquad T_4 = 1380 \text{ K}$$

$$\frac{P_3}{P_4} = \left(\frac{V_4}{V_3}\right)^{k} = 8^{1.4} = 18.38, \qquad P_4 = 0.4795 \text{ MPa}$$

$$\eta_{th} = 1 - \frac{1}{r_v^{k-1}} = 1 - \frac{1}{8^{0.4}} = 1 - \frac{1}{2.3} = 1 - 0.435 = 0.565 = 56.5 \text{ percent}$$

This can be checked by finding the heat rejected.

$$_4q_1 = C_v(T_1 - T_4) = 0.7165(288.2 - 1380) = -782.3 \text{ kJ/kg}$$

$$\eta_{th} = 1 - \frac{782.3}{1800} = 1 - 0.435 = 0.565 = 56.5 \text{ percent}$$

$$w_{net} = 1800 - 782.3 = 1017.7 \text{ kJ/kg} = (v_1 - v_2)\,\text{mep}$$

$$\text{mep} = \frac{1017.7}{(0.827 - 0.1034)} = 1406 \text{ kPa}$$

Note how much higher this mean effective pressure is than that for the Carnot cycle of Example 10.8. A low mean effective pressure means a large piston displacement for a given power output, and a large piston displacement means high frictional losses in an actual engine. In fact, the mean effective pressure of the Carnot cycle of Example 10.8 would scarcely overcome the friction in an actual engine.

10.13 THE AIR-STANDARD DIESEL CYCLE

The air-standard Diesel cycle is shown in Fig. 10.21. This is the ideal cycle for the Diesel engine, which is also called the compression-ignition engine.

In this cycle the heat is transferred to the working fluid at constant pressure. This process corresponds to the injection and burning of the fuel in the actual engine. Since the gas is expanding during the heat addition in the air-standard cycle, the heat transfer must be just sufficient to maintain constant pressure. When state 3 is reached the heat addition ceases and the gas undergoes an isentropic expansion, process 3–4, until the piston reaches crank-end dead center. As in the air-standard Otto cycle, a constant-volume rejection of heat at crank-end dead center replaces the exhaust and intake processes of the actual engine.

The efficiency of the Diesel cycle is given by the relation

$$\eta_{th} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{C_v(T_4 - T_1)}{C_p(T_3 - T_2)} = 1 - \frac{T_1(T_4/T_1 - 1)}{kT_2(T_3/T_2 - 1)} \tag{10.5}$$

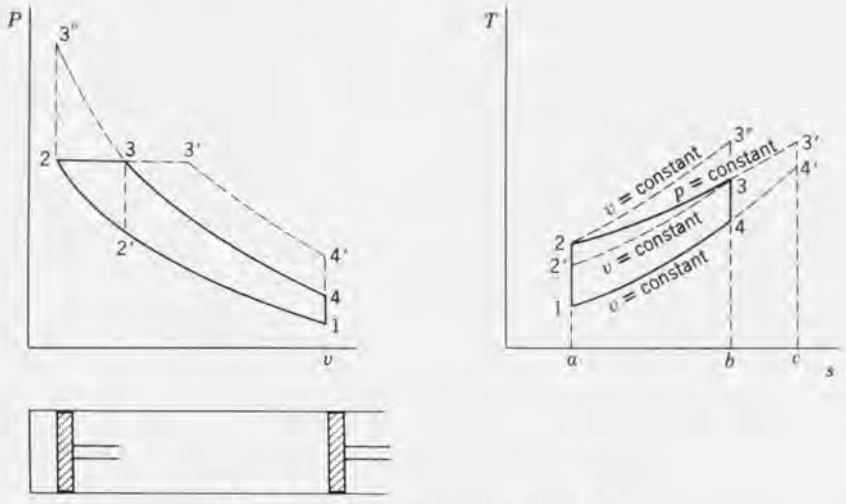


FIGURE 10.21 The air-standard Diesel cycle.

It is important to note that the isentropic compression ratio is greater than the isentropic expansion ratio in the Diesel cycle. In addition, for a given state before compression and a given compression ratio (that is, given states 1 and 2), the cycle efficiency decreases as the maximum temperature increases. This is evident from the T–s diagram, because the constant-pressure and constant-volume lines converge, and increasing the temperature from 3 to 3′ requires a large addition of heat (area 3–3′–c–b–3) and results in a relatively small increase in work (area 3–3′–4′–4–3).

There are a number of comparisons between the Otto cycle and the Diesel cycle, but here we will note only two. Consider Otto cycle 1–2–3″–4–1 and Diesel cycle 1–2–3–4–1, which have the same state at the beginning of the compression stroke and the same piston displacement and compression ratio. It is evident from the T–s diagram that the Otto cycle has the higher efficiency. In practice, however, the Diesel engine can operate on a higher compression ratio than the spark-ignition engine. The reason is that in the spark-ignition engine an air–fuel mixture is compressed, and detonation (spark knock) becomes a serious problem if too high a compression ratio is used. This problem does not exist in the Diesel engine because only air is compressed during the compression stroke.

Therefore, we might compare an Otto cycle with a Diesel cycle and in each case select a compression ratio that might be achieved in practice. Such a comparison can be made by considering Otto cycle 1–2′–3–4–1 and Diesel cycle 1–2–3–4–1. The maximum pressure and temperature is the same for both cycles, which means that the Otto cycle has a lower compression ratio than the Diesel cycle. It is evident from the T–s diagram that in this case the Diesel cycle has the higher efficiency. Thus, the conclusions drawn from a comparison of these two cycles must always be related to the basis on which the comparison has been made.

The actual compression-ignition open cycle differs from the air-standard Diesel cycle in much the same way that the spark-ignition open cycle differs from the air-standard Otto cycle.

EXAMPLE 10.10

An air-standard Diesel cycle has a compression ratio of 18, and the heat transferred to the working fluid per cycle is 1800 kJ/kg. At the beginning of the compression process the pressure is 0.1 MPa and the temperature is 15°C. Determine

1. The pressure and temperature at each point in the cycle.
2. The thermal efficiency.
3. The mean effective pressure.

System: Air inside cylinder.

Diagram: Figure 10.21.

State information: $P_1 = 0.1$ MPa, $T_1 = 288.2$ K.

Process information: Four processes known (Fig. 10.21). Also $r_v = 18$ and $q_H = 1800$ kJ/kg.

Model: Ideal gas, constant specific heat, value at 300 K.

Analysis:

Second law for compression process 1–2:

$$s_2 = s_1$$

so that

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{k}$$

First law for heat addition process 2–3:

$$q_H = {}_2q_3 = C_p(T_3 - T_2)$$

Second law for expansion process 3–4:

$$s_4 = s_3$$

so that

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{k-1}$$

In addition,

$$\eta_{th} = \frac{w_{net}}{q_H}, \qquad \text{mep} = \frac{w_{net}}{v_1 - v_2}$$

Solution

$$v_1 = \frac{0.287 \times 288.2}{100} = 0.827 \text{ m}^3/\text{kg}$$

$$v_2 = \frac{v_1}{18} = \frac{0.827}{18} = 0.045\,95 \text{ m}^3/\text{kg}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1} = 18^{0.4} = 3.1777, \qquad T_2 = 915.8 \text{ K}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^k = 18^{1.4} = 57.2, \qquad P_2 = 5.72 \text{ MPa}$$

$$q_H = {}_2q_3 = C_p(T_3 - T_2) = 1800 \text{ kJ/kg}$$

$$T_3 - T_2 = \frac{1800}{1.0035} = 1794, \qquad T_3 = 2710 \text{ K}$$

$$\frac{V_3}{V_2} = \frac{T_3}{T_2} = \frac{2710}{915.8} = 2.959, \qquad v_3 = 0.135\,98 \text{ m}^3/\text{kg}$$

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{k-1} = \left(\frac{0.827}{0.135\,98}\right)^{0.4} = 2.0588, \qquad T_4 = 1316 \text{ K}$$

$$q_L = {}_4q_1 = C_v(T_1 - T_4) = 0.7165(288.2 - 1316) = -736.6 \text{ kJ/kg}$$

$$w_{\text{net}} = 1800 - 736.6 = 1063.4 \text{ kJ/kg}$$

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_H} = \frac{1063.4}{1800} = 59.1 \text{ percent}$$

$$\text{mep} = \frac{w_{\text{net}}}{v_1 - v_2} = \frac{1063.4}{0.827 - 0.045\,95} = 1362 \text{ kPa}$$

10.14 THE ERICSSON AND STIRLING CYCLES

We briefly consider the Ericsson and Stirling cycles, not so much because they are extensively used, but rather because they serve to demonstrate how a regenerator can often be incorporated in a cycle to give a significant increase in efficiency. This principle finds extensive application in turbines as well as in certain reciprocating devices. The Stirling cycle is shown on the P–v and T–s diagrams of Fig. 10.22. Heat is transferred to the working fluid during the constant-volume process 2–3 and during the isothermal expansion process 3–4. Heat is rejected during the constant-volume process 4–1 and also during the isothermal compression process 1–2. The significance of this cycle in conjunction with a regenerator is discussed shortly.

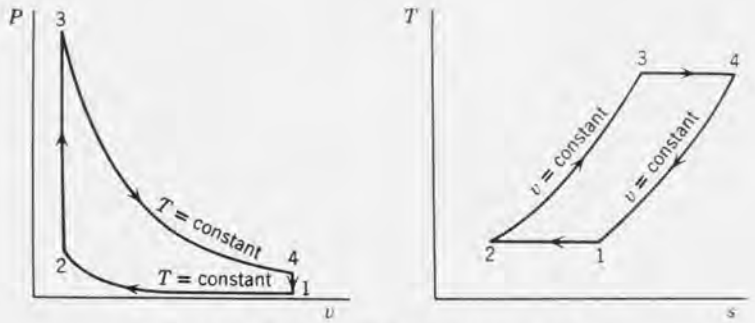


FIGURE 10.22 The air-standard Stirling cycle.

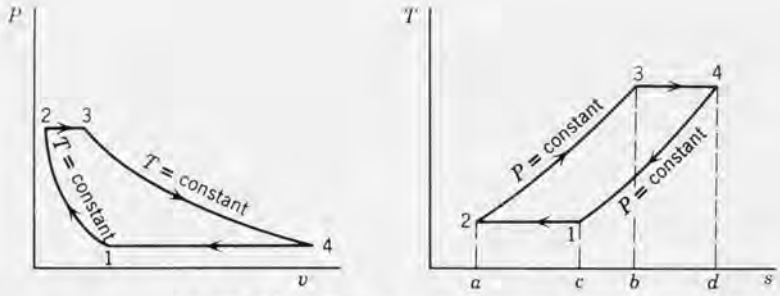


FIGURE 10.23 The air-standard Ericsson cycle.

The Ericsson cycle is shown on the P–v and T–s diagrams of Fig. 10.23. This cycle differs from the Stirling cycle in that the constant-volume processes of the Stirling cycle are replaced by constant-pressure processes. In both cycles there is an isothermal compression and expansion.

The importance of both cycles lies in the possibility of their including a regenerator; by so doing the air-standard Stirling and Ericsson cycles may have an efficiency equal to that of a Carnot cycle operating between the same temperatures. This inclusion of a regenerator may be demonstrated by considering Fig. 10.24, in which the Ericsson cycle is accomplished in a device that is essentially a gas turbine. If we assume an ideal heat-transfer process in the regenerator, that is, no pressure drop and an infinitesimal temperature difference between the two streams, and the reversible compression and expansion processes, then this device operates on the Ericsson cycle.

Note that the heat transfer to the gas between states 2 and 3, area 2–3–b–a–2, is exactly equal to the heat transfer from the gas between states 4 and 1, area 1–4–d–c–1. Thus, all Q_H takes place in the isothermal turbine between states 3 and 4, and Q_L takes place in the isothermal compressor between states 1 and 2. Since all the heat is supplied and rejected isothermally, the efficiency of this cycle equals the efficiency of a Carnot cycle operating between the same temperatures. A similar cycle could be developed that would approximate the Stirling cycle.

The difficulties in achieving such a cycle are primarily those associated with heat transfer. It is difficult to achieve an isothermal compression or expansion in a machine operating at a reasonable speed, and there will be pressure drops in the

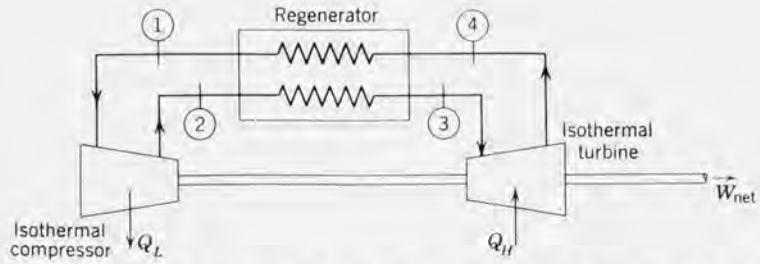


FIGURE 10.24 Schematic arrangement of an engine operating on the Ericsson cycle and utilizing a regenerator.

regenerator and a temperature difference between the two streams flowing through the regenerator. However, the gas turbine with intercooling and regenerators, which is described in Section 10.17, is a practical way of approaching the Ericsson cycle. There have also been attempts to approach the Stirling cycle by using regenerators.

10.15 THE BRAYTON CYCLE

The air-standard Brayton cycle is the ideal cycle for the simple gas turbine. The simple open-cycle gas turbine utilizing an internal-combustion process and the simple closed-cycle gas turbine, which utilizes heat-transfer processes, are both shown schematically in Fig. 10.25. The air-standard Brayton cycle is shown on the P–v and T–s diagrams of Fig. 10.26.

The efficiency of the air-standard Brayton cycle is found as follows:

$$\eta_{th} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{C_p(T_4 - T_1)}{C_p(T_3 - T_2)} = 1 - \frac{T_1(T_4/T_1 - 1)}{T_2(T_3/T_2 - 1)}$$

We note, however, that

$$\frac{P_3}{P_4} = \frac{P_2}{P_1}$$

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{k/(k-1)} = \frac{P_3}{P_4} = \left(\frac{T_3}{T_4}\right)^{k/(k-1)}$$

$$\frac{T_3}{T_4} = \frac{T_2}{T_1} \qquad \therefore \frac{T_3}{T_2} = \frac{T_4}{T_1} \qquad \text{and} \qquad \frac{T_3}{T_2} - 1 = \frac{T_4}{T_1} - 1$$

$$\eta_{th} = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{(P_2/P_1)^{(k-1)/k}} \tag{10.6}$$

The efficiency of the air-standard Brayton cycle is therefore a function of the isentropic pressure ratio; Figure 10.27 shows a plot of efficiency versus pressure ratio. The fact that efficiency increases with pressure ratio is evident from the T–s diagram of Fig. 10.26, because increasing the pressure ratio changes the cycle

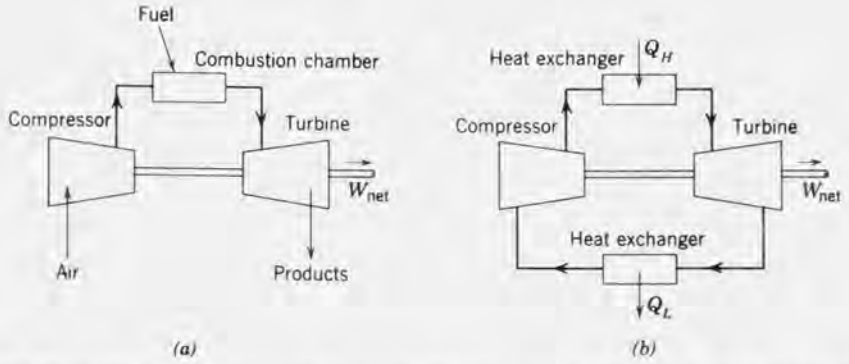


FIGURE 10.25 A gas turbine operating on the Brayton cycle. (*a*) Open cycle. (*b*) Closed cycle.

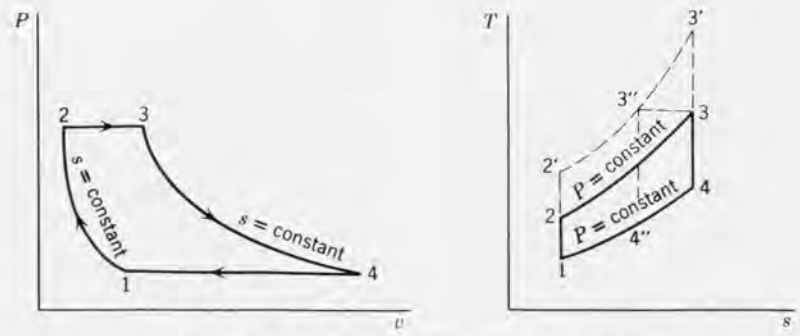


FIGURE 10.26 The air-standard Brayton cycle.

from 1–2–3–4–1 to 1–2′–3′–4–1. The latter cycle has a greater heat supply and the same heat rejected as the original cycle; therefore, it has a greater efficiency. Note that the latter cycle has a higher maximum temperature, T'_3, than the original cycle, T_3. In the actual gas turbine the maximum temperature of the gas entering the turbine is fixed by metallurgical considerations. Therefore, if we fix the temperature T_3 and increase the pressure ratio, the resulting cycle is 1–2′–3″–4″–1. This cycle would have a higher efficiency than the original cycle, but the work per kilogram of working fluid is thereby changed.

With the advent of nuclear reactors, the closed-cycle gas turbine has become more important. Heat is transferred, either directly or via a second fluid, from the fuel in the nuclear reactor to the working fluid in the gas turbine. Heat is rejected from the working fluid to the surroundings.

The actual gas-turbine engine differs from the ideal cycle primarily because of irreversibilities in the compressor and turbine, and because of pressure drop in the flow passages and combustion chamber (or in the heat exchanger of a closed-cycle turbine). Thus, the state points in a simple open-cycle gas turbine might be as shown in Fig. 10.28.

The efficiencies of the compressor and turbine are defined in relation to isentropic processes. With the states designated as in Fig. 10.28, the definitions of compressor

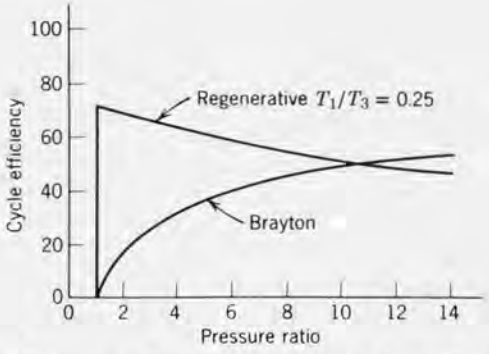


FIGURE 10.27 Cycle efficiency as a function of pressure ratio for the Brayton and regenerative cycles.

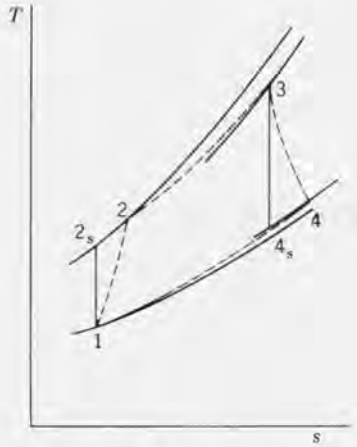


FIGURE 10.28 Effect of inefficencies on the gas-turbine cycle.

and turbine efficiencies are

$$\eta_{\text{comp}} = \frac{h_{2s} - h_1}{h_2 - h_1} \tag{10.7}$$

$$\eta_{\text{turb}} = \frac{h_3 - h_4}{h_3 - h_{4s}} \tag{10.8}$$

Another important feature of the Brayton cycle is the large amount of compressor work (also called back work) compared to turbine work. Thus, the compressor might require from 40 to 80 percent of the output of the turbine. This is particularly important when the actual cycle is considered, because the effect of the losses is to require a larger amount of compression work from a smaller amount of turbine work, and thus, the overall efficiency drops very rapidly with a decrease in the efficiencies of the compressor and turbine. In fact, if these efficiencies drop below about 60 percent, all the work of the turbine will be required to drive the compressor, and the overall efficiency will be zero. This is in sharp contrast to the Rankine cycle, where only 1 or 2 percent of the turbine work is required to drive the pump. The reason for this is that for a reversible steady-state, steady-flow process with negligible change in kinetic and potential energy, the work is equal to $-\int v\,dP$. Because we are pumping a liquid in the Rankine cycle, the specific volume is very low compared to the specific volume of the gas in a gas turbine. This matter is illustrated in the following examples.

EXAMPLE 10.11

In an air-standard Brayton cycle the air enters the compressor at 0.1 MPa, 15°C. The pressure leaving the compressor is 1.0 MPa, and the maximum temperature in the cycle is 1100°C. Determine

1. The pressure and temperature at each point in the cycle.
2. The compressor work, turbine work, and cycle efficiency.

For each of the control volumes analyzed, the model is ideal gas with constant specific heat, value at 300 K, and each process is SSSF with no kinetic or potential energy changes. The diagram for this example is Fig. 10.26.

Control volume: Compressor.
Inlet state: P_1, T_1 known; state fixed.
Exit state: P_2 known.
Analysis:

First law: $w_c = h_2 - h_1$ (Note that the compressor work w_c is here defined as work input to the compressor.)

Second law: $s_2 = s_1$

so that $$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}$$

Solution

$$\left(\frac{P_2}{P_1}\right)^{(k-1)/k} = 10^{0.286} = 1.932, \qquad T_2 = 556.8 \text{ K}$$

$$w_c = h_2 - h_1 = C_p(T_2 - T_1)$$
$$= 1.0035(556.8 - 288.2) = 269.5 \text{ kJ/kg}$$

Control volume: Turbine.
Inlet state: P_3 $(=P_2)$ known, T_3 known; state fixed.
Exit state: P_4 $(=P_1)$ known.
Analysis:

First law: $w_t = h_3 - h_4$

Second law: $s_3 = s_4$

so that $$\frac{T_3}{T_4} = \left(\frac{P_3}{P_4}\right)^{(k-1)/k}$$

Solution

$$\left(\frac{P_3}{P_4}\right)^{(k-1)/k} = 10^{0.286} = 1.932, \qquad T_4 = 710.8 \text{ K}$$

$$w_t = h_3 - h_4 = C_p(T_3 - T_4)$$
$$= 1.0035(1373.2 - 710.8) = 664.7 \text{ kJ/kg}$$
$$w_{\text{net}} = w_t - w_c = 664.7 - 269.5 = 395.2 \text{ kJ/kg}$$

Control volume: High-temperature heat exchanger.
Inlet state: State 2 fixed (as given).
Exit state: State 3 fixed (as given).
Analysis:

First law: $q_H = h_3 - h_2 = C_p(T_3 - T_2)$

Solution

$$q_H = h_3 - h_2 = C_p(T_3 - T_2) = 1.0035(1373.2 - 556.8) = 819.3 \text{ kJ/kg}$$

Control volume: Low-temperature heat exchanger.
Inlet state: State 4 fixed (above).
Exit state: State 1 fixed (above).
Analysis:

First law: $$q_L = h_4 - h_1 = C_p(T_4 - T_1)$$

Solution

$$q_L = h_4 - h_1 = C_p(T_4 - T_1) = 1.0035(710.8 - 288.2) = 424.1 \text{ kJ/kg}$$

Therefore,

$$\eta_{th} = \frac{w_{net}}{q_H} = \frac{395.2}{819.3} = 48.2 \text{ percent}$$

This may be checked by using Eq. 10.6.

$$\eta_{th} = 1 - \frac{1}{(P_2/P_1)^{(k-1)/k}} = 1 - \frac{1}{10^{0.286}} = 48.2 \text{ percent}$$

EXAMPLE 10.12

Consider a gas turbine with air entering the compressor under the same conditions as in Example 10.11 and leaving at a pressure of 1.0 MPa. The maximum temperature is 1100°C. Assume a compressor efficiency of 80 percent, a turbine efficiency of 85 percent, and a pressure drop between the compressor and turbine of 15 kPa. Determine the compressor work, turbine work, and cycle efficiency.

As in the previous example, for each control volume the model is ideal gas, constant specific heat, value at 300 K, and each process is SSSF with no kinetic or potential energy changes. In this example the diagram is Fig. 10.28.

Control volume: Compressor.
Inlet state: P_1, T_1 known; state fixed.
Exit state: P_2 known.
Analysis:

First law, real process: $$w_c = h_2 - h_1$$

Second law, ideal process: $$s_{2s} = s_1$$

so that $$\frac{T_{2s}}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}$$

In addition,

$$\eta_c = \frac{h_{2s} - h_1}{h_2 - h_1} = \frac{T_{2s} - T_1}{T_2 - T_1}$$

Solution

$$\left(\frac{P_2}{P_1}\right)^{(k-1)/k} = \frac{T_{2s}}{T_1} = 10^{0.286} = 1.932, \qquad T_{2s} = 556.8 \text{ K}$$

$$\eta_c = \frac{h_{2s} - h_1}{h_2 - h_1} = \frac{T_{2s} - T_1}{T_2 - T_1} = \frac{556.8 - 288.2}{T_2 - T_1} = 0.80$$

$$T_2 - T_1 = \frac{556.8 - 288.2}{0.80} = 335.8, \qquad T_2 = 624.0 \text{ K}$$

$$w_c = h_2 - h_1 = C_p(T_2 - T_1)$$
$$= 1.0035(624.0 - 288.2) = 337.0 \text{ kJ/kg}$$

Control volume: Turbine.
Inlet state: P_3 (P_2 – drop) known, T_3 known; state fixed.
Exit state: P_4 known.
Analysis:

First law, real process: $w_t = h_3 - h_4$

Second law, ideal process: $s_{4s} = s_3$

so that $$\frac{T_3}{T_{4s}} = \left(\frac{P_3}{P_4}\right)^{(k-1)/k}$$

In addition,

$$\eta_t = \frac{h_3 - h_4}{h_3 - h_{4s}} = \frac{T_3 - T_4}{T_3 - T_{4s}}$$

Solution

$$P_3 = P_2 - \text{pressure drop} = 1.0 - 0.015 = 0.985 \text{ MPa}$$

$$\left(\frac{P_3}{P_4}\right)^{(k-1)/k} = \frac{T_3}{T_{4s}} = 9.85^{0.286} = 1.9236, \qquad T_{4s} = 713.9 \text{ K}$$

$$\eta_t = \frac{h_3 - h_4}{h_3 - h_{4s}} = \frac{T_3 - T_4}{T_3 - T_{4s}} = 0.85$$

$$T_3 - T_4 = 0.85(1373.2 - 713.9) = 560.4$$

$$T_4 = 812.8 \text{ K}$$

$$w_t = h_3 - h_4 = C_p(T_3 - T_4)$$
$$= 1.0035(1373.2 - 812.8) = 562.4 \text{ kJ/kg}$$

$$w_{\text{net}} = w_t - w_c = 562.4 - 337.0 = 225.4 \text{ kJ/kg}$$

Control volume: High-temperature heat exchanger.
Inlet state: State 2 fixed (as given).
Exit state: State 3 fixed (as given).
Analysis:

First law: $q_H = h_3 - h_2$

Solution

$$q_H = h_3 - h_2 = C_p(T_3 - T_2)$$
$$= 1.0035(1373.2 - 624.0) = 751.8 \text{ kJ/kg}$$

so that

$$\eta_{th} = \frac{w_{net}}{q_H} = \frac{225.4}{751.8} = 30.0 \text{ percent}$$

The following comparisons can be made between Examples 10.11 and 10.12.

	w_c	w_t	w_{net}	q_H	η_{th}
Example 10.11 (Ideal)	269.5	664.7	395.2	819.3	48.2
Example 10.12 (Actual)	337.0	562.4	225.4	751.8	30.0

As stated previously, the irreversibilities decrease the turbine work and increase the compressor work. Since the net work is the difference between these two, it decreases very rapidly as compressor and turbine efficiencies decrease. The development of compressors and turbines of high efficiency is therefore an important aspect of the development of gas turbines.

Note that in the ideal cycle (Example 10.11) about 41 percent of the turbine work is required to drive the compressor and 59 percent is delivered as net work. In the actual turbine (Example 10.12) 60 percent of the turbine work is required to drive the compressor and 40 percent is delivered as net work. Thus, if the net power of this unit is to be 10 000 kW, a 25 000-kW turbine and a 15 000-kW compressor are required. This result demonstrates that a gas turbine has a high back-work ratio.

10.16 THE SIMPLE GAS-TURBINE CYCLE WITH A REGENERATOR

The efficiency of the gas-turbine cycle may be improved by introducing a regenerator. The simple open-cycle gas-turbine cycle with a regenerator is shown in Fig. 10.29, and the corresponding ideal air-standard cycle with a regenerator is shown on the P–v and T–s diagrams. In cycle 1–2–x–3–4–y–1, the temperature of the exhaust gas leaving the turbine in state 4 is higher than the temperature of the gas leaving the compressor. Therefore, heat can be transferred from the exhaust gases to the high-pressure gases leaving the compressor. If this is done in a counterflow heat exchanger, which is known as a regenerator, the temperature of the high-pressure gas leaving the regenerator, T_x, may, in the ideal case, have a temperature equal to T_4, the temperature of the gas leaving the turbine. Heat transfer from the external source is necessary only to increase the temperature from T_x to T_3. Area x–3–d–b–x represents the heat transferred, and area y–1–a–c–y represents the heat rejected.

The influence of pressure ratio on the simple gas-turbine cycle with a regenerator is shown by considering cycle 1–2′–3′–4–1. In this cycle the temperature of the

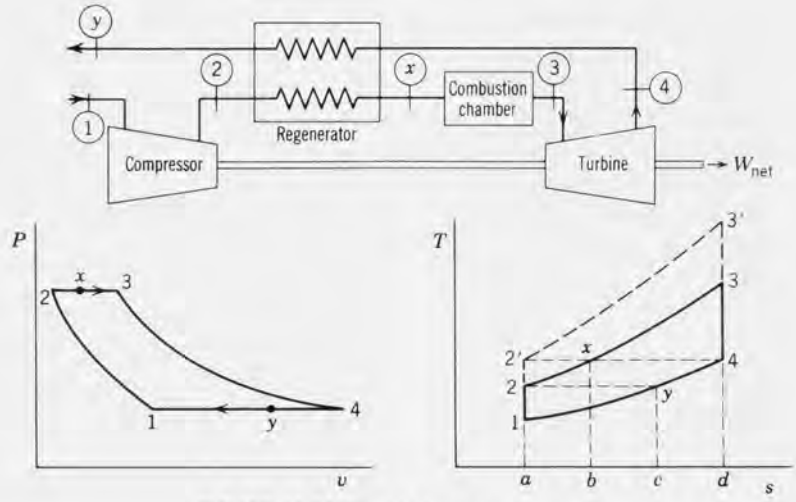


FIGURE 10.29 The ideal regenerative cycle.

exhaust gas leaving the turbine is just equal to the temperature of the gas leaving the compressor; therefore, there is no possibility of utilizing a regenerator. This can be shown more exactly by determining the efficiency of the ideal gas-turbine cycle with a regenerator.

The efficiency of this cycle with regeneration is found as follows, where the states are as given in Fig. 10.29.

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_H} = \frac{w_t - w_c}{q_H}$$

$$q_H = C_p(T_3 - T_x)$$

$$w_t = C_p(T_3 - T_4)$$

But for an ideal regenerator, $T_4 = T_x$, and therefore $q_H = w_t$. Consequently,

$$\eta_{\text{th}} = 1 - \frac{w_c}{w_t} = 1 - \frac{C_p(T_2 - T_1)}{C_p(T_3 - T_4)}$$

$$= 1 - \frac{T_1(T_2/T_1 - 1)}{T_3(1 - T_4/T_3)} = 1 - \frac{T_1}{T_3}\frac{[(P_2/P_1)^{(k-1)/k} - 1]}{[1 - (P_1/P_2)^{(k-1)/k}]}$$

$$\eta_{\text{th}} = 1 - \frac{T_1}{T_3}\left(\frac{P_2}{P_1}\right)^{(k-1)/k}$$

Thus, for the ideal cycle with regeneration the thermal efficiency depends not only on the pressure ratio but also on the ratio of the minimum to maximum temperature. We note that, in contrast to the Brayton cycle, the efficiency decreases with an increase in pressure ratio. The thermal efficiency versus pressure ratio for this cycle is plotted in Fig. 10.27 for a value of

$$\frac{T_1}{T_3} = 0.25$$

The effectiveness or efficiency of a regenerator is given by the regenerator efficiency, which can best be defined by reference to Fig. 10.30. State x represents the high-pressure gas leaving the regenerator. In the ideal regenerator there would be only an infinitesimal temperature difference between the two streams, and the high-pressure gas would leave the regenerator at temperature T'_x, and $T'_x = T_4$. In an actual regenerator, which must operate with a finite temperature difference T_x, the actual temperature leaving the regenerator is therefore less than T'_x. The regenerator efficiency is defined by

$$\eta_{\text{reg}} = \frac{h_x - h_2}{h'_x - h_2}$$

If the specific heat is assumed to be constant, the regenerator efficiency is also given by the relation

$$\eta_{\text{reg}} = \frac{T_x - T_2}{T'_x - T_2}$$

It should be pointed out that a higher efficiency can be achieved by using a regenerator with a greater heat-transfer area. However, this also increases the pressure drop, which represents a loss, and both the pressure drop and the regenerator efficiency must be considered in determining which regenerator gives maximum thermal efficiency for the cycle. From an economic point of view, the cost of the regenerator must be weighed against the saving that can be effected by its use.

EXAMPLE 10.13

If an ideal regenerator is incorporated into the cycle of Example 10.11, determine the thermal efficiency of the cycle.

The diagram for this example is Fig. 10.30. Values are from Example 10.11. Therefore, for the analysis of the high-temperature heat exchanger (combustion chamber), from the first law,

$$q_H = h_3 - h_x$$

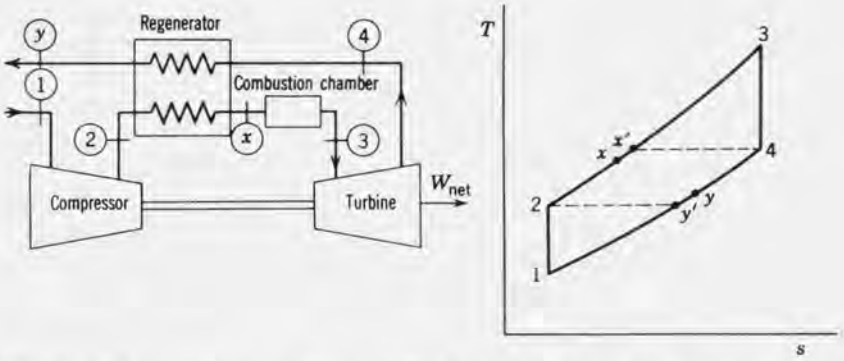


FIGURE 10.30 Temperature-entropy diagram to illustrate the definition of regenerator efficiency.

so that the solution is

$$T_x = T_4 = 710.8 \text{ K}$$

$$q_H = h_3 - h_x = C_p(T_3 - T_x) = 1.0035(1373.2 - 710.8) = 664.7 \text{ kJ/kg}$$

$$w_{net} = 395.2 \text{ kJ/kg} \quad \text{(from Example 10.11)}$$

$$\eta_{th} = \frac{395.2}{664.7} = 59.5 \text{ percent}$$

10.17 THE IDEAL GAS-TURBINE CYCLE USING MULTISTAGE COMPRESSION WITH INTERCOOLING, MULTISTAGE EXPANSION WITH REHEATING, AND A REGENERATOR

In Section 10.14 it was pointed out that when an ideal regenerator was incorporated into the Ericsson cycle, an efficiency equal to the efficiency of the corresponding Carnot cycle could be attained. It was also pointed out that in practice it is impossible to approach at all closely the reversible isothermal compression and expansion required in the Ericsson cycle.

The practical approach to this cycle is to use multistage compression with intercooling between stages, multistage expansion with reheat between stages, and a regenerator. Figure 10.31 shows a cycle with two stages of compression and two stages of expansion. The air-standard cycle is given on the corresponding T–s diagram. It may be shown that for this cycle the maximum efficiency is obtained if equal pressure ratios are maintained across the two compressors and the two turbines. In this ideal cycle it is assumed that the temperature of the air leaving the intercooler, T_3, is equal to the temperature of the air entering the first stage of compression, T_1, and that the temperature after reheating, T_8, is equal to the temperature entering the first turbine, T_6. Furthermore, in the ideal cycle it is assumed that the temperature of the high-pressure air leaving the regenerator, T_5, is equal to the temperature of the low-pressure air leaving the turbine, T_9.

If a large number of stages of compression and expansion are used, it is evident that the Ericsson cycle is approached. This is shown in Fig. 10.32. In practice, the economical limit to the number of stages is usually two or three. The turbine and compressor losses and pressure drops that have already been discussed would be involved in any actual unit employing this cycle.

There are a variety of ways in which the turbines and the compressors using this cycle can be utilized. Two possible arrangements for closed cycles are shown in Fig. 10.33. One advantage frequently sought in a given arrangement is ease of control of the unit under various loads. Detailed discussion of this point, however, is beyond the scope of this text.

10.18 THE AIR-STANDARD CYCLE FOR JET PROPULSION

The last air-standard power cycle we will consider is utilized in jet propulsion. In this cycle the work done by the turbine is just sufficient to drive the compressor.

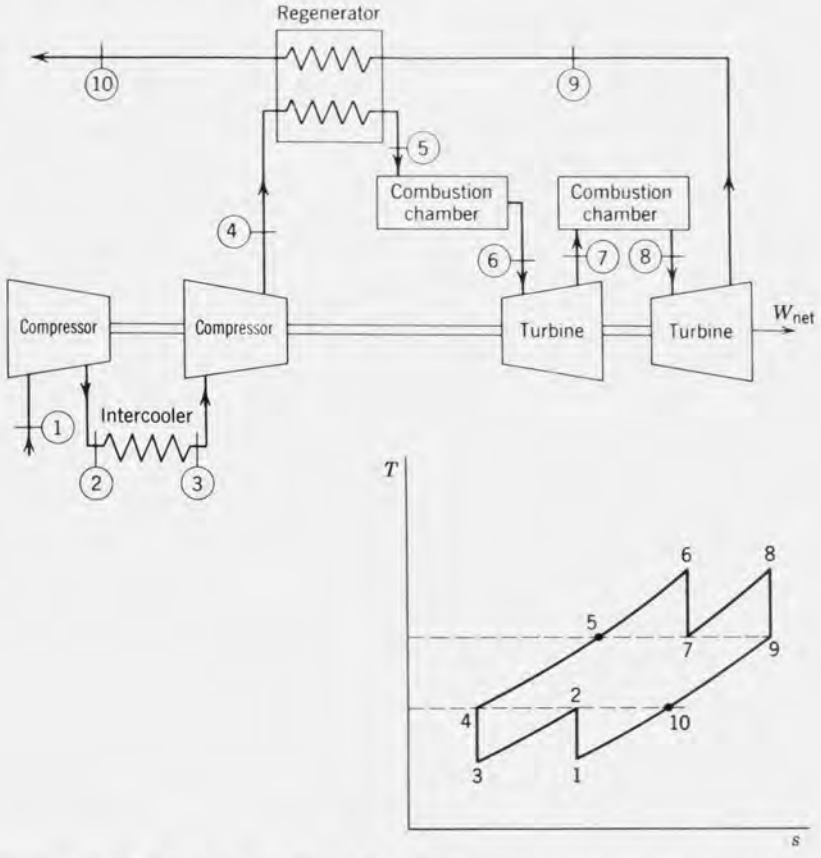


FIGURE 10.31 The ideal gas-turbine cycle utilizing intercooling, reheat, and a regenerator.

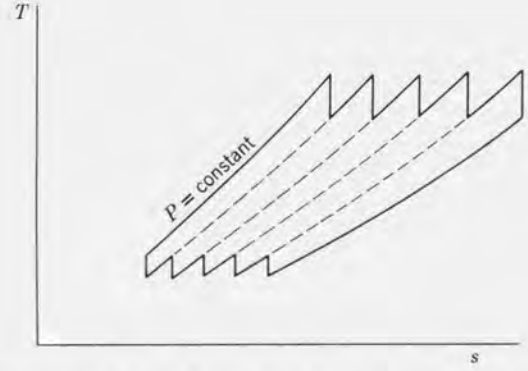


FIGURE 10.32 Temperature—entropy diagram that shows how the gas-turbine cycle with many stages approaches the Ericsson cycle.

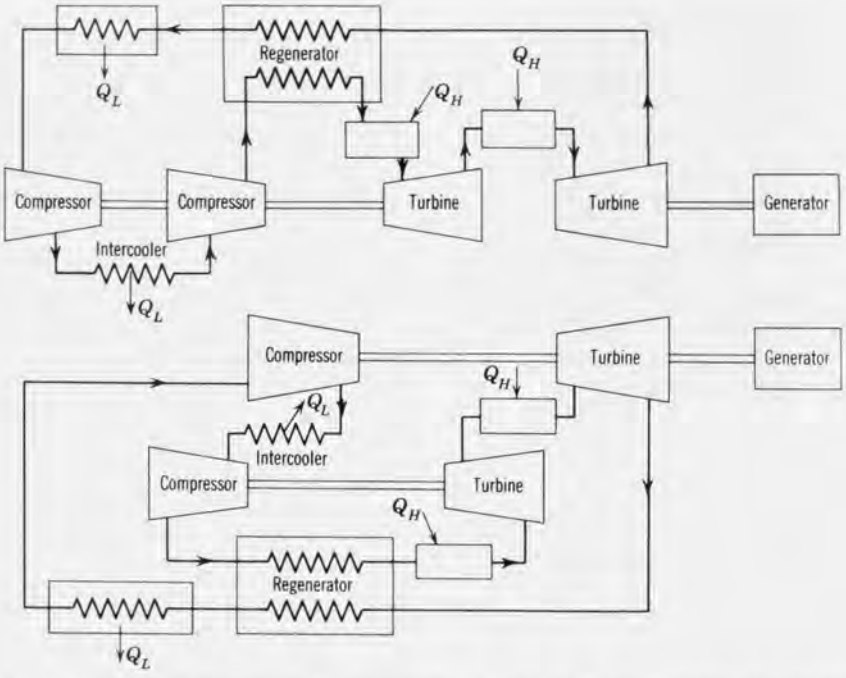


FIGURE 10.33 Some arrangements of components that may be utilized in stationary gas-turbine power plants.

The gases are expanded in the turbine to a pressure for which the turbine work is just equal to the compressor work. The exhaust pressure of the turbine will then be greater than that of the surroundings, and the gas can be expanded in a nozzle to the pressure of the surroundings. Since the gases leave at a high velocity, the change in momentum that the gases undergo gives a thrust to the aircraft in which the engine is installed. The air-standard cycle for this situation is shown in Fig. 10.34.

Since all the principles explaining this cycle have already been covered, the example that follows will conclude our consideration of air-standard power cycles.

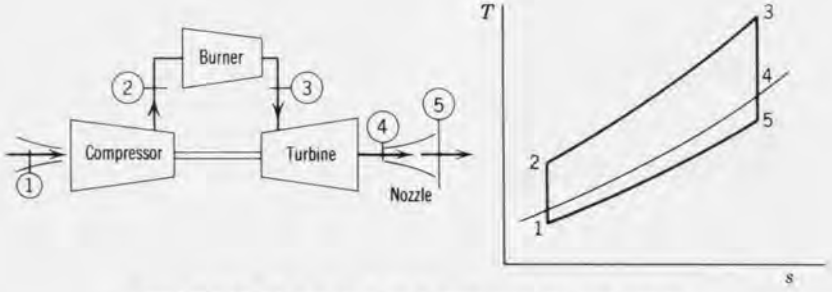


FIGURE 10.34 The ideal gas-turbine cycle for a jet engine.

EXAMPLE 10.14

Consider an ideal cycle in which air enters the compressor at 0.1 MPa, 15°C. The pressure leaving the compressor is 1.0 MPa and the maximum temperature is 1100°C. The air expands in the turbine to a pressure at which the turbine work is just equal to the compressor work. On leaving the turbine, the air expands in a nozzle to 0.1 MPa. The process is reversible and adiabatic. Determine the velocity of the air leaving the nozzle.

The model used is ideal gas, constant specific heat, value at 300 K, and each process is SSSF with no potential energy change. The only kinetic energy change occurs in the nozzle. The diagram is shown in Fig. 10.34.

The compressor analysis is the same as in Example 10.11. From the results of that solution,

$$P_1 = 0.1 \text{ MPa}, \qquad T_1 = 288.2 \text{ K}$$
$$P_2 = 1.0 \text{ MPa}, \qquad T_2 = 556.8 \text{ K}$$
$$w_c = 269.5 \text{ kJ/kg}$$

The turbine analysis is also the same as in Example 10.11. Here, however,

$$P_3 = 1.0 \text{ MPa}, \qquad T_3 = 1373.2 \text{ K}$$
$$w_c = w_t = C_p(T_3 - T_4) = 269.5 \text{ kJ/kg}$$
$$T_3 - T_4 = \frac{269.5}{1.0035} = 268.6, \qquad T_4 = 1104.6 \text{ K}$$

so that

$$\frac{T_3}{T_4} = \left(\frac{P_3}{P_4}\right)^{(k-1)/k} = \frac{1373.2}{1104.6} = 1.2432$$
$$\frac{P_3}{P_4} = 2.142, \qquad P_4 = 0.4668 \text{ MPa}$$

Control volume: Nozzle.
Inlet state: State 4 fixed (above).
Exit state: P_5 known.
Analysis:

First law: $$h_4 = h_5 + \frac{\mathbf{V}_5^2}{2}$$

Second law: $$s_4 = s_5$$

Solution

Since P_5 is 0.1 MPa, from the second law we find that $T_5 = 710.8$ K.

$$\mathbf{V}_5^2 = 2C_{p0}(T_4 - T_5)$$
$$\mathbf{V}_5^2 = 2 \times 1000 \times 1.0035(1104.6 - 710.8)$$
$$\mathbf{V}_5 = 889 \text{ m/s}$$

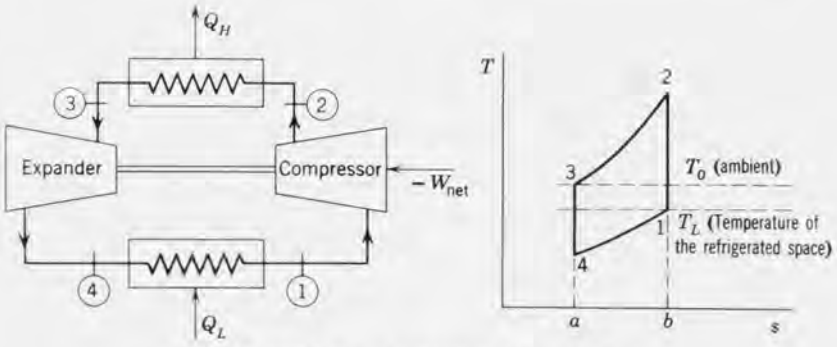


FIGURE 10.35 The air-standard refrigeration cycle.

AIR-STANDARD REFRIGERATION CYCLE

10.19 THE AIR-STANDARD REFRIGERATION CYCLE

The final section of this chapter concerns the air-standard refrigeration cycle. Its major use in practice is in the liquefaction of air and other gases and in certain special situations that require refrigeration, such as aircraft cooling systems.

The simplest form of the air-standard refrigeration cycle, which is essentially the reverse of the Brayton cycle, is shown in Fig. 10.35. The compressor and expander might be either reciprocating or rotary. After compression from 1 to 2, the air is cooled as heat is transferred to the surroundings at temperature T_0. The air is then expanded in process 3–4 to the pressure entering the compressor, and the temperature drops to T_4 in the expander. Heat may then be transferred to the air until temperature T_L is reached. The work for this cycle is represented by area 1–2–3–4–1, and the refrigeration effect is represented by area 4–1–b–a–4. The coefficient of performance is the ratio of these two areas.

In practice, this cycle has been used to cool aircraft in an open cycle. A simplified form is shown in Fig. 10.36. Upon leaving the expander, the cool air is blown directly into the cabin, thus providing the cooling effect where needed.

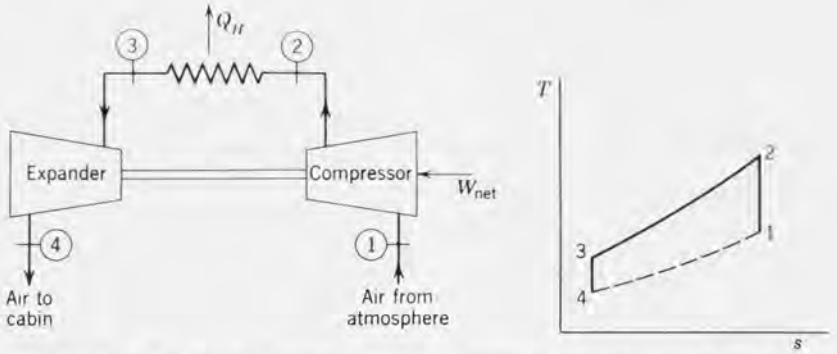


FIGURE 10.36 An air refrigeration cycle that might be utilized for aircraft cooling.

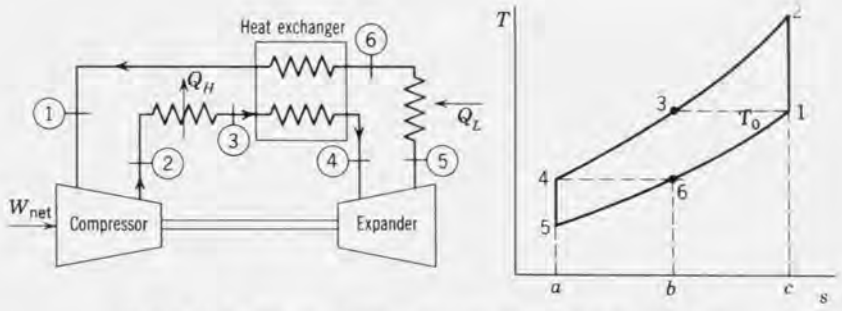


FIGURE 10.37 The air refrigeration cycle utilizing a heat exchanger.

When counterflow heat exchangers are incorporated, very low temperatures can be obtained. This is essentially the cycle used in low-pressure air liquefaction plants and in other liquefaction devices such as the Collins helium liquefier. The ideal cycle is as shown in Fig. 10.37. It is evident that the expander operates at very low temperature, which presents unique problems to the designer in providing lubrication and choosing materials.

EXAMPLE 10.15

Consider the simple air-standard refrigeration cycle of Fig. 10.35. Air enters the compressor at 0.1 MPa, −20°C, and leaves at 0.5 MPa. Air enters the expander at 15°C. Determine

1. The coefficient of performance for this cycle.
2. The rate at which air must enter the compressor to provide 1 kW of refrigeration.

For each control volume in this example, the model is ideal gas with constant specific heat, value at 300 K, and each process is SSSF with no kinetic or potential energy changes. The diagram for this example is Fig. 10.35.

Control volume: Compressor.
Inlet state: P_1, T_1 known; state fixed.
Exit state: P_2 known.
Analysis:

First law: $w_c = h_2 - h_1$ (Here w_c designates work into the compressor.)

Second law: $s_1 = s_2$

so that $$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}$$

Solution

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} = 5^{0.286} = 1.5845, \qquad T_2 = 401.2 \text{ K}$$

$$w_c = h_2 - h_1 = C_p(T_2 - T_1)$$
$$= 1.0035(401.2 - 253.2) = 148.5 \text{ kJ/kg}$$

Control volume: Expander.
Inlet state: $P_3\ (=P_2)$ known, T_3 known; state fixed.
Exit state: $P_4\ (=P_1)$ known.
Analysis:

First law: $w_t = h_3 - h_4$

Second law: $s_3 = s_4$

so that $\dfrac{T_3}{T_4} = \left(\dfrac{P_3}{P_4}\right)^{(k-1)/k}$

Solution

$$\frac{T_3}{T_4} = \left(\frac{P_3}{P_4}\right)^{(k-1)/k} = 5^{0.286} = 1.5845, \qquad T_4 = 181.9 \text{ K}$$
$$w_t = h_3 - h_4 = 1.0035(288.2 - 181.9) = 106.7 \text{ kJ/kg}$$

Control volume: High-temperature heat exchanger.
Inlet state: State 2 known (as given).
Exit state: State 3 known (as given).
Analysis:

First law: $q_H = h_2 - h_3$ (heat rejected)

Solution

$$q_H = h_2 - h_3 = C_p(T_2 - T_3) = 1.0035(401.2 - 288.2) = 113.4 \text{ kJ/kg}$$

Control volume: Low-temperature heat exchanger.
Inlet state: State 4 known (as given).
Exit state: State 1 known (as given).
Analysis:

First law: $q_L = h_1 - h_4$

Solution

$$q_L = h_1 - h_4 = C_p(T_1 - T_4) = 1.0035(253.2 - 181.9) = 71.6 \text{ kJ/kg}$$

Therefore,

$$w_{\text{net}} = w_c - w_t = 148.5 - 106.7 = 41.8 \text{ kJ/kg}$$
$$\beta = \frac{q_L}{w_{\text{net}}} = \frac{71.6}{41.8} = 1.713$$

To provide 1 kW of refrigeration capacity, we have

$$\dot{m} = \frac{\dot{Q}_L}{q_L} = \frac{1}{71.6} = 0.014 \text{ kg/s}$$

PROBLEMS

10.1 Consider a solar-energy-powered ideal Rankine cycle which uses water as the working fluid. Saturated vapor leaves the solar collector at 150°C, and the condenser pressure is 10 kPa. Determine the thermal efficiency of this cycle.

10.1E Consider a solar-energy-powered ideal Rankine cycle which uses water as the working fluid. Saturated vapor leaves the solar collector at 300 F, and the condenser pressure is 1 lbf/in.^{2}. Determine the thermal efficiency of this cycle.

10.2 A supply of geothermal hot water is to be used as the energy source in an ideal Rankine cycle, with R-22 as the cycle working fluid. Saturated vapor R-22 leaves the boiler at a temperature of 85°C, and the condenser temperature is 40°C.

(a) Calculate the thermal efficiency of this cycle.

(b) If 2 kg/s of geothermal water is available at 95°C, what is the maximum power output of the cycle?

10.3 Consider the ammonia Rankine-cycle power plant shown in Fig. 10.38, a plant which was designed to operate in a location where the ocean water temperature is 25°C near the surface and 5°C at some greater depth.

(a) Determine the turbine power output and the pump power input for the ammonia cycle.

(b) Determine the mass flow rate of water through each heat exchanger.

(c) What is the thermal efficiency of this power plant?

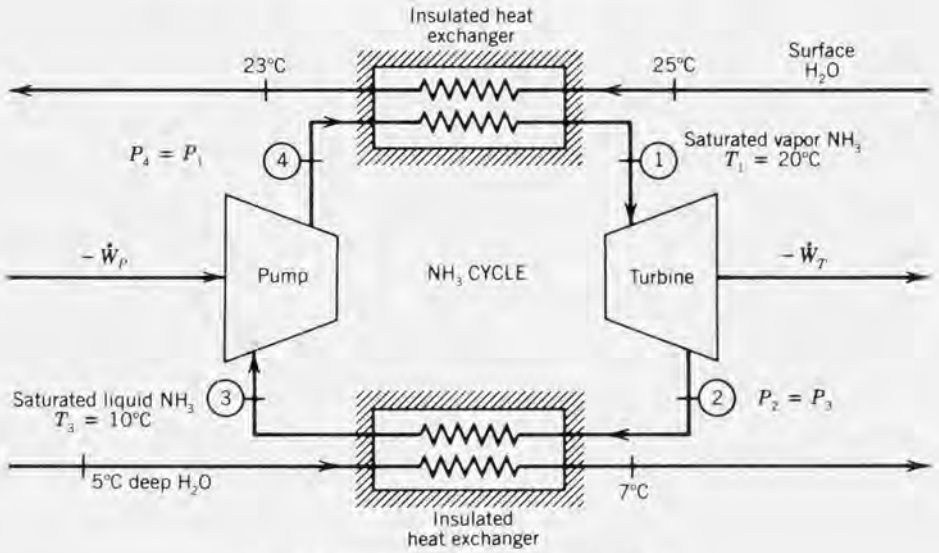


FIGURE 10.38 Sketch for Problem 10.3.

10.4 The effect of turbine exhaust pressure on the performance of an ideal steam Rankine cycle is to be studied. Steam enters the turbine at 3.5 MPa, 350°C. Calculate the thermal efficiency of the cycle and the moisture content of the steam leaving the turbine for turbine exhaust pressures of 5, 10, 50, and 100 kPa. Plot thermal

efficiency versus turbine exhaust pressure for the specified turbine inlet pressure and temperature.

10.5 The effect of turbine inlet pressure on the performance of an ideal steam Rankine cycle is to be studied. Steam enters the turbine at 350°C and exhausts at 10 kPa. Calculate the thermal efficiency of the cycle and the moisture content of the steam leaving the turbine as saturated vapor for turbine inlet pressures of 1, 3.5, 6, and 10 MPa. Plot thermal efficiency versus turbine inlet pressure for the specified turbine inlet temperature and exhaust pressure.

10.6 The effect of turbine inlet temperature on the performance of an ideal steam Rankine cycle is to be studied. Steam enters the turbine at 3.5 MPa and exhausts at 10 kPa. Calculate the thermal efficiency of the cycle and the moisture content of the steam leaving the turbine for turbine inlet temperatures of 350°, 500°, 800°C, and saturated vapor (at 3.5-MPa pressure). Plot thermal efficiency versus turbine inlet temperature for the specified turbine inlet pressure and exhaust pressure.

10.7 Consider a simple ideal Rankine cycle that uses steam as the working fluid. The high-pressure side of the cycle is at a supercritical pressure. Such a cycle has a potential advantage of minimizing local temperature differences between the fluids in the steam generator, such as the instance in which the high-temperature energy source is the hot exhaust gas from a gas-turbine engine. Calculate the thermal efficiency of the cycle if the state entering the turbine is 25 MPa, 500°C, and the condenser pressure is 5 kPa. What is the steam quality at the turbine exit?

10.7E Consider a simple ideal Rankine cycle that uses steam as the working fluid. The high-pressure side of the cycle is at a supercritical pressure. Such a cycle has a potential advantage of minimizing local temperature differences between the fluids in the steam generator, such as the instance in which the high-temperature energy source is the hot exhaust gas from a gas-turbine engine. Calculate the thermal efficiency of the cycle if the state entering the turbine is 3500 lbf/in.^{2}, 1100 F, and the condenser pressure is 1 lbf/in.^{2}. What is the steam quality at the turbine exit?

10.8 Consider an ideal steam reheat cycle in which steam enters the high-pressure turbine at 3.5 MPa, 350°C, and then expands to 0.8 MPa. It is then reheated to 350°C and expands to 10 kPa in the low-pressure turbine. Calculate the thermal efficiency of the cycle and the moisture content of the steam leaving the low-pressure turbine.

10.9 The effect of reheat pressure on the ideal steam reheat cycle is to be studied. Repeat Problem 10.8, using various values other than 0.8 MPa for the reheat pressure.

10.10 The effect of a number of reheat stages on the ideal steam reheat cycle is to be studied. Repeat Problem 10.8 using two reheat stages, one stage at 1.2 MPa and the second at 0.2 MPa, instead of the single reheat stage at 0.8 MPa.

10.11 Consider an ideal steam regenerative cycle in which steam enters the turbine at 3.5 MPa, 350°C, and exhausts to the condenser at 10 kPa. Steam is extracted from the turbine at 0.8 MPa and also at 0.2 MPa for heating the boiler feedwater in two open feedwater heaters. The feedwater leaves each heater at the temperature of the condensing steam. The appropriate pumps are used for the water leaving the condenser and the two feedwater heaters. Calculate the thermal efficiency of the cycle and the net work per kilogram of steam.

10.12 Repeat Problem 10.11, but assume closed instead of open feedwater heaters. A single pump is used to pump the water leaving the condenser up to a boiler pressure

of 3.5 MPa. Condensate from the high-pressure heater is drained through a trap to the low-pressure heater, and that from the low-pressure heater is drained through a trap to the condenser.

10.13 The effect of a number of open feedwater heaters on the thermal efficiency of an ideal cycle is to be studied. Steam leaves the steam generator at 20 MPa, 600°C, and the cycle has a condenser pressure of 10 kPa. Determine the thermal efficiency for each of the following cases.

(a) No feedwater heater.
(b) One feedwater heater operating at 1.0 MPa.
(c) Two feedwater heaters, one operating at 3.0 MPa and the other at 0.2 MPa.

10.14 Consider an ideal steam combined reheat and regenerative cycle in which steam enters the high-pressure turbine at 3.5 MPa, 350°C, and is extracted for feedwater heating at 0.8 MPa. The remainder of the steam is reheated to 350°C at this pressure, 0.8 MPa, and is fed to the low-pressure turbine. Steam is extracted from the low-pressure turbine at 0.2 MPa for feedwater heating. The condenser pressure is 10 kPa. Both feedwater heaters are open heaters. Calculate the thermal efficiency of the cycle and the net work per kilogram of steam.

10.14E Consider an ideal steam combined reheat and regenerative cycle in which steam enters the high-pressure turbine at 500 lbf/in.^{2}, 700 F, and is extracted for feedwater heating at 120 lbf/in.^{2}. The remainder of the steam is reheated to 700 F at this pressure, 120 lbf/in.^{2}, and is fed to the low-pressure turbine. Steam is extracted from the low-pressure turbine at 20 lbf/in.^{2} for feedwater heating. The condenser pressure is 2 lbf/in.^{2}. Both feedwater heaters are open heaters. Calculate the thermal efficiency of the cycle and the net work per pound-mass of steam.

10.15 An ideal steam power plant is designed to operate on the combined reheat and regenerative cycle and to produce a net power output of 10 MW. Steam enters the high-pressure turbine at 8 MPa, 550°C, and is expanded to 0.6 MPa, at which pressure some of the steam is fed to an open feedwater heater, and the remainder is reheated to 550°C. The reheated steam is then expanded in the low-pressure turbine to 10 kPa.

(a) Determine the steam flow rate to the high-pressure turbine.
(b) Determine the size of motor required to drive each of the pumps.
(c) If the increase in the condenser cooling water temperature is restricted to a maximum of 10°C, what is the flow rate of the cooling water?
(d) If the steam velocity in the turbine–condenser connecting pipe is restricted to a maximum of 100 m/s, what is the diameter of the connecting pipe?

10.16 In a particular nuclear power plant the nuclear reactor is so designed that the maximum temperature in the steam cycle is 450°C. The steam-condensing temperature is fixed at 40°C. The plan is to build a steam power plant that has one open feedwater heater. Select what you consider to be a reasonable ideal steam cycle within these specifications, determine its thermal efficiency, and explain why the particular pressures involved were selected.

10.17 Steam leaves a power plant steam generator at 3.5 MPa, 350°C, and enters the turbine at 3.4 MPa, 325°C. The isentropic turbine efficiency is 88 percent, and the turbine exhaust pressure is 10 kPa. Condensate leaves the condenser and enters the pump at 35°C, 10 kPa. The isentropic pump efficiency is 80 percent, and the

discharge pressure is 3.7 MPa. The feedwater enters the steam generator at 3.6 MPa, 30°C. Calculate the following.

(a) The thermal efficiency of the cycle.

(b) The irreversibility of the process in the line between the steam generator exit and the turbine inlet, assuming an ambient temperature of 25°C.

10.17E Steam leaves a power plant steam generator at 500 lbf/in.^{2}, 650 F, and enters the turbine at 490 lbf/in.^{2}, 625 F. The isentropic turbine efficiency is 88 percent, and the turbine exhaust pressure is 1.7 lbf/in.^{2}. Condensate leaves the condenser and enters the pump at 110 F, 1.7 lbf/in.^{2}. The isentropic pump efficiency is 80 percent, and the discharge pressure is 520 lbf/in.^{2}. The feedwater enters the steam generator at 510 lbf/in.^{2}, 100 F. Calculate the following.

(a) The thermal efficiency of the cycle.

(b) The irreversibility of the process in the line between the steam generator exit and the turbine inlet, assuming an ambient temperature of 77 F.

10.18 In a particular reheat-cycle power plant, steam enters the high-pressure turbine at 5 MPa, 450°C, expands to 0.5 MPa, after which it is reheated to 450°C. The steam is then expanded through the low-pressure turbine to 7.5 kPa. Liquid water leaves the condenser at 30°C, is pumped to 5 MPa, and is then returned to the steam generator. Each turbine is adiabatic with an isentropic efficiency of 87 percent, and the pump efficiency is 82 percent. If the total power output of the turbines is 10 000 kW, determine

(a) The mass flow rate of steam.

(b) The pump power input.

(c) The thermal efficiency of the power plant.

10.19 In one type of nuclear power plant, heat is transferred in the nuclear reactor to liquid sodium. The liquid sodium is then pumped through a heat exchanger where heat is transferred to boiling water. Saturated vapor steam at 5 MPa exits this heat exchanger and is then superheated to 600°C in an external gas-fired superheater. The steam enters the turbine, which has one (open-type) feedwater extraction at 0.4 MPa. The isentropic turbine efficiency is 87 percent, and the condenser pressure is 7.5 kPa. Determine the heat transfer in the reactor and in the superheater to produce a net power output of 1 MW.

10.20 A certain industrial application has the following steam requirement: one 5-kg/s stream at a pressure of 0.5 MPa and one 5-kg/s stream at 1.4 MPa (both saturated or slightly superheated vapor). Instead of installing a low-pressure boiler to generate this steam, the designers plan to obtain it by cogeneration, whereby the steam required will be the exhaust from a steam turbine. A high-pressure boiler generating steam at 10 MPa, 500°C, is therefore installed to supply steam to the turbine. The required amount is withdrawn at 1.4 MPa, and the remainder is expanded in the low-pressure end of the turbine to 0.5 MPa. Assuming that the high-pressure and low-pressure turbines each have an isentropic efficiency of 85 percent, determine the following.

(a) The power output of the turbine.

(b) The heat-transfer rate required in the boiler compared with the rate needed were the steam generated in a low-pressure boiler without cogeneration. Assume that for each, 20°C liquid water is pumped to the required pressure and fed to the boiler.

10.21 Consider the following preliminary design specifications for a supercritical steam power plant cycle. The maximum pressure will be 30 MPa, and the maximum temperature will be 600°C. The temperature of the cooling water is such that 10-kPa pressure can be maintained in the condensers. Turbine isentropic efficiencies of at least 87 percent can be expected.

(a) Do you recommend any reheat for this cycle? If so, how many stages of reheat and at what pressures? Give reasons for your decisions.

(b) Do you recommend feedwater heaters? If so, how many and at what pressures would they operate? Should they be open or closed feedwater heaters?

(c) Estimate the thermal efficiency of the cycle that you recommend.

10.21E Consider the following preliminary design specifications for a supercritical steam power plant cycle. The maximum pressure will be 4000 lbf/in.^{2}, and the maximum temperature will be 1100 F. The temperature of the cooling water is such that 1-lbf/in.^{2} pressure can be maintained in the condensers. Turbine isentropic efficiencies of at least 87 percent can be expected.

(a) Do you recommend any reheat for this cycle? If so, how many stages of reheat and at what pressures? Give reasons for your decisions.

(b) Do you recommend feedwater heaters? If so, how many and at what pressures would they operate? Should they be open or closed feedwater heaters?

(c) Estimate the thermal efficiency of the cycle that you recommend.

10.22 In both power and refrigeration cycles that operate over a wide temperature range, it is frequently advantageous to use more than one working fluid. Two fluids that have been used together in power plants are mercury and water; this is referred to as a binary system. The advantage of this system is that mercury has a much lower vapor pressure than water; therefore, it is possible for an isothermal boiling process in the mercury to take place at a high temperature (much higher than the critical temperature of water) but at a moderate pressure. Such a binary system is shown in Fig. 10.39. The temperatures and pressures for an ideal cycle are shown on the corresponding T–s diagram. The maximum temperature in the steam cycle, that leaving the superheater at point 4, is 500°C. Determine

(a) The kilograms of mercury condensed in the mercury condenser per kilogram of water boiled.

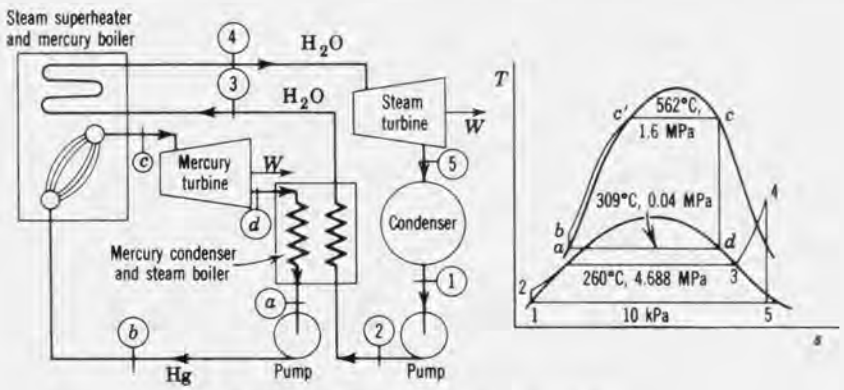


FIGURE 10.39 Sketch for Problem 10.22

(b) The thermal efficiency of this ideal cycle.

From tables of thermodynamic properties for mercury, the following saturation data are known.

P, MPa	T_g, °C	h_f, kJ/kg	h_g, kJ/kg	s_f, kJ/kgK	s_g, kJ/kgK
0.04	309	42.21	335.64	0.1034	0.6073
1.6	562	75.37	364.04	0.1498	0.4954

10.23 Consider an ideal refrigeration cycle that has a condenser temperature of 45°C and an evaporator temperature of −15°C. Determine the coefficient of performance of this refrigerator for the working fluids R-12 and R-22.

10.24 The environmentally safe refrigerant R-134a is one of the replacements for R-12 in refrigeration systems. Repeat Problem 10.23 for R-134a (Fig. A.4), and compare the result with that for R-12.

10.25 Consider an ideal heat pump that has a condenser temperature of 50°C and an evaporator temperature of 0°C. Determine the coefficient of performance of this heat pump for the working fluids R-12, R-22, and ammonia.

10.25E Consider an ideal heat pump that has a condenser temperature of 120F and an evaporator temperature of 30F. Determine the coefficient of performance of this heat pump for the working fluids R-12, R-22, and ammonia.

10.26 The effect of the evaporator temperature on the coefficient of performance of a heat pump is to be studied. Consider an ideal cycle with R-22 as the working fluid and a condenser temperature of 40°C. Plot a curve for the coefficient of performance versus the evaporator temperature for temperature values from 15 to −25°C.

10.27 How the difference between the temperature of the refrigerant in the condenser and the temperature of the surroundings affects the amount of cycle power required is to be studied. For this study consider an ideal refrigeration cycle with R-22 as the working fluid, surroundings having a temperature of 30°C, and an evaporator whose temperature is −15°C. Plot a curve of power input per kilowatt of refrigeration for differences of 0 to 40°C between the temperatures of the surroundings and of the condenser.

10.28 How the difference between the temperature of the refrigerated cold space and the temperature of the refrigerant in the evaporator affects the amount of cycle power required is to be studied. For this study consider an ideal refrigeration cycle with R-22 as the working fluid, a condenser temperature of 50°C, and a cold space temperature of −15°C. Plot a curve of power input per kilowatt of refrigeration for differences of 0 to 30°C between the temperatures of the cold space and of the refrigerant in the evaporator.

10.29 A small heat pump unit is used to heat water for a hot-water supply. Assume that the unit uses R-22 and operates on the ideal refrigeration cycle. The evaporator temperature is 15°C and the condenser temperature is 60°C. If the amount of hot water needed is 0.1 kg/s, determine the amount of energy saved by using the heat pump instead of directly heating the water from 15 to 60°C.

10.30 In both power and refrigeration cycles that operate over a wide temperature range, it is frequently advantageous to use more than one working fluid. In refrigeration

systems this is commonly referred to as a cascade system. Consider such a system composed of two ideal refrigeration cycles, as shown in Fig. 10.40. This system is designed to use environmentally safe refrigerants as the two working fluids. The high-temperature cycle uses R-22. Saturated liquid leaves the condenser at 40°C, and saturated vapor leaves the heat exchanger at −20°C. The low-temperature cycle uses a different refrigerant, R-23 (Fig. A.3). Saturated vapor leaves the evaporator at −80°C, and saturated liquid leaves the heat exchanger at −10°C. Calculate

(a) The ratio of the mass flow rates through the two cycles.
(b) The coefficient of performance of the system.

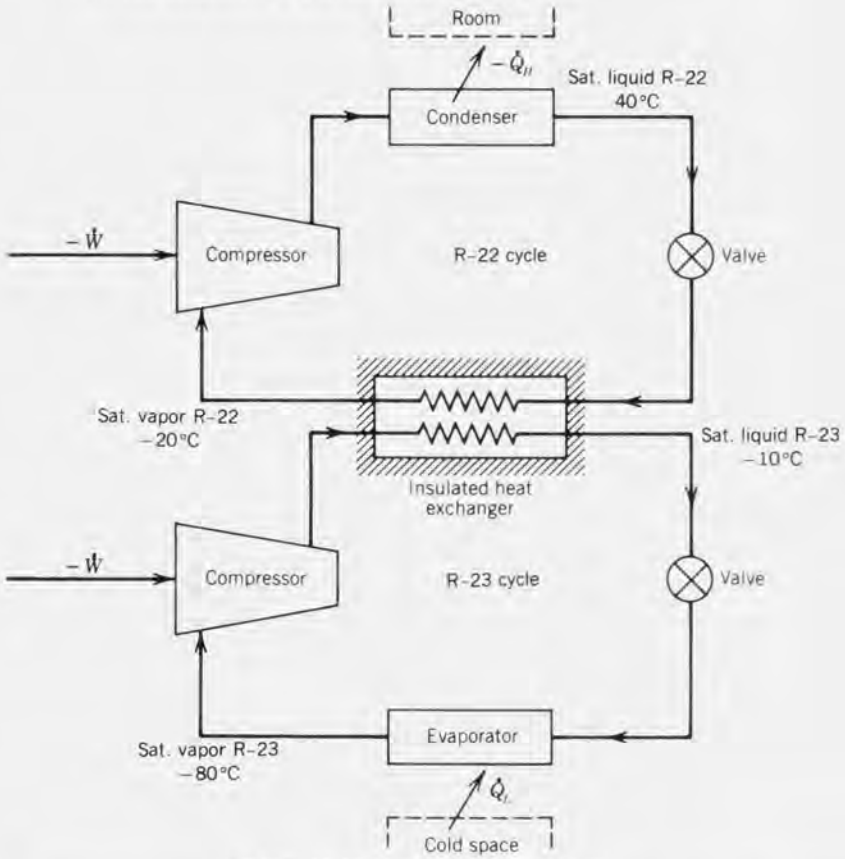


FIGURE 10.40 Sketch for Problem 10.30.

10.31 One means of improving the performance of a refrigeration system that operates over a wide temperature range is to use a two-stage compressor. Consider an ideal refrigeration system of this type that uses R-12 as the working fluid, as shown in Fig. 10.41. Saturated liquid leaves the condenser at 40°C and is throttled to −20°C. The liquid and vapor at this temperature are separated, and the liquid is throttled to the evaporator temperature, −70°C. Vapor leaving the evaporator is compressed to the saturation pressure corresponding to −20°C, after which it is mixed with the vapor leaving the flash chamber. It may be assumed that both the flash chamber and the mixing chamber are well insulated to prevent heat transfer from the ambient. Vapor leaving the mixing chamber is compressed in the second

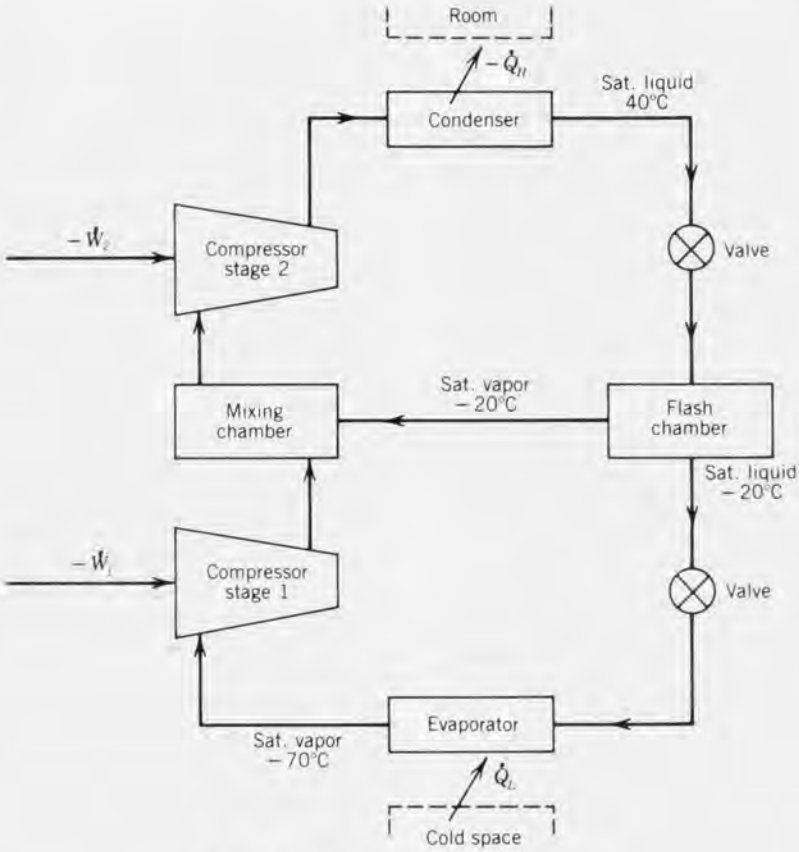


FIGURE 10.41 Sketch for Problem 10.31.

stage of the compressor to the saturation pressure corresponding to the condenser temperature, 40°C. Determine

(a) The coefficient of performance of the system.

(b) The coefficient of performance of a simple ideal refrigeration cycle operating over the same condenser and evaporator temperature ranges as those of the two-stage compressor unit studied in this problem.

10.32 The refrigerant R-22 is used as the working fluid in a conventional heat pump cycle. Saturated vapor enters the compressor of this unit at 10°C; its exit temperature from the compressor is measured and found to be 85°C. If the isentropic efficiency of the compressor is estimated to be 70 percent, what is the coefficient of performance of the heat pump?

10.32E The refrigerant R-22 is used as the working fluid in a conventional heat pump cycle. Saturated vapor enters the compressor of this unit at 50 F; its exit temperature from the compressor is measured and found to be 185 F. If the isentropic efficiency of the compressor is estimated to be 70 percent, what is the coefficient of performance of the heat pump?

10.33 In an actual refrigeration cycle using R-12 as the working fluid, the refrigerant flow rate is 0.05 kg/s. Vapor enters the compressor at 150 kPa, −10°C, and leaves

at 1.2 MPa, 75°C. The power input to the compressor is measured and found to be 2.4 kW. The refrigerant enters the expansion valve at 1.15 MPa, 40°C, and leaves the evaporator at 175 kPa, −15°C. Determine

(a) The irreversibility during the compression process.
(b) The refrigeration capacity.
(c) The coefficient of performance for this cycle.

10.34 Consider an ideal dual-loop heat-powered refrigeration cycle using R-12 as the working fluid, as shown in Fig. 10.42. Saturated vapor at 105°C leaves the boiler and expands in the turbine to the condenser pressure. Saturated vapor at −15°C leaves the evaporator and is compressed to the condenser pressure. The ratio of flows through the two loops is such that the turbine produces just enough power to drive the compressor. The two exiting streams mix together and enter the condenser. Saturated liquid leaving the condenser at 45°C is then separated into two streams in the necessary proportions. Determine

(a) The ratio of mass flow rate through the power loop to that through the refrigeration loop.
(b) The performance of the cycle, in terms of the ratio Q_L/Q_H.

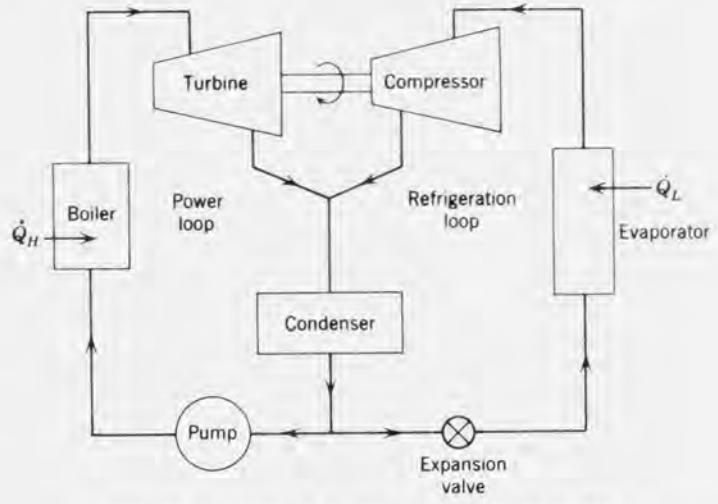


FIGURE 10.42 Sketch for Problems 10.34 and 10.34E.

10.34E Consider an ideal dual-loop heat-powered refrigeration cycle using R-12 as the working fluid, as shown in Fig. 10.42. Saturated vapor at 220 F leaves the boiler and expands in the turbine to the condenser pressure. Saturated vapor at 0 F leaves the evaporator and is compressed to the condenser pressure. The ratio of flows through the two loops is such that the turbine produces just enough power to drive the compressor. The two exiting streams mix together and enter the condenser. Saturated liquid leaving the condenser at 110 F is then separated into two streams in the necessary proportions. Determine

(a) The ratio of mass flow rate through the power loop to that through the refrigeration loop.
(b) The performance of the cycle, in terms of the ratio Q_L/Q_H.

10.35 A jet ejector, a device with no moving parts, functions as the equivalent of a coupled turbine–compressor unit (see Problems 9.24 and 9.29). Thus, the turbine–compressor in the dual-loop cycle of Fig. 10.42 could be replaced by a jet ejector. The primary stream of the jet ejector enters from the boiler, the secondary stream enters from the evaporator, and the discharge flows to the condenser. Alternatively, a jet ejector may be used with water as the working fluid. The purpose of the device is to chill water, usually for an air-conditioning system. In this application the physical setup is as shown in Fig. 10.43. Using the data given on the diagram, evaluate the performance of this cycle in terms of the ratio Q_L/Q_H.

(a) Assume an ideal cycle.
(b) Assume an ejector efficiency of 20 percent (see Problem 9.29).

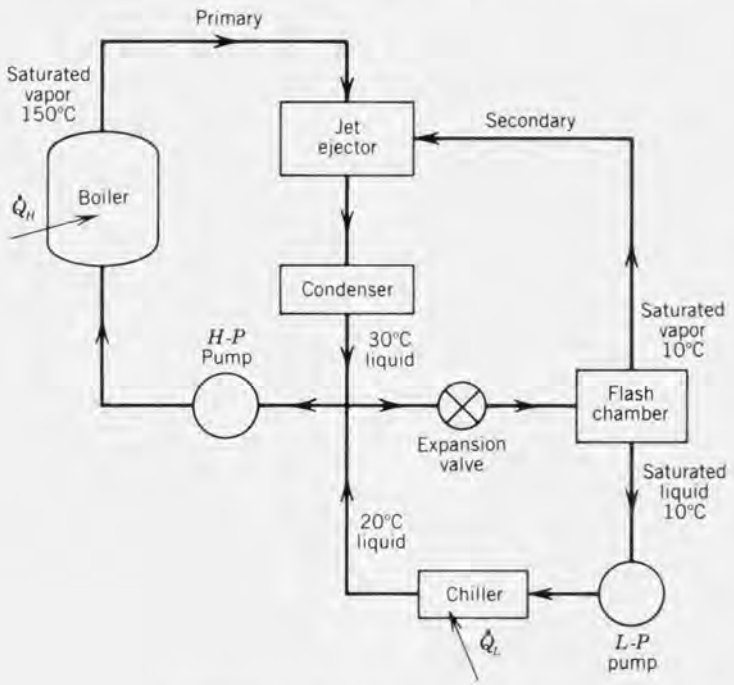


FIGURE 10.43 Sketch for Problem 10.35.

10.36 Consider a small ammonia absorption refrigeration cycle that is powered by solar energy and is to be used as an air conditioner. Saturated-vapor ammonia leaves the generator at 50°C, and saturated vapor leaves the evaporator at 10°C. If 7000 kJ of heat is required in the generator (solar collector) per kilogram of ammonia vapor generated, determine the overall performance of this system.

10.37 The performance of an ammonia absorption cycle refrigerator is to be compared with that of a similar vapor-compression system. Consider an absorption system having an evaporator temperature of −10°C and a condenser temperature of 48°C. The generator temperature in this system is 150°C. In this cycle 0.42 kJ is transferred to the ammonia in the evaporator for each kilojoule transferred from the high-temperature source to the ammonia solution in the generator. To make the comparison, assume that a reservoir is available at 150°C, and that heat is transferred

from this reservoir to a reversible engine that rejects heat to the surroundings at 25°C. This work is then used to drive an ideal vapor-compression system with ammonia as the refrigerant. Compare the amount of refrigeration that can be achieved per kilojoule from the high-temperature source with the 0.42 kJ that can be achieved in the absorption system.

10.38 A stoichiometric mixture of gasoline and air has an energy release upon combustion of approximately 2800 kJ/kg of the mixture. To approximate an actual spark-ignition engine using such a mixture, consider an air-standard Otto cycle that has a heat addition of 2800 kJ/kg of air, a compression ratio of 9, and a pressure and temperature at the beginning of the compression process of 100 kPa, 20°C. Assuming constant specific heat, with the value from Table A.9, determine

(a) The maximum pressure and temperature of the cycle.
(b) The thermal efficiency of the cycle.
(c) The mean effective pressure.

10.38E A stoichiometric mixture of gasoline and air has an energy release upon combustion of approximately 1200 Btu/lbm of the mixture. To approximate an actual spark-ignition engine using such a mixture, consider an air-standard Otto cycle that has a heat addition of 1200 Btu/lbm of air, a compression ratio of 9, and a pressure and temperature at the beginning of the compression process of 14.7 lbf/in.^{2}, 70 F. Assuming constant specific heat, with the value from Table A.9, determine

(a) The maximum pressure and temperature of the cycle.
(b) The thermal efficiency of the cycle.
(c) The mean effective pressure.

10.39 Repeat Problem 10.38, but assume variable specific heat. The ideal-gas air tables, Table A.11, are recommended for this calculation (and specific heat from Fig. 5.10 at high temperature).

10.40 When methanol (probably produced from coal) is considered as an alternative fuel to gasoline for automotive engines, it is recognized that the engine can be designed with a higher compression ratio, say 12 instead of 9, but that the energy release upon combustion for a stoichiometric mixture with air is slightly smaller, about 2700 kJ/kg. Repeat Problem 10.38 using these values, and compare the results.

10.41 It has been determined experimentally that the power stroke expansion in an internal-combustion engine can be approximated reasonably as a polytropic process with a value of the polytropic exponent n somewhat smaller than the specific heat ratio k. Repeat Problem 10.38 but assume that the expansion process is reversible and polytropic (instead of the isentropic expansion of the Otto cycle) with a value of n equal to 1.25.

10.42 In an air-standard Otto cycle, all the heat transfer q_H occurs at constant volume. It would be more realistic to assume that part of the q_H occurs after the piston has started to move downward in the expansion stroke. Therefore, consider a cycle identical to the Otto cycle, except that the first two-thirds of the total q_H occurs at constant volume and the final one-third occurs at constant pressure. Assume that the total q_H in this cycle is 2400 kJ/kg, that the pressure and temperature at the beginning of the compression process are 100 kPa, 25°C, and that the compression ratio is 10. Calculate the maximum pressure and temperature and the thermal efficiency of this cycle. Compare the results with those of a conventional Otto cycle having the same given variables.

10.42E In an air-standard Otto cycle, all the heat transfer q_H occurs at constant volume. It would be more realistic to assume that part of the q_H occurs after the piston has started to move downward in the expansion stroke. Therefore, consider a cycle identical to the Otto cycle, except that the first two-thirds of the total q_H occurs at constant volume and the final one-third occurs at constant pressure. Assume that the total q_H in this cycle is 1100 Btu/lbm, that the pressure and temperature at the beginning of the compression process are 14.7 lbf/in.^{2}, 70 F, and that the compression ratio is 10. Calculate the maximum pressure and temperature and the thermal efficiency of this cycle. Compare the results with those of a conventional Otto cycle having the same given variables.

10.43 Consider an ideal air-standard Diesel cycle in which the state before the compression process is 100 kPa, 300 K, and the compression ratio is 18. What maximum temperature must the cycle register to have a thermal efficiency of 60 percent?

10.43E Consider an ideal air-standard Diesel cycle in which the state before the compression process is 14.7 lbf/in.^{2}, 80 F, and the compression ratio is 18. What maximum temperature must the cycle register to have a thermal efficiency of 60 percent?

10.44 A simple Rankine cycle with R-22 as the working fluid is to be used as a bottoming cycle for an electrical generating facility driven by a Diesel engine. (The exhaust gas from the Diesel cycle is used as the high-temperature energy source in the R-22 boiler.) Diesel inlet conditions are 100 kPa, 20°C, the compression ratio is 20, and the maximum temperature in the cycle is 2800°C. Saturated-vapor R-22 leaves the bottoming cycle boiler at 110°C, and the condenser temperature is 30°C. The power output of the Diesel engine is 1.0 MW. Assuming ideal cycles throughout, determine

(a) The flow rate required in the Diesel cycle.

(b) The power output of the bottoming cycle, assuming that the Diesel exhaust is cooled to 200°C in the R-22 boiler.

10.45 Consider an ideal Stirling-cycle engine in which the pressure and temperature at the beginning of the isothermal compression process are 100 kPa, 25°C, the compression ratio is 6, and the maximum temperature in the cycle is 1100°C. Calculate

(a) The maximum pressure in the cycle.

(b) The thermal efficiency of the cycle with and without regenerators.

10.45E Consider an ideal Stirling-cycle engine in which the pressure and temperature at the beginning of the isothermal compression process are 14.7 lbf/in.^{2}, 80 F, the compression ratio is 6, and the maximum temperature in the cycle is 2000 F. Calculate

(a) The maximum pressure in the cycle.

(b) The thermal efficiency of the cycle with and without regenerators.

10.46 Consider an ideal air-standard Ericsson cycle that has an ideal regenerator. The amount of high-temperature heat supplied is 1000 kJ/kg; it is supplied at a temperature of 1500 K. Heat is rejected in the cycle at a temperature of 300 K, and the cycle pressure at the beginning of the isothermal compression process is 100 kPa. Determine the compressor work and the turbine work per kilogram of air and the thermal efficiency of the cycle.

10.47 Consider an ideal air-standard Stirling cycle with an ideal regenerator. The minimum pressure and temperature in the cycle are 100 kPa, 25°C, the compression ratio is 10, and the maximum temperature in the cycle is 1000°C. Analyze each of the four processes in this cycle for work and heat transfer, and determine the overall performance of the engine.

10.48 Consider an ideal air-standard Brayton cycle in which the pressure and temperature of the air entering the compressor are 100 kPa, 20°C, and the pressure ratio across the compressor is 12 to 1. The maximum temperature in the cycle is 1100°C, and the air flow rate is 10 kg/s. Assume constant specific heat for the air, with the value from Table A.9.

(a) Determine the compressor work, the turbine work, and the thermal efficiency of the cycle.

(b) If this cycle were to be used for a reciprocating machine, what would be the mean effective pressure? Would you recommend the Brayton cycle for a reciprocating machine?

10.49 Repeat Problem 10.48, but assume variable specific heat for the air.

10.50 An ideal regenerator is incorporated into the ideal air-standard Brayton cycle of Problem 10.48. Calculate the thermal efficiency of the cycle with this modification.

10.51 Consider a large stationary gas-turbine power plant that operates on the ideal Brayton cycle and delivers a power output of 100 MW to an electric generator. The minimum temperature in the cycle is 300 K, and the maximum temperature is 1600 K. The minimum pressure in the cycle is 100 kPa, and the compressor pressure ratio is 14.

(a) Calculate the power output of the turbine. What fraction of the turbine output is required to drive the compressor?

(b) What is the thermal efficiency of the cycle?

10.51E Consider a large stationary gas-turbine power plant that operates on the ideal Brayton cycle and delivers a power output of 100 000 hp to an electric generator. The minimum temperature in the cycle is 540 R, and the maximum temperature is 2900 R. The minimum pressure in the cycle is 1 atm, and the compressor pressure ratio is 14.

(a) Calculate the power output of the turbine. What fraction of the turbine output is required to drive the compressor?

(b) What is the thermal efficiency of the cycle?

10.52 Repeat Problem 10.51, but assume that the compressor has an isentropic efficiency of 85 percent and the turbine an isentropic efficiency of 88 percent.

10.53 Repeat Problem 10.52, but include a regenerator with 75 percent efficiency to the cycle.

10.54 The gas-turbine cycle shown in Fig. 10.44 is to be used as an automotive engine. In the first turbine, the gas expands to pressure P_5, just low enough for this turbine to drive the compressor. The gas is then expanded through a second turbine connected to the drive wheels. The data for this engine are as shown in the figure. Consider the working fluid to be air throughout the entire cycle, and assume that all processes are ideal. Determine

(a) The intermediate pressure P_5.

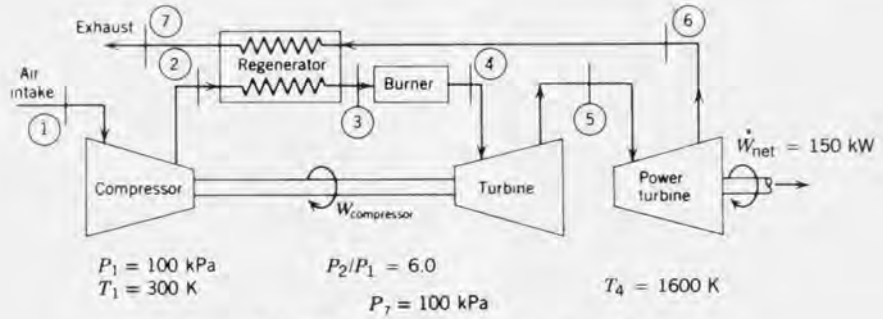


FIGURE 10.44 Sketch for Problem 10.54.

(b) The net work output of the engine per kilogram of air, and the mass flow rate through the engine.

(c) The air temperature entering the burner T_3, and the thermal efficiency of the engine.

10.55 Repeat Problem 10.54, but assume that the compressor has an efficiency of 82 percent, that both turbines have efficiencies of 87 percent, and that the regenerator efficiency is 70 percent. Also assume that friction causes pressure drops in the burner and on both sides of the regenerator. In each case, the pressure drop is estimated to be 2 percent of the inlet pressure to that component of the system.

10.56 The power plant shown in Fig. 10.45 combines a gas-turbine cycle and a steam-turbine cycle. The following data are known for the gas-turbine cycle. Air enters the compressor at 100 kPa, 25°C, the compressor pressure ratio is 14, and the isentropic compressor efficiency is 87 percent; the heater input rate is 60 MW; the turbine inlet temperature is 1250°C, the exhaust pressure is 100 kPa, and the isentropic turbine efficiency is 87 percent; the cycle exhaust temperature from the heat exchanger is 200°C. The following data are known for the steam-turbine cycle. The pump inlet state is saturated liquid at 10 kPa, the pump exit pressure is 12.5 MPa, and the isentropic pump efficiency is 85 percent; turbine inlet temperature is 500°C and the isentropic turbine efficiency is 87 percent. Determine

(a) The mass flow rate of air in the gas-turbine cycle.
(b) The mass flow rate of water in the steam cycle.
(c) The overall thermal efficiency of the combined cycle.

10.57 A gas-turbine engine is to be used for pumping natural gas through a cross-country pipeline. The required power input from this engine to the natural gas compressor is 1.0 MW. A simple open cycle with a regenerator will be used for this application. Since a supply of fuel is readily available, and since some of these units may be located in relatively isolated places, low maintenance costs are more important than efficiency. Making assumptions for the isentropic efficiencies of the compressor and turbine and also for the regenerator efficiency, recommend a cycle. For the gas-turbine engine unit, determine the power output of the turbine, the power input to the compressor, and the thermal efficiency of the engine.

10.58 Consider an ideal gas-turbine cycle with two stages of compression and two stages of expansion. The pressure ratio across each compressor stage and each turbine stage is 8 to 1. The pressure at the entrance to the first compressor is 100 kPa, the temperature entering each compressor is 20°C, and the temperature entering each

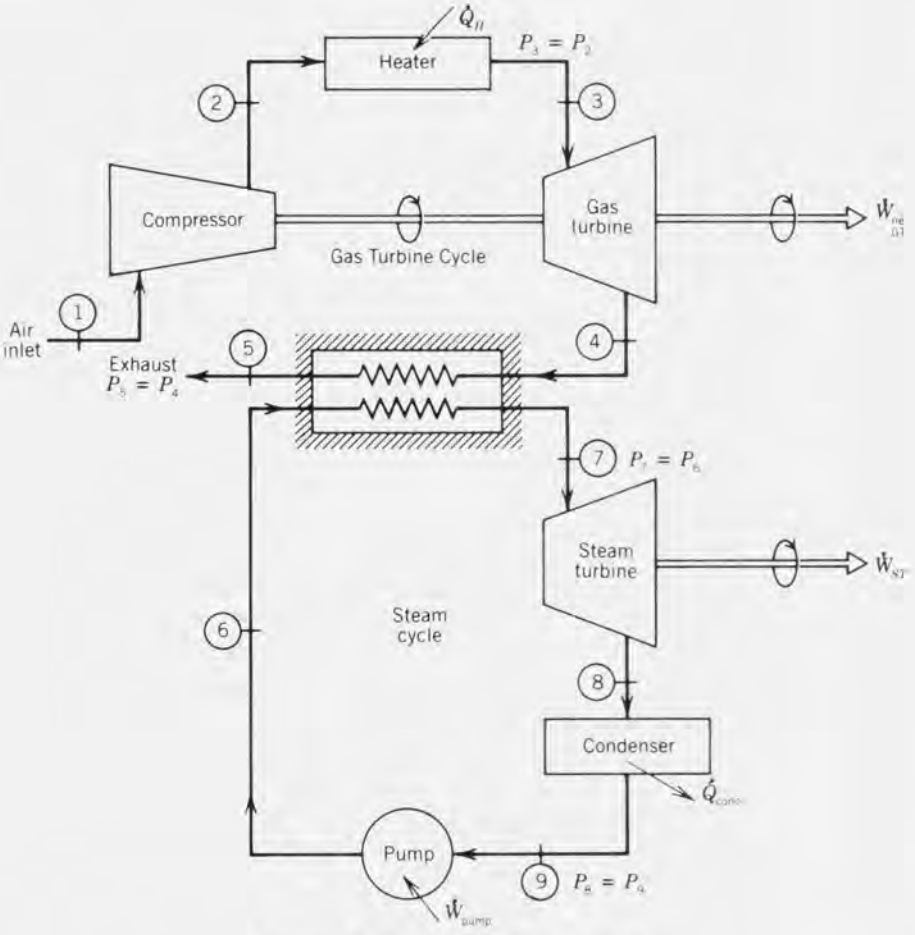


FIGURE 10.45 Sketch for Problem 10.56.

turbine is 1100°C. An ideal regenerator is also incorporated into the cycle. Determine the compressor work, the turbine work, and the thermal efficiency of the cycle.

10.59 Repeat Problem 10.58, but assume that each compressor stage and each turbine stage has an isentropic efficiency of 85 percent. Also assume that the regenerator has an efficiency of 70 percent.

10.60 Consider an ideal air-standard cycle for a gas-turbine, jet propulsion unit, such as that shown in Fig. 10.34. The pressure and temperature entering the compressor are 100 kPa, 290 K. The pressure ratio across the compressor is 14 to 1, and the turbine inlet temperature is 1500 K. When the air leaves the turbine, it enters the nozzle and expands to 100 kPa. Determine the pressure at the nozzle inlet and the velocity of the air leaving the nozzle.

10.61 Repeat Problem 10.60, but assume that the isentropic compressor efficiency is 87 percent, the isentropic turbine efficiency is 89 percent, and the isentropic nozzle efficiency is 96 percent.

10.62 A jet aircraft is flying at an altitude of 4900 m, where the ambient pressure is approximately 55 kPa and the ambient temperature is $-18°C$. The velocity of the aircraft is 280 m/s, and the pressure ratio across the compressor is 14. Devise an air-standard cycle that approximates this engine, and determine the velocity (relative to the aircraft) of the air leaving the engine. Assume that the air has been expanded to the ambient pressure. In addition, assume a maximum gas temperature of 1450 K in the engine.

10.63 A heat exchanger is incorporated into an ideal air-standard refrigeration cycle, as shown in Fig. 10.46. It may be assumed that both the compression and expansion are reversible adiabatic processes in this ideal case. Determine the coefficient of performance for the cycle.

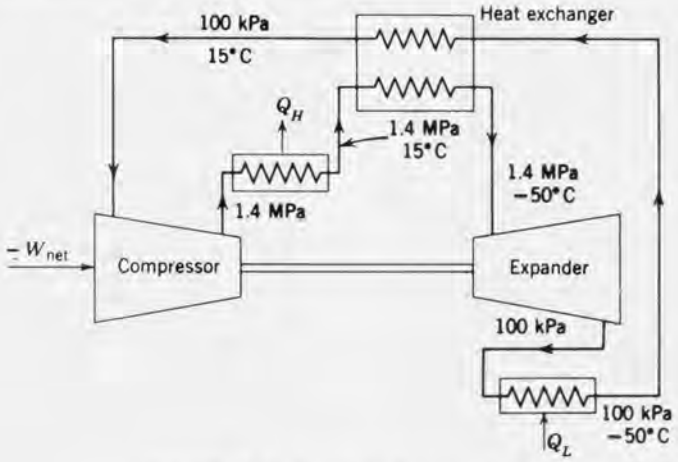


FIGURE 10.46 Sketch for Problem 10.63.

10.64 Repeat Problem 10.63, but assume an isentropic efficiency of 75 percent for both the compressor and the expander.

10.65 Repeat Problems 10.63 and 10.64, but assume that helium is the cycle's working fluid instead of air. Discuss the significance of the results.

COMPUTER PROBLEMS

10.1C Write a program to solve the general case of Problems 10.4, 10.5, and 10.6. The effects of turbine exhaust pressure, inlet pressure, and inlet temperature on the ideal Rankine steam cycle are to be studied.

10.2C Extend the program of Problem 10.1C to include the effects of turbine and pump isentropic efficiencies.

10.3C Write a program to solve the general case of Problems 10.8, 10.9, and 10.10. The effects of reheat pressure and the number of reheats on the ideal reheat steam cycle are to be studied.

10.4C Extend the program of Problem 10.3C to include the effects of turbine and pump isentropic efficiencies.

10.5C Write a program to solve the general case of Problems 10.11, 10.12, and 10.13. The effects of feedwater heater extraction pressure, the number of heaters, and open-versus-closed heaters on the ideal regenerative steam cycle are to be studied.

10.6C Extend the program of Problem 10.5C to include the effects of turbine and pump isentropic efficiencies.

10.7C Write a program to solve the general case of Problem 10.14. The effect of feedwater heater extraction pressure on a combined reheat and regenerative steam cycle is to be studied. The effects of turbine and pump isentropic efficiencies should also be included.

10.8C Write a program to solve the general case of Problem 10.20. The effects of the high pressure and temperature and also the state of the two process streams on the performance of the cogeneration plant are to be studied.

10.9C Write a program to solve the general case of Problem 10.23. The ideal refrigeration–heat pump cycle using ammonia as the working fluid is to be studied. The study should include ranges of condenser temperature and evaporator temperature appropriate to the operation of refrigerators, air-conditioning systems, and heat pumps.

10.10C Write a program to solve the following problem. The effects of varying parameters on the performance of an air-standard Brayton cycle are to be determined. Consider a compressor inlet condition of 100 kPa, 20°C, and assume constant specific heat. The thermal efficiency of the cycle and the net work output per kilogram should be determined for all combinations of the following variables.

(a) Compressor pressure ratio of 6, 9, 12, and 15.
(b) Maximum cycle temperature of 900°C, 1100°C, 1300°C, and 1500°C.
(c) Compressor and turbine isentropic efficiencies each 100, 90, 80, and 70 percent.

10.11C Write a program to solve the following problem. The effect of variable specific heat on the results of Problem 10.10C is to be studied. Use, as necessary, the ideal-gas "enthalpy" and "relative pressure" functions that are curve-fitted polynomial functions of temperature from Table A.11 values.

10.12C Write a program to solve the following problem. Consider an ideal Otto cycle operating with nitrogen gas as the working fluid. The condition at the beginning of the compression process is 100 kPa, 20°C. Assume variable specific heat according to the equation in Table A.10. Determine the net work output per kilogram and the cycle thermal efficiency for various combinations of compression ratio and maximum cycle temperature. Compare the results with those found when constant specific heat is assumed.

10.13C Write a program to solve the following problem. The performances of the ideal Otto and Diesel cycles are to be compared. Repeat Problem 10.12C for the Diesel cycle operating with nitrogen gas as the working fluid. Use the specific heat equation given in Table A.10.

10.14C Write a program to solve the following problem. The effect of the number of stages on the performance of an ideal gas-turbine cycle having intercooling, reheat, and a regenerator, as shown in Fig. 10.31 (for two stages), is to be studied. Assume that the inlet condition, point 1, is 100 kPa, 20°C, and that the total pressure ratio,

the maximum temperature in the cycle, and the number of stages (equal number of compressor and turbine stages) are all variable. Each stage has an equal pressure ratio. Determine the net work output per kilogram and the thermal efficiency of the cycle for various combinations of these variables.

10.15C Write a program to solve the following problem. The effect of variable specific heat on the results of Problem 10.14C is to be studied. Repeat that problem, but use the ideal-gas polynomial functions for air developed in the program of Problem 10.11C.

10.16C Write a program to solve the following problem. We wish to study the effect of irreversible component processes on the results of Problem 10.15C. Repeat that problems for various values of the isentropic efficiencies of the compressor and turbine and for various values of the regenerator efficiency.

10.17C Write a program to solve the following problem. We wish to study the performance of an air-standard refrigeration cycle incorporating a heat exchanger, as shown in Fig. 10.46. The pressure and temperature at the inlet to the compressor are 100 kPa, 15°C. The pressure ratio across the compressor and expander and also the isentropic efficiencies of the compressor and expander are to be taken as variables in this study.

10.18C Write a program to solve the general case of the combined-cycle power plant of Problem 10.56, as shown in Fig. 10.45. The gas-turbine cycle compressor pressure ratio and the turbine inlet temperature are to be taken as input variables, as are the maximum pressure and temperature in the steam cycle.

11

AN INTRODUCTION TO THE THERMODYNAMICS OF MIXTURES

Up to this point in our development of thermodynamics, we have considered primarily pure substances. A large number of processes, however, use mixtures of different pure substances. Sometimes these mixtures are referred to as solutions—particularly in the liquid and solid phases.

This chapter introduces the thermodynamics of mixtures and solutions. The word "introduces" should be emphasized because the thermodynamics of mixtures and solutions is a rather complex subject, and a detailed presentation is beyond the scope of this book. The focus will be on mixtures of ideal gases and a simplified, but very useful model of certain mixtures, such as air and water vapor, in which one of the components may also be in a condensed (solid or liquid) phase. An attempt has been made to present the material so that this introduction can lead directly to a more comprehensive study of mixtures.

An understanding of the material in this chapter is a necessary foundation for the consideration of chemical reactions and chemical and phase equilibrium. These topics are covered in the chapters that follow.

11.1 GENERAL CONSIDERATIONS AND MIXTURES OF IDEAL GASES

In any mixture, the mole fraction of component i is defined as

$$y_i = \frac{n_i}{n} \tag{11.1}$$

where n_i, is the number of moles of component i, and n is the total number of moles in the mixture.

Similarly, the mass fraction mf_i is

$$\mathrm{mf}_i = \frac{m_i}{m} \tag{11.2}$$

where m_i is the mass of component i and m is the total mass of the mixture.

Consider a mixture of two gases (not necessarily ideal gases) such as that shown in Fig. 11.1. What properties can we experimentally measure for such a mixture? Certainly we can measure the pressure, temperature, volume, and mass of the mixture. We can also experimentally measure the composition of the mixture and thus determine the mole and mass fractions.

Suppose that this mixture undergoes a process or a chemical reaction and we wish to perform a thermodynamic analysis of this process or reaction. What type of thermodynamic data would we use in performing such an analysis? One possibility would be to have tables of thermodynamic properties of mixtures. The number of possible mixtures is very large, however, both because there are many substances to choose from, and because the relative amounts of each substance in a mixture can vary. We would need a library full of tables of thermodynamic properties to handle all possible situations. It would be much simpler if we could determine the thermodynamic properties of a mixture from the properties of the pure components. This is in essence the approach used in dealing with ideal gases and certain other simplified models of mixtures.

One exception to this procedure is a particular mixture that is encountered very frequently, the most familiar being air. Tables and charts of the thermodynamic properties of air are available. However, even in this case, it is necessary to define the composition of the "air" for which the tables are given, because the composition of the atmosphere varies with altitude, with the number of pollutants, and with other variables at a given location. The composition of air on which air tables are usually based is as follows:

Component	*Percent on Mole Basis*
Nitrogen	78.10
Oxygen	20.95
Argon	0.92
Carbon dioxide and trace elements	0.03

Consider again the mixture of Fig. 11.1. For the general case the properties of the mixture are defined in terms of the partial molal properties of the individual components. A partial molal property is defined as the value of a property, such as internal energy, for a given component as it exists in the mixture. With this definition, the internal energy of the mixture of Fig. 11.1 would be

$$U_{\text{mix}} = n_A \overline{U}_A + n_B \overline{U}_B \tag{11.3}$$

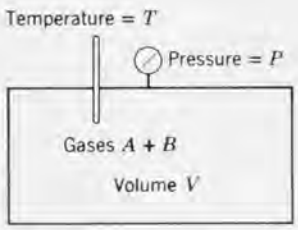


FIGURE 11.1 A mixture of two gases.

where $\overline{U}$ designates the partial molal internal energy. Similar equations can be written for other properties. This matter will be developed further in Chapters 12 and 14.

In this chapter we focus on mixtures of ideal gases. We assume that each component is uninfluenced by the presence of the other components, and that each component can be treated as an ideal gas. In an actual case of a gaseous mixture at high pressure, this assumption would probably not be true because of the nature of the interaction between the molecules of the different components.

Two models are used in analyzing the mixtures of gases—the Dalton model and the Amagat model.

DALTON MODEL

For the Dalton model, the properties of each component are considered as though each component existed separately at the volume and temperature of the mixture, as shown in Fig. 11.2.

Consider this model for the special case in which both the mixture and the separated components can be considered an ideal gas.

For the mixture:

$$PV = n\overline{R}T \qquad n = n_A + n_B \tag{11.4}$$

For the components:

$$P_AV = n_A\overline{R}T \qquad P_BV = n_B\overline{R}T \tag{11.5}$$

On substituting, we have

$$n = n_A + n_B$$

$$\frac{PV}{\overline{R}T} = \frac{P_AV}{\overline{R}T} + \frac{P_BV}{\overline{R}T} \tag{11.6}$$

or

$$P = P_A + P_B$$

where P_A and P_B are referred to as partial pressures. Thus, for a mixture of ideal gases, the pressure is the sum of the partial pressures of the individual components.

It should be stressed that the term partial pressure is relevant only for ideal gases. This concept assumes that the molecules of each component are uninfluenced by the other components, and that the total pressure is the sum of partial pressures

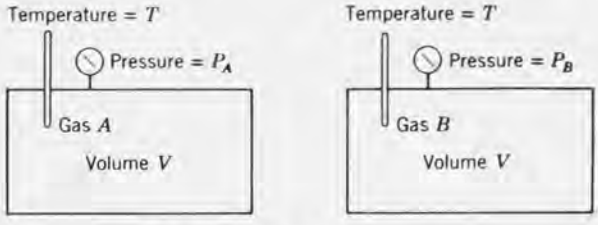


FIGURE 11.2 The Dalton model.

of the individual components. It should also be noted that partial pressure is not a partial molal property in the sense defined by Eq. 11.3, since partial molal properties relate only to the extensive properties.

AMAGAT MODEL

In the Amagat model the properties of each component are considered as though each component existed separately at the pressure and temperature of the mixture, as shown in Fig. 11.3. The volumes of A and B under these conditions are V_A and V_B, respectively.

In the general case, the sum of the volumes when separated—$V_A + V_B$—need not be equal to the volume of the mixture. However, let us consider the special case in which both the separated components and the mixture are considered to be ideal gases. We can write

For the mixture:

$$PV = n\bar{R}T \qquad n = n_A + n_B \tag{11.7}$$

For the components:

$$PV_A = n_A\bar{R}T \qquad PV_B = n_B\bar{R}T \tag{11.8}$$

On substituting, we have,

$$n = n_A + n_B$$

$$\frac{PV}{\bar{R}T} = \frac{PV_A}{\bar{R}T} + \frac{PV_B}{\bar{R}T}$$

Therefore,

$$V_A + V_B = V$$

or

$$\frac{V_A}{V} + \frac{V_B}{V} = 1 \tag{11.9}$$

where V_A/V and V_B/V are the volume fractions.

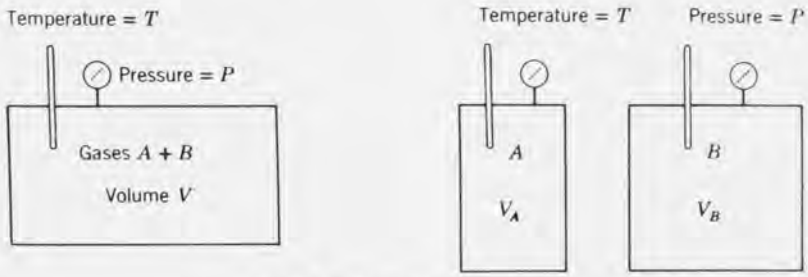


FIGURE 11.3 The Amagat model.

Thus, for ideal gases, Amagat's model leads to the conclusion that the sum of the volume fractions is unity, and that there would be no volume change if the components are mixed while holding the temperature and pressure constant.

From Eqs. 11.4, 11.5, 11.7, and 11.8, it is evident that

$$\frac{V_A}{V} = \frac{n_A}{n} = \frac{P_A}{P}$$

$$\frac{V_A}{V} = y_A = \frac{P_A}{P} \tag{11.10}$$

That is, for each component of a mixture of ideal gases, the volume fraction, the mole fraction, and the ratio of the partial pressure to the total pressure are equal.

In determining the internal energy, enthalpy, and entropy of a mixture of ideal gases, the Dalton model proves useful because the assumption is made that each constituent behaves as though it occupies the entire volume by itself. Thus, the internal energy, enthalpy, and entropy can be evaluated as the sum of the respective properties of the constituent gases at the condition at which the component exists in the mixture. Since for ideal gases the internal energy and enthalpy are functions only of temperature, it follows that

$$U = n\bar{u} = n_A\bar{u}_A + n_B\bar{u}_B \tag{11.11}$$

$$H = n\bar{h} = n_A\bar{h}_A + n_B\bar{h}_B \tag{11.12}$$

where $\bar{u}_A$ and $\bar{h}_A$ are the internal energy and enthalpy per mole for pure A, and $\bar{u}_B$ and $\bar{h}_B$ are the same quantities for pure B. All the quantities are at the temperature of the mixture.

The entropy of an ideal gas is a function of pressure as well as of temperature. Since each component exists in the mixture at its partial pressure,

$$S = n\bar{s} = n_A\bar{s}_A + n_B\bar{s}_B \tag{11.13}$$

where $\bar{s}_A$ is the entropy per mole for pure A at T and P_A (the partial pressure of A), and $\bar{s}_B$ is the entropy per mole for pure B at T and P_B.

EXAMPLE 11.1

A volumetric analysis of a gaseous mixture yields the following results:

Component	*Percent by Volume*
CO_2	12.0
O_2	4.0
N_2	82.0
CO	2.0

Determine the analysis on a mass basis. Determine the molecular weight and the gas constant on a mass basis for the mixture. Assume ideal-gas behavior.

System: Gas mixture.

State: Composition known.

TABLE 11.1

Constituent	Percent by Volume	Mole Fraction		Molecular Weight		Mass, kg per kmol of Mixture	Analysis on Mass Basis, percent
CO_2	12	0.12	×	44.0	=	5.28	$\frac{5.28}{30.08} = 17.55$
O_2	4	0.04	×	32.0	=	1.28	$\frac{1.28}{30.08} = 4.26$
N_2	82	0.82	×	28.0	=	22.96	$\frac{22.96}{30.08} = 76.33$
CO	2	0.02	×	28.0	=	0.56	$\frac{0.56}{30.08} = 1.86$
						30.08	100.00

Solution

It is convenient to set up and solve the problem as shown in Table 11.1. From this table, we note that

$$\text{Molecular weight of mixture} = 30.08$$

Therefore,

$$R \text{ for mixture} = \frac{\overline{R}}{M} = \frac{8.3144}{30.08} = 0.2764 \text{ kJ/kg K}$$

If the analysis has been given on a mass basis and the mole fraction or volumetric analysis is desired, the procedure shown in Table 11.2 can be used.

$$M = \frac{1}{\text{kmol/kg mixture}} = \frac{1}{0.033\,24} = 30.08$$

$$R = \frac{\overline{R}}{M} = \frac{8.3144}{30.08} = 0.2764 \text{ kJ/kg K}$$

TABLE 11.2

Constituent	Mass Fraction		Molecular Weight		kmol per kg of Mixture	Mole Fraction	Volumetric Analysis, percent
CO_2	0.1755	÷	44.0	=	0.003 99	0.120	12.0
O_2	0.0426	÷	32.0	=	0.001 33	0.040	4.0
N_2	0.7633	÷	28.0	=	0.027 26	0.820	82.0
CO	0.0186	÷	28.0	=	0.000 66	0.020	2.0
					0.033 24	1.000	100.0

EXAMPLE 11.2

Let n_A moles of gas A at a given pressure and temperature be mixed with n_B moles of gas B at the same pressure and temperature in an adiabatic constant-volume process, as shown in Fig. 11.4. Determine the increase in entropy for this process.

System: All gas (A and B).

Initial states: P, T known for A and B.

Final state: P, T of mixture known.

Sketch: Figure 11.4.

Analysis and Solution

The final partial pressure of gas A is P_A, and for gas B it is P_B. Since there is no change in temperature, Eq. 8.22 reduces to

$$(S_2 - S_1)_A = -n_A \bar{R} \ln \frac{P_A}{P} = -n_A \bar{R} \ln y_A$$

$$(S_2 - S_1)_B = -n_B \bar{R} \ln \frac{P_B}{P} = -n_B \bar{R} \ln y_B$$

The total change in entropy is the sum of the entropy changes for gases A and B.

$$S_2 - S_1 = -\bar{R}(n_A \ln y_A + n_B \ln y_B)$$

The result of Example 11.2 can readily be generalized to account for the mixing of any number of components at the same temperature and pressure. The result is

$$S_2 - S_1 = -\bar{R} \sum_k n_k \ln y_k \tag{11.14}$$

The interesting thing about this equation is that the increase in entropy depends only on the number of moles of component gases and is independent of the composition of the gas. For example, when 1 mol of oxygen and 1 mol of nitrogen are mixed, the increase in entropy is the same as when 1 mol of hydrogen and 1 mol of nitrogen are mixed. But we also know that if 1 mol of nitrogen is "mixed" with another mole of nitrogen, there is no increase in entropy. The question is how dissimilar must the gases be to have an increase in entropy? The answer lies in our ability to distinguish between the two gases. The entropy increases whenever

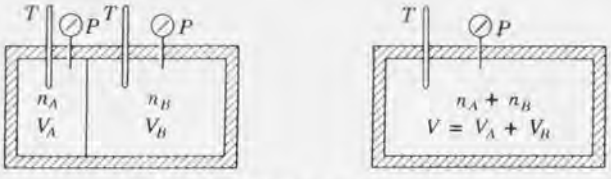


FIGURE 11.4 Sketch for Example 11.2.

we can distinguish between the gases being mixed. When we cannot distinguish between the gases, there is no increase in entropy.

11.2 A SIMPLIFIED MODEL OF A MIXTURE OF GASES AND A VAPOR

Let us now consider a simplification, which is often a reasonable one, of the problem of a mixture of ideal gases that is in contact with a solid or liquid phase of one of the components. The most familiar example is a mixture of air and water vapor in contact with liquid water or ice, as encountered in air conditioning or in drying. We are all familiar with the condensation of water from the atmosphere when it cools on a summer day.

This problem and a number of similar problems can be analyzed quite simply and with considerable accuracy if the following assumptions are made.

1. The solid or liquid phase contains no dissolved gases.
2. The gaseous phase can be treated as a mixture of ideal gases.
3. When the mixture and the condensed phase are at a given pressure and temperature, the equilibrium between the condensed phase and its vapor is not influenced by the presence of the other component. This means that when equilibrium is achieved, the partial pressure of the vapor will be equal to the saturation pressure corresponding to the temperature of the mixture.

Since this approach is used extensively and with considerable accuracy, let us give some attention to the terms that have been defined and the type of problems for which this approach is valid and relevant. In our discussion we will refer to this process as a gas–vapor mixture.

The dew point of a gas–vapor mixture is the temperature at which the vapor condenses or solidifies when it cools at constant pressure. This is shown on the T–s diagram for the vapor, given in Fig. 11.5. Suppose that the temperature of the gaseous mixture and the partial pressure of the vapor in the mixture are such that the vapor is initially superheated at state 1. If the mixture cools at constant pressure, the partial pressure of the vapor remains constant until point 2 is reached

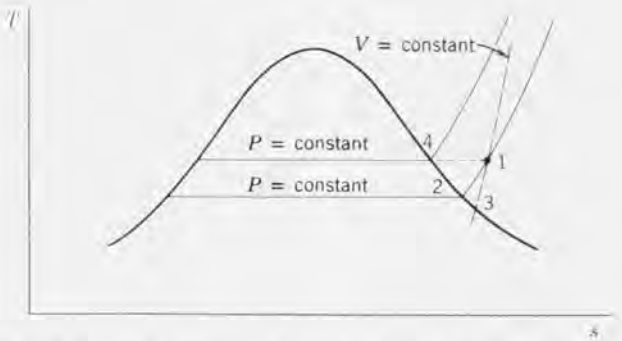


FIGURE 11.5 *Temperature-entropy diagram to show definition of the dew point.*

and then condensation begins. The temperature at state 2 is the dew-point temperature. Line 1–3 on the diagram indicates that if the mixture cools at constant volume, the condensation begins at point 3, which is slightly lower than the dew-point temperature.

If the vapor is at the saturation pressure and temperature, the mixture is referred to as a saturated mixture, and for an air–water vapor mixture, the term "saturated air" is used.

The relative humidity ϕ is defined as the ratio of the mole fraction of the vapor in the mixture to the mole fraction of vapor in a saturated mixture at the same temperature and total pressure. Since the vapor is considered an ideal gas, the definition reduces to the ratio of the partial pressure of the vapor as it exists in the mixture, P_v, to the saturation pressure of the vapor at the same temperature, P_g.

$$\phi = \frac{P_v}{P_g}$$

In terms of the numbers on the T–s diagram of Fig. 11.5, the relative humidity ϕ would be

$$\phi = \frac{P_1}{P_4}$$

Because we consider the vapor to be an ideal gas, the relative humidity can also be defined in terms of specific volume or density.

$$\phi = \frac{P_v}{P_g} = \frac{\rho_v}{\rho_g} = \frac{v_g}{v_v} \tag{11.15}$$

The humidity ratio ω of an air–water vapor mixture is defined as the ratio of the mass of water vapor m_v to the mass of dry air m_a. The term "dry air" emphasizes that only the air and not the water vapor is referred to. The term "specific humidity" is used synonymously with humidity ratio.

$$\omega = \frac{m_v}{m_a} \tag{11.16}$$

This definition is identical for any other gas–vapor mixture, and the subscript a refers to the gas, exclusive of the vapor. Since we consider both the vapor and the mixture to be ideal gases, a very useful expression for the humidity ratio in terms of partial pressures and molecular weights can be developed.

$$m_v = \frac{P_v V}{R_v T} = \frac{P_v V M_v}{\bar{R} T}, \quad m_a = \frac{P_a V}{R_a T} = \frac{P_a V M_a}{\bar{R} T}$$

Then

$$\omega = \frac{P_v V / R_v T}{P_a V / R_a T} = \frac{R_a P_v}{R_v P_a} = \frac{M_v P_v}{M_a P_a} \tag{11.17}$$

For an air–water vapor mixture this equation reduces to

$$\omega = 0.622 \frac{P_v}{P_a} \tag{11.18}$$

The degree of saturation is defined as the ratio of the actual humidity ratio to the humidity ratio of a saturated mixture at the same temperature and total pressure.

An expression for the relation between the relative humidity ϕ and the humidity ratio ω can be found by solving Eqs. 11.15 and 11.18 for P_v and equating them. The resulting relation for an air–water vapor mixture is

$$\phi = \frac{\omega P_a}{0.622 P_g} \tag{11.19}$$

A few words should also be said about the nature of the process that occurs when a gas–vapor mixture cools at constant pressure. Suppose that the vapor is initially superheated at state 1 in Fig. 11.6. As the mixture cools at constant pressure, the partial pressure of the vapor remains constant until the dew point is reached at point 2, where the vapor in the mixture is saturated. The initial condensate is at state 4 and is in equilibrium with the vapor at state 2. As the temperature lowers further, more of the vapor condenses, which lowers the partial pressure of the vapor in the mixture. The vapor that remains in the mixture is always saturated, and the liquid or solid is in equilibrium with it. For example, when the temperature is reduced to T_3, the vapor in the mixture is at state 3. Its partial pressure is the saturation pressure corresponds to T_3. The liquid in equilibrium with it is at state 5.

EXAMPLE 11.3

Consider 100 m^3 of an air–water vapor mixture at 0.1 MPa, 35°C, 70 percent relative humidity. Calculate the humidity ratio, dew point, mass of air, and mass of vapor.

System: Mixture.

State: P, T, ϕ known; state fixed.

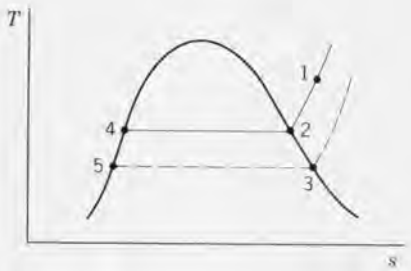


FIGURE 11.6 Temperature-entropy diagram to show the cooling of a gas-vapor mixture at a constant pressure.

Analysis and Solution

From Eq. 11.15 and the steam tables,

$$\phi = 0.70 = \frac{P_v}{P_g}$$

$$P_v = 0.70(5.628) = 3.94 \text{ kPa}$$

The dew point is the saturation temperature corresponding to this pressure, which is 28.6°C.

The partial pressure of the air is

$$P_a = P - P_v = 100 - 3.94 = 96.06 \text{ kPa}$$

The humidity ratio can be calculated from Eq. 11.18.

$$\omega = 0.622 \times \frac{P_v}{P_a} = 0.622 \times \frac{3.94}{96.06} = 0.0255$$

The mass of air is

$$m_a = \frac{P_a V}{R_a T} = \frac{96.06 \times 100}{0.287 \times 308.2} = 108.6 \text{ kg}$$

The mass of the vapor can be calculated using the humidity ratio or the ideal-gas equation of state.

$$m_v = \omega m_a = 0.0255(108.6) = 2.77 \text{ kg}$$

$$m_v = \frac{3.94 \times 100}{0.461\,52 \times 308.2} = 2.77 \text{ kg}$$

EXAMPLE 11.4

Calculate the amount of water vapor condensed if the mixture of Example 11.3 is cooled to 5°C in a constant-pressure process.

System: Mixture.

Initial state: *Known* (*Example* 11.3).

Final state: T known.

Process: Constant pressure.

Analysis: At the final temperature, 5°C, the mixture is saturated, since this is below the dew-point temperature. Therefore,

$$P_{v2} = P_{g2}, \qquad P_{a2} = P - P_{v2}$$

and

$$\omega_2 = 0.622 \frac{P_{v2}}{P_{a2}}$$

From the conservation of mass, it follows that the amount of water condensed is equal to the difference between the initial and final masses of water vapor, or

$$\text{Mass of vapor condensed} = m_a(\omega_1 - \omega_2)$$

Solution

$$P_{v2} = P_{g2} = 0.8721 \text{ kPa}$$
$$P_{a2} = 100 - 0.8721 = 99.128 \text{ kPa}$$
$$\omega_2 = 0.622 \times \frac{0.8721}{99.128} = 0.0055$$
$$\text{Mass of vapor condensed} = m_a(\omega_1 - \omega_2) = 108.6(0.0255 - 0.0055) = 2.172 \text{ kg}$$

11.3 THE FIRST LAW APPLIED TO GAS-VAPOR MIXTURES

When the first law of thermodynamics is applied to gas–vapor mixtures, to calculate changes of internal energy and enthalpy, it is helpful to realize that because of our assumption that ideal gases are involved, the various components can be treated separately. Therefore, in dealing with air–water vapor mixtures, we find the changes in enthalpy of the water vapor from the steam tables, and the ideal-gas relations can be applied to the air. These points are illustrated by Examples 11.5 and 11.6.

EXAMPLE 11.5

An air-conditioning unit is shown in Fig. 11.7, with pressure, temperature, and relative-humidity data. Calculate the heat transfer per kilogram of dry air, assuming that changes in kinetic energy are negligible.

Control volume: Duct, excluding cooling coils.

Inlet state: Known (Fig. 11.7).

Exit state: Known (Fig. 11.7).

Process: SSSF, no kinetic or potential energy changes.

Model: Air—ideal gas, constant specific heat, value at 300 K. Water—steam tables. (Since the water vapor at these low pressures is considered an ideal gas, the enthalpy of the water vapor is a function of the temperature only. Therefore, the enthalpy of slightly superheated water vapor is equal to the enthalpy of saturated vapor at the same temperature.)

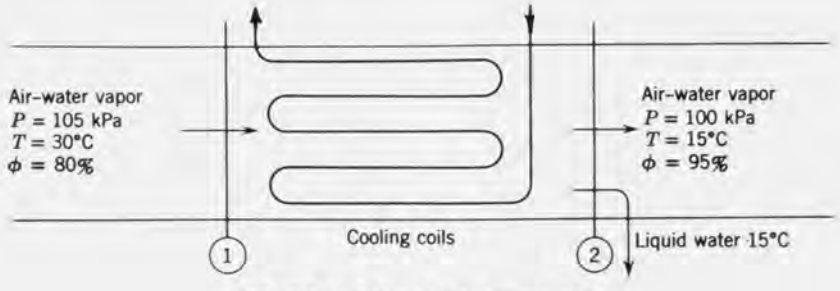


FIGURE 11.7 Sketch for Example 11.5.

Analysis:

Continuity, air and water:

$$\dot{m}_{a1} = \dot{m}_{a2}$$
$$\dot{m}_{v1} = \dot{m}_{v2} + \dot{m}_{l2}$$

First law:

$$\dot{Q}_{c.v.} + \sum \dot{m}_i h_i = \sum \dot{m}_e h_e$$
$$\dot{Q}_{c.v.} + \dot{m}_a h_{a1} + \dot{m}_{v1} h_{v1} = \dot{m}_a h_{a2} + \dot{m}_{v2} h_{v2} + \dot{m}_{l2} h_{l2}$$

If we divide this equation by $\dot{m}_a$, introduce the continuity equation for the water, and note that $\dot{m}_v = \omega \dot{m}_a$, we can write the first law in the form

$$\frac{\dot{Q}_{c.v.}}{\dot{m}_a} + h_{a1} + \omega_1 h_{v1} = h_{a2} + \omega_2 h_{v2} + (\omega_1 - \omega_2) h_{l2}$$

Solution

The humidity ratios are calculated as follows:

$$P_{v1} = \phi P_{g1} = 0.80(4.246) = 3.397 \text{ kPa}$$
$$\omega_1 = \frac{R_a}{R_v} \frac{P_{v1}}{P_{a1}} = 0.622 \times \frac{3.397}{105 - 3.4} = 0.0208$$
$$P_{v2} = \phi_2 P_{g2} = 0.95(1.7051) = 1.620 \text{ kPa}$$
$$\omega_2 = \frac{R_a}{R_v} \times \frac{P_{v2}}{P_{a2}} = 0.622 \times \frac{1.62}{100 - 1.62} = 0.0102$$

Substituting gives

$$\dot{Q}_{c.v.}/\dot{m}_a + h_{a1} + \omega_1 h_{v1} = h_{a2} + \omega_2 h_{v2} + (\omega_1 - \omega_2) h_{l2}$$
$$\dot{Q}_{c.v.}/\dot{m}_a = 1.0035(15 - 30) + 0.0102(2528.9) - 0.0208(2556.3) + (0.0208 - 0.0102)(62.99)$$
$$= -41.76 \text{ kJ/kg dry air}$$

EXAMPLE 11.6

A tank has a volume of 0.5 m^3 and contains nitrogen and water vapor. The temperature of the mixture is 50°C and the total pressure is 2 MPa. The partial pressure of the water vapor is 5 kPa. Calculate the heat transferred when the contents of the tank are cooled to 10°C.

System: Nitrogen and water.

Initial state: P_1, T_1 known; state fixed.

Final state: T_2 known.

Process: Constant volume.

Model: Ideal-gas mixture; constant specific heat for nitrogen; steam tables for water.

Analysis: This is a constant-volume process. Since the work is zero, the first law reduces to

$$Q = U_2 - U_1 = m_{N_2} C_{v(N_2)}(T_2 - T_1) + (m_2 u_2)_v + (m_2 u_2)_l - (m_1 u_1)_v$$

This equation assumes that some of the vapor condensed. This assumption must be checked, however, as shown in the solution.

Solution

The mass of nitrogen and water vapor can be calculated using the ideal-gas equation of state.

$$m_{N_2} = \frac{P_{N_2} V}{R_{N_2} T} = \frac{1995 \times 0.5}{0.2968 \times 323.2} = 10.39 \text{ kg}$$

$$m_{v1} = \frac{P_{v1} V}{R_v T} = \frac{5 \times 0.5}{0.461\,52 \times 323.2} = 0.016\,76 \text{ kg}$$

If condensation takes place, the final state of the vapor will be saturated vapor at 10°C. Therefore,

$$m_{v2} = \frac{P_{v2} V}{R_v T} = \frac{1.2276 \times 0.5}{0.461\,52 \times 283.2} = 0.004\,70 \text{ kg}$$

Since this amount is less than the original mass of vapor, there must have been condensation.

The mass of liquid that is condensed, m_{l2}, is

$$m_{l2} = m_{v1} - m_{v2} = 0.016\,76 - 0.004\,70 = 0.012\,06 \text{ kg}$$

The internal energy of the water vapor is equal to the internal energy of saturated water vapor at the same temperature. Therefore,

$$\begin{aligned} u_{v1} &= 2443.5 \text{ kJ/kg} \\ u_{v2} &= 2389.2 \text{ kJ/kg} \\ u_{l2} &= 42.0 \text{ kJ/kg} \\ Q_{c.v.} &= 10.39 \times 0.7448(10 - 50) + 0.0047(2389.2) \\ &\quad + 0.012\,06(42.0) - 0.016\,76(2443.5) \\ &= -338.8 \text{ kJ} \end{aligned}$$

11.4 THE ADIABATIC SATURATION PROCESS

An important process for an air–water vapor mixture is the adiabatic saturation process. In this process, an air–vapor mixture comes in contact with a body of water in a well-insulated duct (Fig. 11.8). If the initial relative humidity is less than 100 percent, some of the water will evaporate and the temperature of the air–vapor mixture will decrease. If the mixture leaving the duct is saturated and if the process is adiabatic, the temperature of the mixture on leaving is known as the adiabatic

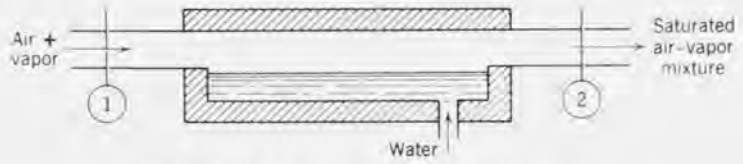


FIGURE 11.8 The adiabatic saturation process.

saturation temperature. For this to take place as a steady-flow process, make-up water at the adiabatic saturation temperature is added at the same rate that water is evaporated. The pressure is assumed to be constant.

Considering the adiabatic saturation process to be a steady-state, steady-flow process and neglecting changes in kinetic and potential energy reduces the first law to

$$\begin{aligned} h_{a1} + \omega_1 h_{v1} + (\omega_2 - \omega_1)h_{l2} &= h_{a2} + \omega_2 h_{v2} \\ \omega_1(h_{v1} - h_{l2}) &= C_{pa}(T_2 - T_1) + \omega_2(h_{v2} - h_{l2}) \\ \omega_1(h_{v1} - h_{l2}) &= C_{pa}(T_2 - T_1) + \omega_2 h_{fg2} \end{aligned} \tag{11.20}$$

The most significant point to be made about the adiabatic saturation process is that the adiabatic saturation temperature, the temperature of the mixture when it leaves the duct, is a function of the pressure, temperature, and relative humidity of the entering air–vapor mixture and of the exit pressure. Thus, the relative humidity and the humidity ratio of the entering air–vapor mixture can be determined from the measurements of the pressure and temperature of the air–vapor mixture entering and leaving the adiabatic saturator. Since these measurements are relatively easy to make, this is one means of determining the humidity of an air–vapor mixture.

EXAMPLE 11.7

The pressure of the mixture entering and leaving the adiabatic saturator is 0.1 MPa, the entering temperature is 30°C, and the temperature leaving is 20°C, which is the adiabatic saturation temperature. Calculate the humidity ratio and relative humidity of the air–water vapor mixture entering.

Control volume: Adiabatic saturator.

Inlet state: P_1, T_1 known.

Exit state: P_2, T_2 known; $\phi_2 = 100$ percent; state fixed.

Process: SSSF, adiabatic saturation (Fig. 11.8).

Model: Ideal-gas mixture, constant specific heat for air, steam tables for water.

Analysis: Continuity and first law, Eq. 11.20.

Solution

Since the water vapor leaving is saturated, $P_{v2} = P_{g2}$, and ω_2 can be calculated.

$$\omega_2 = 0.622 \times \frac{2.339}{100 - 2.34} = 0.0149$$

In addition, ω_1 can be calculated using Eq. 11.20.

$$\omega_1 = \frac{C_{pa}(T_2 - T_1) + \omega_2 h_{fg2}}{h_{v1} - h_{l2}}$$

$$\omega_1 = \frac{1.0035(20 - 30) + 0.0149 \times 2454.1}{2556.3 - 83.96} = 0.0107$$

$$\omega_1 = 0.0107 = 0.622 \times \frac{P_{v1}}{100 - P_{v1}}$$

$$P_{v1} = 1.691 \text{ kPa}$$

$$\phi_1 = \frac{P_{v1}}{P_{g1}} = \frac{1.691}{4.246} = 0.398$$

11.5 WET-BULB AND DRY-BULB TEMPERATURES

The humidity of air–water vapor mixtures has traditionally been measured with a device called a psychrometer, which uses the flow of air past wet-bulb and dry-bulb thermometers. The bulb of the wet-bulb thermometer is covered with a cotton wick that is saturated with water. The dry-bulb thermometer is used simply to measure the temperature of the air. The airflow can be maintained by a fan, as shown in the continuous-flow psychrometer depicted in Fig. 11.9.

The processes that take place at the wet-bulb thermometer are somewhat complicated. First, if the air–water vapor mixture is not saturated, some of the water in the wick evaporates and diffuses into the surrounding air, which cools the water in the wick. As soon as the temperature of the water drops, however, heat is transferred to the water from both the air and the thermometer, with corresponding cooling. A steady state, determined by heat and mass transfer rates, will be reached, in which the wet-bulb thermometer temperature is lower than the dry-bulb temperature.

It can be argued that this evaporative cooling process is very similar, but not identical, to the adiabatic saturation process described and analyzed in Section 11.4. In fact, the adiabatic saturation temperature is often termed the thermodynamic wet-bulb temperature. It is clear, however, that the wet-bulb temperature

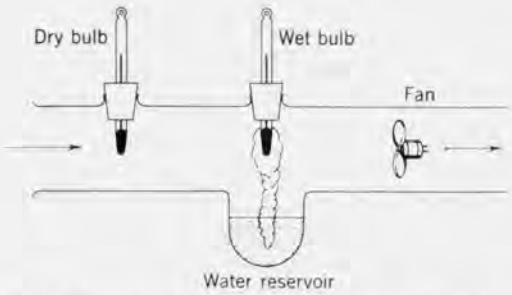


FIGURE 11.9 Steady-flow apparatus for measuring wet- and dry-bulb temperatures.

as measured by a psychrometer is influenced by heat and mass transfer rates, which depend, for example, on the airflow velocity and not simply on thermodynamic equilibrium properties. It does happen that the two temperatures are very close for air–water vapor mixtures at atmospheric temperature and pressure, and they will be assumed to be equivalent in this text.

In recent years, humidity measurements have been made using other phenomena and other devices, primarily electronic devices for convenience and simplicity. For example, some substances tend to change in length, in shape, or in electrical capacitance, or in a number of other ways, when they absorb moisture. They are therefore sensitive to the amount of moisture in the atmosphere. An instrument making use of such a substance can be calibrated to measure the humidity of air–water vapor mixtures. The instrument output can be programmed to furnish any of the desired parameters, such as relative humidity, humidity ratio, or wet-bulb temperature.

11.6 THE PSYCHROMETRIC CHART

Properties of air–water vapor mixtures are given in graphical form on psychrometric charts. These charts are available in a number of different forms, and only their principal features are considered here.

The basic psychrometric chart plots the dry-bulb temperature (abscissa) versus the humidity ratio (ordinate). If we fix the total pressure for which the chart is to be constructed (in our chart, Fig. A.6, this is 1 bar or 0.1 MPa), lines of constant relative humidity and wet-bulb temperature can be drawn on the chart, because for a given dry-bulb temperature, total pressure, and humidity ratio, the relative humidity and wet-bulb temperature are fixed. The partial pressure of the water vapor is fixed by the humidity ratio and total pressure, and therefore a second ordinate scale that indicates the partial pressure of the water vapor can be constructed.

Most psychrometric charts give the enthalpy of an air–vapor mixture per kilogram of dry air. The values assume that the enthalpy of the dry air is zero at $-20^{\circ}C$, and the enthalpy of the vapor is taken from the steam tables (which are based on the assumption that the enthalpy of saturated liquid is zero at $0^{\circ}C$). This procedure is satisfactory because we are usually concerned only with differences in enthalpy. The fact that lines of constant enthalpy are essentially parallel to lines of constant wet-bulb temperature is evident because the wet-bulb temperature is essentially equal to the adiabatic saturation temperature. Thus, in Fig. 11.8, if we neglect the enthalpy of the liquid entering the adiabatic saturator, the enthalpy of the air-vapor mixture entering is equal to the enthalpy of the saturated air–vapor mixture leaving, and a given adiabatic saturation temperature fixes the enthalpy of the mixture entering.

Some charts that give corrections for variation from standard atmospheric pressures are available. Before using a particular chart, one should fully understand the assumptions made in constructing it, and whether it is applicable to the particular problem at hand.

PROBLEMS

11.1 A carbureted internal-combustion engine is converted to run on methane gas. The air–fuel ratio in the cylinder is to be 20 to 1 on a mass basis. How many moles of oxygen per mole of methane are there in the cylinder?

11.2 The mixture specified in Problem 11.1 is at 90 kPa, 30°C, at the beginning of the compression stroke in the engine cycle. The engine compression ratio (volume ratio) is 9 to 1. Assuming that the compression is reversible and adiabatic, determine the pressure and temperature at the end of the compression stroke. Determine also the compression work input per kilogram of mixture.

11.3 At a certain point in a coal gasification process, a sample of the gas is taken and stored in a 1-L cylinder. An analysis of this mixture yields the following results:

Component	*Percent by Volume*
H_2	35
CO	50
CO_2	15

Determine

(a) The mixture composition on a mass basis.
(b) The mass of sample in the cylinder at 100 kPa, 20°C.
(c) The amount of heat that must be transferred to heat the sample at constant volume from the initial state to 100°C.

11.4 The gas mixture from Problem 11.3 is compressed in a reversible adiabatic process from the initial state in the sample cylinder to a volume of 0.2 L. Determine the final temperature of the mixture and the work done during this process.

11.5 Two insulated tanks A and B are connected by a valve. Tank A has a volume of 1 m^3 and initially contains argon at 300 kPa, 10°C. Tank B has a volume of 2 m^3 and initially contains ethane at 200 kPa, 50°C. The valve is opened and remains open until the resulting gas mixture comes to a uniform state. Determine

(a) The final pressure and temperature.
(b) The entropy change for the process.

11.5E Two insulated tanks A and B are connected by a valve. Tank A has a volume of 30 ft^3 and initially contains argon at 50 lbf/$in.^2$, 50 F. Tank B has a volume of 60 ft^3 and initially contains ethane at 30 lbf/$in.^2$, 120 F. The valve is opened and remains open until the resulting gas mixture comes to a uniform state. Determine

(a) The final pressure and temperature.
(b) The entropy change for the process.

11.6 Recent developments in semipermeable membrane technology have been successfully applied to a number of industrial gas separation processes. One particular application is the partial removal of oxygen from air that is to be fed through a grain elevator storage facility. Ambient air (assume 79 mole percent nitrogen, 21 mole percent oxygen) is to be compressed to an appropriate pressure, cooled to ambient temperature, 25°C, and then fed through a bundle of hollow polymer fibers that selectively absorb oxygen, to the extent that the exiting mixture at 120 kPa, 25°C, contains only 5 percent oxygen. The absorbed oxygen is bled off

through the fiber walls at 40 kPa, 25°C, to a vacuum pump. What is the minimum inlet air pressure to the fiber bundle?

11.7 A spherical balloon has an initial diameter of 1 m and contains argon gas at 200 kPa, 40°C. The balloon is connected by a valve to a 500-L rigid tank containing carbon dioxide at 100 kPa, 100°C. The valve is opened, and eventually the balloon and tank reach a uniform state in which the pressure is 185 kPa. In the range of variables of this process, it may be assumed that the pressure inside the balloon is always directly proportional to its diameter. Considering the balloon and tank as a system, calculate the final temperature and the heat transfer for the process.

11.7E A spherical balloon has an initial diameter of 3 ft and contains argon gas at 30 lbf/in.^{2}, 100 F. The balloon is connected by a valve to a 20-ft^3 rigid tank containing carbon dioxide at 15 lbf/in.^{2}, 200 F. The valve is opened, and eventually the balloon and tank reach a uniform state in which the pressure is 25 lbf/in.^{2}. In the range of variables of this process, it may be assumed that the pressure inside the balloon is always directly proportional to its diameter. Considering the balloon and tank as a system, calculate the final temperature and the heat transfer for the process.

11.8 A 100-L insulated tank contains nitrogen gas at 200 kPa and ambient temperature 25°C. The tank is connected by a valve to a supply line flowing carbon dioxide at 1.2 MPa, 90°C. A mixture of 50 mole percent nitrogen and 50 mole percent carbon dioxide is to be obtained by opening the valve and allowing flow into the tank until an appropriate pressure is reached. At this point the valve closed. What is this pressure? The tank eventually cools to ambient temperature. Calculate the net entropy change for the overall process.

11.9 A large SSSF air separation plant takes in ambient air (79 percent N_2 and 21 percent O_2 by volume) at 100 kPa, 20°C, at the rate of 1 kmol/s. It discharges a stream of pure O_2 gas at 200 kPa, 100°C, and a stream of pure N_2 gas at 100 kPa, 20°C. The plant operates on an electrical power input of 2000 kW. Calculate the net rate of entropy change for the process.

11.9E A large SSSF air separation plant takes in ambient air (79 percent N_2 and 21 percent O_2 by volume) at 14.7 lbf/in.^{2}, 70 F, at the rate of 2 lb mol/s. It discharges a stream of pure O_2 gas at 30 lbf/in.^{2}, 200 F, and a stream of pure N_2 gas at 14.7 lbf/in.^{2}, 70 F. The plant operates on an electrical power input of 2000 kW. Calculate the net rate of entropy change for the process.

11.10 The only known sources of helium are the atmosphere (mole fraction approximately 5×10^{-6}) and natural gas. A large unit is being constructed to separate 100 m^3/s of natural gas, assumed to be 0.001 He mole fraction and 0.999 CH_4. The gas enters the unit at 150 kPa, 10°C. Pure helium exits at 100 kPa, 20°C, and pure methane exits at 140 kPa, 30°C. Any heat transfer is with the surroundings at 20°C. Is an electrical power input of 3000 kW sufficient to drive this unit?

11.11 A 0.2-m^3 insulated, rigid vessel is divided into two equal parts A and B by an insulated partition, as shown in Fig. 11.10. The partition will support a pressure difference of up to 400 kPa before breaking. Side A contains methane and side B contains carbon dioxide. Both sides are initially at 1 MPa, 30°C. A valve on side B is opened, and carbon dioxide flows out. It may be assumed that any carbon dioxide remaining inside side B undergoes a reversible adiabatic expansion while there is flow out of the vessel. Eventually, the partition breaks, and the valve is

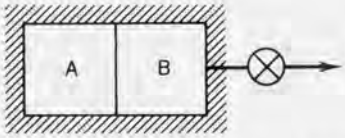


FIGURE 11.10 Sketch for Problem 11.11.

closed. Calculate the net entropy change for the process that begins when the valve is closed.

11.12 Consider a room of dimensions 4 m × 6 m × 2.5 m that contains an air–water vapor mixture at 100 kPa, 15°C, and 20 percent relative humidity. How much water would have to be added to this space for the room to be at 100 kPa, 25°C, and have 50 percent relative humidity?

11.12E Consider a room of dimensions 12 ft × 18 ft × 8 ft that contains an air–water vapor mixture at 14.7 lbf/in.^{2}, 60 F, and 20 percent relative humidity. How much water would have to be added to this space for the room to be at 14.7 lbf/in.^{2}, 75 F, and have 50 percent relative humidity?

11.13 The products of combustion of a hydrocarbon fuel with air are analyzed, with the following results:

Component	*Percent by Volume*
CO_2	10.4
CO	0.1
H_2O	11.8
O_2	3.4
N_2	74.3

This gas mixture passes through a SSSF heat exchanger at ambient pressure at the rate of 0.1 kg/s. What is the dew-point temperature? If the mixture is cooled 10°C below the dew-point temperature, how long will it take to collect 10 kg of liquid water?

11.14 A new high-efficiency home heating system includes an air-to-air heat exchanger which uses energy from outgoing stale air to heat the incoming fresh air. If the outside ambient temperature is −10°C and the relative humidity is 30 percent, how much water will have to be added to the incoming air, if it flows in at the rate of 1 m^3/s and must eventually be conditioned to 20°C and 40 percent relative humidity?

11.15 Consider a 500-L rigid tank containing an air–water vapor mixture at 100 kPa, 35°C, with a relative humidity of 70 percent. This system is cooled until the water just begins to condense. Determine the final temperature in the tank and the heat transfer for the process.

11.15E Consider a 10-ft^3 rigid tank containing an air–water vapor mixture at 14.7 lbf/in.^{2}, 90 F, with a relative humidity of 70 percent. This system is cooled until the water just begins to condense. Determine the final temperature in the tank and the heat transfer for the process.

11.16 Ambient air (air plus vapor) enters a steady-flow air-conditioning unit at 102 kPa, 30°C, with a relative humidity of 60 percent. The volume flow rate entering the

unit is 100 L/s. The air–vapor mixture leaves the air-conditioning unit at 95 kPa, 15°C, with a relative humidity of 100 percent. Liquid condensate also leaves the unit at 15°C. Determine the rate of heat transfer for this process.

11.17 A saturated air–water vapor mixture at 20°C, 100 kPa, is contained in a 5-m^3 closed tank in equilibrium with 1 kg of liquid water. The tank is heated to 80°C.

(a) Is there any liquid water at the final state?
(b) Calculate the heat transfer for the process.

11.18 Outdoor ambient air (air plus vapor) enters a steady-flow heater–humidifier unit at 0°C, 100 kPa, 50 percent relative humidity, at the volumetric flow rate of 0.1 m^3/s. Liquid water at 10°C is sprayed into the mixture, and enough heat is transferred that the air–vapor mixture leaves the unit at 30°C, 100 kPa, 35 percent relative humidity. Determine

(a) The mass flow rate of liquid water sprayed into the mixture.
(b) The rate of heat transfer to the unit.

11.18E Outdoor ambient air (air plus vapor) enters a steady-flow heater–humidifier unit at 32 F, 14.7 $lbf/in.^2$, 50 percent relative humidity, at the volumetric flow rate of 5 ft^3/s. Liquid water at 50 F is sprayed into the mixture, and enough heat is transferred that the air–vapor mixture leaves the unit at 85 F, 14.7 $lbf/in.^2$, 35 percent relative humidity. Determine

(a) The mass flow rate of liquid water sprayed into the mixture.
(b) The rate of heat transfer to the unit.

11.19 A new high-efficiency home heating system uses an air-to-air heat exchanger, in which the outgoing stale air heats the incoming fresh air in a counterflow SSSF heat exchanger. The unit is advertised as "recovering 80 percent of the energy" of the outgoing air–vapor stream. Using a reasonable assumption for the meaning of this advertising statement, determine the temperature and relative humidity of the incoming air as it exits the heat exchanger. Assume that the room conditions are 100 kPa, 20°C, 40 percent relative humidity, and the outdoor ambient conditions are 100 kPa, −10°C, 40 percent relative humidity.

11.20 A cylinder fitted with a piston restrained by a linear spring (force directly proportional to distance moved) contains a saturated air–water vapor mixture at 120 kPa, 0.1-m^3 volume and ambient temperature, 20°C. The piston area is 0.2 m^2, and the spring constant is 20 kN/m. This cylinder is attached by a valve to a line flowing dry air at 800 kPa, 40°C. The valve is opened, and air flows into the cylinder until the pressure reaches 200 kPa, at which point the temperature inside is 40°C. Determine

(a) The relative humidity at the final state.
(b) The mass of air entering the cylinder.
(c) The work done during the process. Consider the cylinder a control volume.

11.21 Consider the system and process described in Problem 11.20. For this process

(a) Calculate the heat transfer.
(b) Show that the process does not violate the second law.

11.22 One means of air-conditioning hot summer air is by evaporative cooling, which is a process similar to the SSSF adiabatic saturation process. Consider outdoor

ambient air at 35°C, 100 kPa, 30 percent relative humidity. What is the maximum amount of cooling that can be achieved by such a technique? What disadvantage is there to this approach? Solve this problem using

(a) A first-law analysis.
(b) The psychrometric chart, Fig. A.6.

11.23 The air-conditioning by simple evaporative cooling discussed in Problem 11.22 is to be modified by adding a dehumidification process before the water spray cooling process. This dehumidification is to be achieved as shown in Fig. 11.11, by using a desiccant material, which absorbs water on one side of a rotating-drum heat exchanger. The desiccant is regenerated by being heated to a high temperature on the other side of the rotating-drum heat exchanger. The high temperature drives out the water. The state conditions are as shown in the diagram. All pressures are assumed to be 100 kPa. Calculate the relative humidity of the cool air supplied to the room at state 4, and the heat transfer per unit mass of air that needs to be supplied to the unit in the heater.

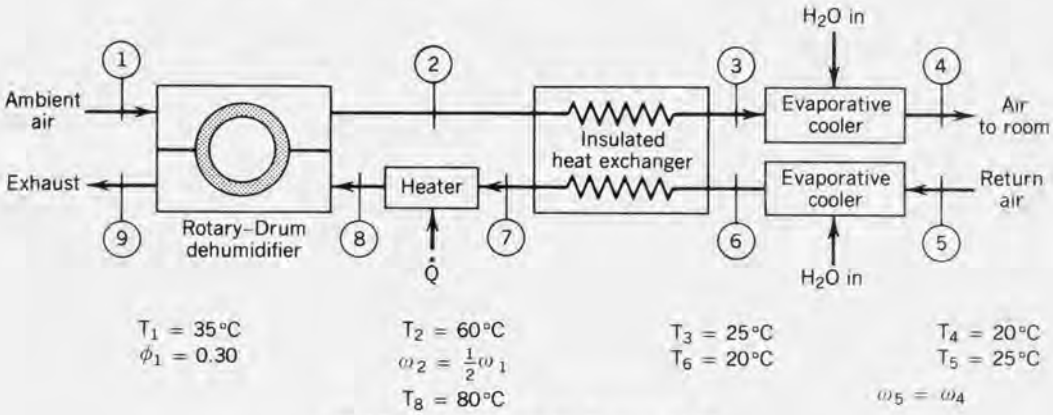


FIGURE 11.11 Sketch for Problem 11.23.

11.24 A combination air cooler and dehumidification unit receives outside ambient air at 35°C, 100 kPa, 90 percent relative humidity. This air–water vapor mixture is first cooled to a low temperature to condense the proper amount of water. The air–vapor mixture is then heated and leaves the unit at 20°C, 100 kPa, 30 percent relative humidity. The volume flow rate of the air–vapor mixture at the exit conditions is 0.01 m^3/s.

(a) Find the temperature to which the mixture is initially cooled and the mass of water condensed per kilogram of dry air. Show the process that the water undergoes on a T–s diagram.

(b) Assuming that all the liquid water condensed leaves the unit at the minimum temperature, calculate the overall heat transfer rate.

11.24E A combination air cooler and dehumidification unit receives outside ambient air at 100 F, 14.7 lbf/in.^{2}, 90 percent relative humidity. This air–water vapor mixture is first cooled to a low temperature to condense the proper amount of water. The air–vapor mixture is then heated and leaves the unit at 70 F, 14.7 lbf/in.^{2}, 30 percent relative humidity. The volume flow rate of the air–vapor mixture at the exit conditions is 0.2 ft^3/s.

(a) Find the temperature to which the mixture is initially cooled and the mass of water condensed per pound-mass of dry air. Show the process that the water undergoes on a T–s diagram.

(b) Assuming that all the liquid water condensed leaves the unit at the minimum temperature, calculate the overall heat transfer rate.

11.25 Ambient air at 100 kPa, 30°C, 40 percent relative humidity is conditioned to 100 kPa, 20°C, 50 percent relative humidity in a SSSF process in the following manner. One stream is cooled at constant pressure to 5°C, and any liquid water condensate is trapped out. The air–vapor stream from this cooler is then mixed with an unconditioned stream to produce the desired state. Calculate

(a) The ratio of the mass flow rates of the two streams.
(b) The required heat transfer in the cooler.

11.26 A 300-L rigid vessel initially contains an air–water vapor mixture at 150 kPa, 40°C, with a relative humidity of 10 percent. A supply line connected to this vessel by a valve carries steam at 600 kPa, 200°C. The valve is opened, and steam flows into the vessel until the relative humidity of the resultant air–water vapor mixture is 90 percent. The valve is then closed. Sufficient heat is transferred from the vessel that the temperature inside remains at 40°C during this process. Determine the heat transfer for the process, the mass of steam entering the vessel, and the final pressure inside the vessel.

11.26E A 10-ft^3 rigid vessel initially contains an air–water vapor mixture at 20 lbf/in.^{2}, 100 F, with a relative humidity of 10 percent. A supply line connected to this vessel by a valve carries steam at 100 lbf/in.^{2}, 400 F. The valve is opened, and steam flows into the vessel until the relative humidity of the resultant air–water vapor mixture is 90 percent. The valve is then closed. Sufficient heat is transferred from the vessel that the temperature inside remains at 100 F during this process. Determine the heat transfer for the process, the mass of steam entering the vessel, and the final pressure inside the vessel.

11.27 Steam power plants often utilize large cooling towers to cool the condenser cooling water so that it can be recirculated and reused in the condenser. The process is essentially adiabatic evaporative cooling, in which part of the cooling water stream is lost and must therefore be made up before returning to the condenser. Consider the case shown schematically in Fig. 11.12, in which 1000 kg/s of warm water at

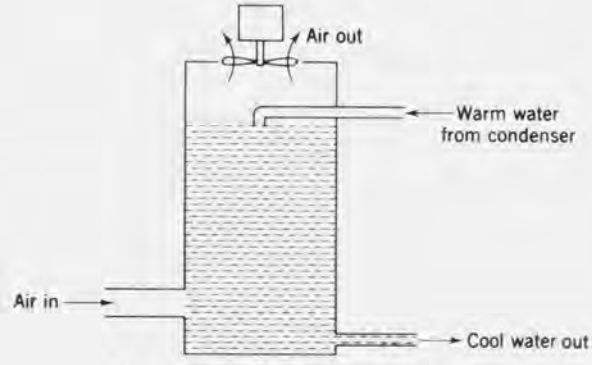


FIGURE 11.12 Sketch for Problem 11.27.

32°C (from the condenser) enters the top of the cooling tower, and the cooled water leaves the bottom at 20°C. The air–water vapor mixture enters the bottom of the cooling tower at 100 kPa. It has a dry-bulb temperature of 18°C and a wet-bulb temperature of 10°C. The air–water vapor mixture leaves the tower at 95 kPa, 30°C, and a relative humidity of 85 percent. Determine the kilograms of dry air per second that must be used and the fraction of the incoming water that evaporates and is lost.

11.28 A vertical cylinder is fitted with a piston held in place by a pin. The initial volume is 200 L and the cylinder contains an air–water vapor mixture at 100 kPa, 25°C, with a wet-bulb temperature of 15°C. The pin is removed, and at the same time a valve on the bottom of the cylinder is opened, allowing the mixture to flow out. A cylinder pressure of 150 kPa is required to balance the piston. The valve is closed when the cylinder volume reaches 100 L, at which point the temperature inside is 15°C.

(a) Is there any liquid water in the cylinder in the final state?

(b) Calculate the heat transfer to the cylinder during the process.

(c) Taking a control volume around the cylinder, calculate the entropy change of the control volume and that of the surroundings.

11.28E A vertical cylinder is fitted with a piston held in place by a pin. The initial volume is 4 ft^3, and the cylinder contains an air–water vapor mixture at 14.7 $lbf/in.^2$, 75 F, with a wet-bulb temperature of 60 F. The pin is removed, and at the same time a valve on the bottom of the cylinder is opened, allowing the mixture to flow out. A cylinder pressure of 20 $lbf/in.^2$ is required to balance the piston. The valve is closed when the cylinder volume reaches 2 ft^3, at which point the temperature inside is 60 F.

(a) Is there any liquid water in the cylinder in the final state?

(b) Calculate the heat transfer to the cylinder during the process.

(c) Taking a control volume around the cylinder, calculate the entropy change of the control volume and that of the surroundings.

11.29 A steady supply of air is available from a line at 200 kPa, 30°C. This line is supplied by compressing ambient air (20°C, 100 kPa, 15°C wet-bulb temperature). No provision has been made to remove water vapor. The line is connected by a valve to a 500-L tank that initially contains water at 80°C, 99 percent quality. The valve is opened until the pressure inside reaches 200 kPa, at which point the temperature inside is 40°C.

(a) How much liquid water is in the tank in the final state?

(b) Calculate the heat transfer from the tank.

(c) Calculate the net entropy change for the tank-filling process (do not include the air-line compressor).

11.30 Ambient air is at a condition of 100 kPa, 35°C, 50 percent relative humidity. A steady stream of air at 100 kPa, 23°C, 70 percent relative humidity, is to be produced, by first cooling one stream to an appropriate temperature to condense out the proper amount of water and then mixing this conditioned stream adiabatically with a second one at ambient conditions. What is the ratio of the two flow rates? To what temperature must the first stream be cooled?

11.30E Ambient air is at a condition of 14.7 $lbf/in.^2$, 95 F, 50 percent relative humidity. A steady stream of air at 14.7 $lbf/in.^2$, 73 F, 70 percent relative humidity, is to be

produced by first cooling one stream to an appropriate temperature to condense out the proper amount of water and then mixing this conditioned stream adiabatically with a second one at ambient conditions. What is the ratio of the two flow rates? To what temperature must the first stream be cooled?

COMPUTER PROBLEMS

11.1C Write a program to solve the general case of Problem 11.5, in which the two volumes and the initial state properties of the argon and ethane are input variables.

11.2C Write a program to solve the general case of Problem 11.8, in which the nitrogen initial state, the carbon dioxide supply line state, and the desired mixture percentages are input variables.

11.3C Write a program to solve the general case of Problem 11.14 (only for ambient temperatures above 0°C), in which the outdoor ambient state and the desired indoor state are program input variables. For this and later program convenience and independence, curve-fit an equation to represent water liquid–vapor saturation pressure as a function of temperature. Use steam table data for the range 0.01°C to 40°C. The form of the equation should be log P_g as a polynomial in T, powers -1 to $+4$.

11.4C Extend the solution range of Problem 11.3C to allow for outdoor ambient temperatures as low as -30°C.

11.5C Use the equation developed in Problem 11.3C as the starting point in writing a program that will perform all the functions of the psychrometric chart, Fig. A.6. For program convenience, curve-fit equations for water saturated-liquid enthalpy and saturated-vapor enthalpy as polynomial functions of temperature (powers 0

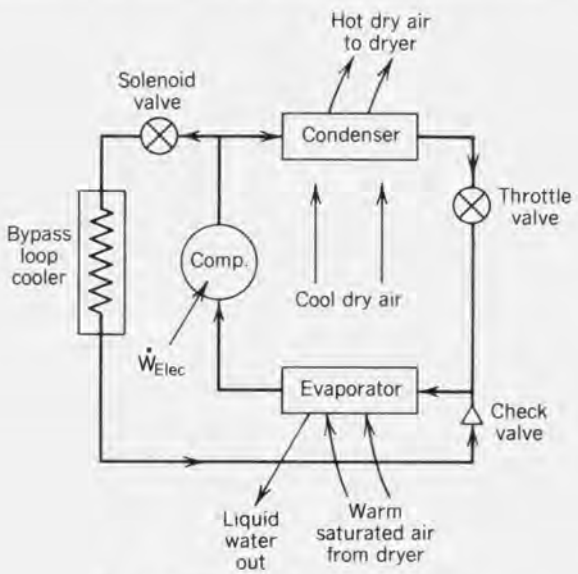


FIGURE 11.13 Sketch for Problem 11.8C.

to 3), as was done earlier for saturation pressure. The final "psychrometric chart" program input parameters are to be pressure, temperature, and one of the following: wet-bulb temperature, relative humidity, or humidity ratio.

11.6C Write a program to solve the general case of Problem 11.18, using the program developed in Problem 11.5C. The outdoor ambient state and the desired indoor state are to be input variables.

11.7C Extend the result of Problem 11.6C to include a second-law analysis. Curve-fit water saturated-liquid entropy and saturated-vapor entropy as polynomial functions of temperature, as was done for enthalpies in Problem 11.5C.

11.8C A heat pump clothes dryer, the principle of which is shown in Fig. 11.13, is to be designed. Warm (and increasing with time) saturated air comes from the clothes dryer and is cooled by flowing over the evaporator coils, thereby condensing out water. The dry air is then heated by passing over the condenser coils. The hot, dry air returns to the clothes dryer. An electrically controlled bypass loop allows control of the air temperature to a maximum of 70°C, and it is also possible to flow air over the evaporator and condenser coils at different rates. Consider the heat pump cycle to be an ideal cycle using ammonia as the working fluid. Evaluate the performance of this clothes dryer as a function of time for a variety of operating conditions.

12

THERMODYNAMIC RELATIONS

We have already defined and used several thermodynamic properties. Among these are pressure, specific volume, density, temperature, mass, internal energy, enthalpy, entropy, constant-pressure specific heat, constant-volume specific heat, and the Joule–Thomson coefficient. Two other properties, the Helmholtz function and the Gibbs function, have been introduced and will be used more extensively in the following chapters. Finally, we have had occasion to use tables of thermodynamic properties for a number of different substances.

One important question is now raised, namely which of the thermodynamic properties can be experimentally measured? We can answer this question by considering the measurements we can make in the laboratory. Some of the properties such as internal energy and entropy cannot be measured directly and must be calculated from other experimental data. If we carefully consider all these thermodynamic properties, we conclude that there are only four that can be directly measured: pressure, temperature, volume, and mass.

This observation leads to a second question, namely how can values of thermodynamic properties that cannot be measured be determined from experimental data on properties that can be measured? In answering this question, we will develop certain general thermodynamic relations. Because there are millions of such equations that can be written, our study will be limited to certain basic considerations, with particular reference to the determination of thermodynamic properties from experimental data. We will also consider such related matters as generalized charts and equations of state.

12.1 TWO IMPORTANT RELATIONS

This chapter concerns partial derivatives, and two important relations are reviewed here. Consider a variable z that is a continuous function of x and y.

$$z = f(x, y)$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

It is convenient to write this function in the form

$$dz = M\,dx + N\,dy \tag{12.1}$$

where

$$M = \left(\frac{\partial z}{\partial x}\right)_y = \text{partial derivative of } z \text{ with respect to } x \text{ (the variable } y \text{ being held constant)}$$

$$N = \left(\frac{\partial z}{\partial y}\right)_x = \text{partial derivative of } z \text{ with respect to } y \text{ (the variable } x \text{ being held constant)}$$

The physical significance of partial derivatives as they relate to the properties of a pure substance can be explained by referring to Fig. 12.1, which shows a P–v–T surface of the superheated vapor region of a pure substance. It shows constant-temperature, constant-pressure, and constant-specific volume planes that intersect at point b on the surface. Thus, the partial derivative $(\partial P/\partial v)_T$ is the slope of curve abc at point b. Line de represents the tangent to curve abc at point b. A similar interpretation can be made of the partial derivatives $(\partial P/\partial T)_v$ and $(\partial v/\partial T)_P$.

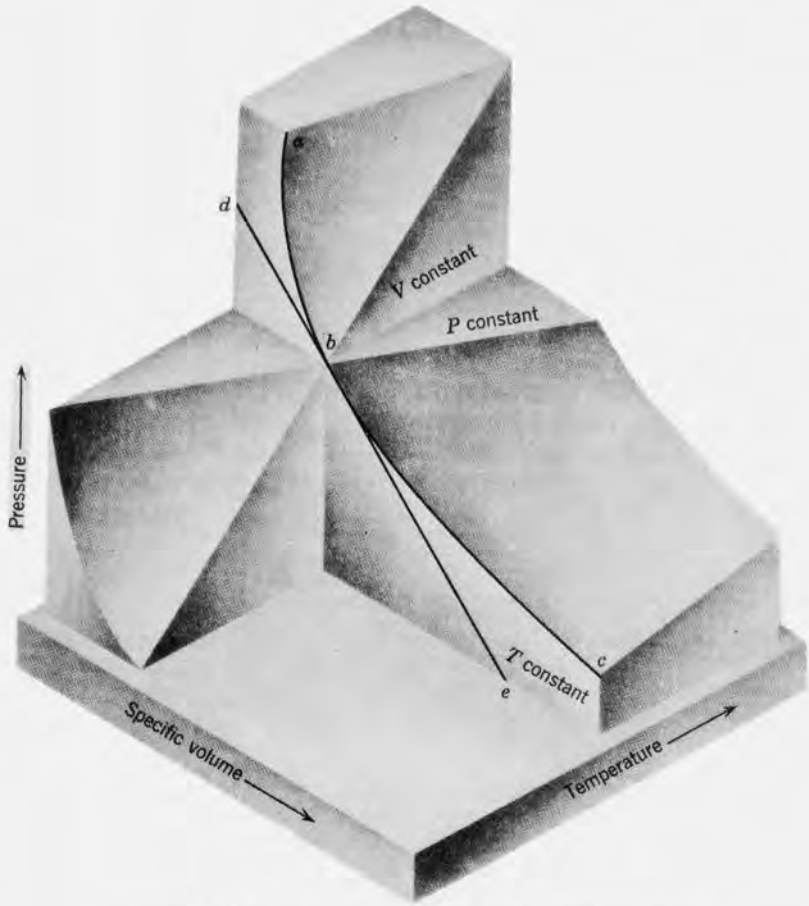


FIGURE 12.1 Schematic representation of partial derivatives.

If we wish to evaluate the partial derivative along a constant-temperature line, the rules for ordinary derivatives can be applied. Thus, we can write for a constant-temperature process

$$\left(\frac{\partial P}{\partial v}\right)_T = \frac{dP_T}{dv_T}$$

and the integration can be performed as usual. This point will be demonstrated later in a number of examples.

Let us return to the consideration of the relation

$$dz = M\,dx + N\,dy$$

If x, y, and z are all point functions (that is, quantities that depend only on the state and are independent of the path), the differentials are exact differentials. When this is so, the following important relation holds:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

The proof of this is

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x\,\partial y}$$
$$\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y\,\partial x}$$

Since the order of differentiation makes no difference when point functions are involved, it follows that

$$\frac{\partial^2 z}{\partial x\,\partial y} = \frac{\partial^2 z}{\partial y\,\partial x}$$
$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

The second important mathematical relation is

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{12.2}$$

The proof of this relation is as follows. Consider three variables x, y, and z. Suppose there exists a relation between the variables of the form

$$x = f(y, z)$$

Then

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \tag{12.3}$$

If this relationship between the three variables is written in the form

$$y = f(x, z)$$

it follows that

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \tag{12.4}$$

Substituting Eq. 12.4 into Eq. 12.3, we have

$$\begin{aligned} dx &= \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\right] + \left(\frac{\partial x}{\partial z}\right)_y dz \\ &= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \end{aligned}$$

There are two independent variables, and we select x and z as these variables. Suppose that $dz = 0$ and $dx \neq 0$. It then follows that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1 \tag{12.5}$$

Similarly, suppose that $dx = 0$ and $dz \neq 0$. It then follows that

$$\begin{aligned} \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y &= 0 \\ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x &= -\left(\frac{\partial x}{\partial z}\right)_y \\ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= -1 \end{aligned}$$

This is Eq. 12.2, which is what we set out to derive.

12.2 THE MAXWELL RELATIONS

Consider a simple compressible system of fixed chemical composition. The Maxwell relations, which can be written for such a system, are four equations relating the properties P, v, T, and s.

The Maxwell relations are most easily derived by considering four relations involving thermodynamic properties. Two of these relations have already been derived and are

$$du = T\,ds - P\,dv \tag{12.6}$$

$$dh = T\,ds + v\,dP \tag{12.7}$$

The other two are derived from the definition of the Helmholtz function, a, and the Gibbs function, g.

$$\begin{aligned} a &= u - Ts \\ da &= du - T\,ds - s\,dT \end{aligned}$$

Substituting Eq. 12.6 into this relation gives the third relation,

$$da = -P\,dv - s\,dT \tag{12.8}$$

Similarly,

$$g = h - Ts$$
$$dg = dh - T\,ds - s\,dT$$

Substituting Eq. 12.7 yields the fourth relation,

$$dg = v\,dP - s\,dT \tag{12.9}$$

Since Eqs. 12.6, 12.7, 12.8, and 12.9 are relations involving properties, we conclude that these are exact differentials and, therefore, are of the general form

$$dz = M\,dx + N\,dy$$

Since

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{12.10}$$

it follows from Eq. 12.6 that

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \tag{12.11}$$

Similarly, from Eqs. 12.7, 12.8, and 12.9, we can write

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \tag{12.12}$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \tag{12.13}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T \tag{12.14}$$

These four equations are known as the Maxwell relations for a simple compressible system. The great usefulness of these equations will be demonstrated in later sections of this chapter. In particular, it should be noted that pressure, temperature, and specific volume can be measured by experimental methods, whereas entropy cannot be determined experimentally. By using the Maxwell relations, we can determine changes in entropy from quantities that can be measured, that is, pressure, temperature, and specific volume.

There are a number of other very useful relations that can be derived from Eqs. 12.6 through 12.9. For example, from Eq. 12.6, we can write the relations

$$\left(\frac{\partial u}{\partial s}\right)_v = T, \qquad \left(\frac{\partial u}{\partial v}\right)_s = -P \tag{12.15}$$

Similarly, from the other equations, we have

$$\left(\frac{\partial h}{\partial s}\right)_P = T, \qquad \left(\frac{\partial h}{\partial P}\right)_s = v$$
$$\left(\frac{\partial a}{\partial v}\right)_T = -P, \qquad \left(\frac{\partial a}{\partial T}\right)_v = -s$$
$$\left(\frac{\partial g}{\partial P}\right)_T = v, \qquad \left(\frac{\partial g}{\partial T}\right)_P = -s \tag{12.16}$$

As already noted, the Maxwell relations are written for a simple compressible substance. It is readily evident, however, that similar Maxwell relations can be written for substances having other effects, such as electrical and magnetic effects. For example, Eq. 8.9 can be written in the form

$$dU = T\,dS - P\,dV + \mathcal{T}\,dL + \mathcal{S}\,d\mathcal{A} + \mu_0\mathcal{H}\,d(V\mathcal{M}) + \mathcal{E}\,dZ + \cdots \quad (12.17)$$

Thus, at constant volume for a substance having only magnetic effects, we can write

$$dU = T\,dS + \mu_0 V\mathcal{H}\,d\mathcal{M}$$

and it follows that for such a substance

$$\left(\frac{\partial T}{\partial \mathcal{M}}\right)_{S,V} = \mu_0 V\left(\frac{\partial \mathcal{H}}{\partial S}\right)_{\mathcal{M},V}$$

Other Maxwell relations similar to Eqs. 12.12 through 12.14 could be written for such a substance. The extension of this approach to other systems, as well as to the interrelation between the various effects that may occur in a given system, is readily evident. For example, suppose a system has both magnetic and surface effects. We could consider a constant entropy process and write

$$\left(\frac{\partial \mathcal{S}}{\partial \mathcal{M}}\right)_{S,\mathcal{A},V} = \mu_0 V\left(\frac{\partial \mathcal{H}}{\partial \mathcal{A}}\right)_{S,\mathcal{M},V}$$

EXAMPLE 12.1

From an examination of the properties of compressed-liquid water, as given in Table A.1.4 of the Appendix, we find that the entropy of compressed liquid is greater than the entropy of saturated liquid for a temperature of 0°C, and is less than the entropy of saturated liquid for all the other temperatures listed. Explain why this conclusion follows from other thermodynamic data.

System: Water.

Solution

Suppose we increase the pressure of liquid water that is initially saturated and keep the temperature constant. The change of entropy for the water during this process can be found by integrating the following Maxwell relation, Eq. 12.14:

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

Therefore, the sign of the entropy change depends on the sign of the term $(\partial v/\partial T)_P$. The physical significance of this term is that it involves the change in specific volume of water as the temperature changes but the pressure remains constant. As water at moderate pressures and 0°C is heated in a constant-pressure process, the specific volume decreases until the point of maximum density is reached at approximately 4°C, after which it increases. This is shown on a v–T diagram in Fig. 12.2. Thus, the quantity $(\partial v/\partial T)_P$ is the slope of the curve in Fig. 12.2. Since this slope is negative at 0°C, the quantity $(\partial s/\partial P)_T$ is positive at 0°C. At the point

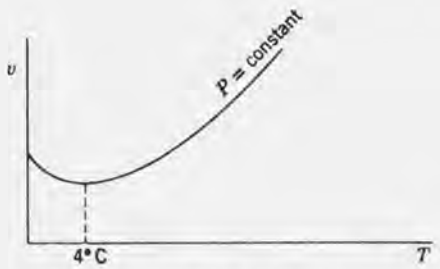


FIGURE 12.2 Sketch for Example 12.1.

of maximum density, the slope is zero and, therefore, the constant-pressure line shown in Fig. 8.7 crosses the saturated-liquid line at the point of maximum density.

12.3 THE PROPERTY RELATION FOR MIXTURES

In Chapter 11 the partial molal property was briefly introduced, but, the consideration of mixtures was limited to ideal gases. There was no need at that point for further expansion of the subject. We now continue this subject with a view toward developing the property relations for mixtures. This subject will be particularly relevant to our consideration of chemical equilibrium in Chapter 14.

For a mixture, any extensive property X is a function of the temperature and pressure of the mixture and the number of moles of each component. Thus, for a mixture of two components,

$$X = f(T, P, n_A, n_B)$$

Therefore,

$$dX_{T,P} = \left(\frac{\partial X}{\partial n_A}\right)_{T,P,n_B} dn_A + \left(\frac{\partial X}{\partial n_B}\right)_{T,P,n_A} dn_B \tag{12.18}$$

Since at constant temperature and pressure an extensive property is directly proportional to the mass, Eq. 12.18 can be integrated to give

$$X_{T,P} = \overline{X}_A n_A + \overline{X}_B n_B \tag{12.19}$$

where

$$\overline{X}_A = \left(\frac{\partial X}{\partial n_A}\right)_{T,P,n_B}, \qquad \overline{X}_B = \left(\frac{\partial X}{\partial n_B}\right)_{T,P,n_A}$$

Here $\overline{X}$ is defined as the partial molal property for a component in a mixture. It is particularly important to note that the partial molal property is defined under conditions of constant temperature and pressure. Note that Eq. 12.19 has the same form as Eq. 11.3.

The partial molal property is particularly significant when a mixture undergoes a chemical reaction. Suppose a mixture consists of components A and B, and a chemical reaction takes place so that the number of moles of A is changed by dn_A

and the number of moles of B by dn_B. The temperature and the pressure remain constant. What is the change in internal energy of the mixture during this process? From Eq. 12.19 we conclude that

$$dU_{T,P} = \overline{U}_A \, dn_A + \overline{U}_B \, dn_B \tag{12.20}$$

where $\overline{U}_A$ and $\overline{U}_B$ are the partial molal internal energy of A and B, respectively. Equation 12.20 suggests that the partial molal internal energy of each component can also be defined as the internal energy of the component as it exists in the mixture.

In Section 12.2 we considered a number of property relations for systems of fixed mass such as

$$dU = T \, dS - P \, dV$$

We note that in this equation, temperature is the intensive property or potential function associated with entropy, and pressure is the intensive property associated with volume. Suppose we have a chemical reaction such as described in the last paragraph. How would we modify this property relation for this situation? Intuitively we might write the equation

$$dU = T \, dS - P \, dV + \mu_A \, dn_A + \mu_B \, dn_B \tag{12.21}$$

where μ_A is the intensive property or potential function associated with n_A, and similarly μ_B for n_B. This potential function is called the chemical potential.

To derive an expression for this chemical potential, we examine Eq. 12.21 and conclude that it might be reasonable to write an expression for U in the form

$$U = f(S, V, n_A, n_B)$$

Therefore,

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_A,n_B} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_A,n_B} dV + \left(\frac{\partial U}{\partial n_A}\right)_{S,V,n_B} dn_A + \left(\frac{\partial U}{\partial n_B}\right)_{S,V,n_A} dn_B$$

Since the expressions

$$\left(\frac{\partial U}{\partial S}\right)_{V,n_A,n_B} \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_{S,n_A,n_B}$$

imply constant composition, it follows from Eq. 12.15 that

$$\left(\frac{\partial U}{\partial S}\right)_{V,n_A,n_B} = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_{S,n_A,n_B} = -P$$

Thus

$$dU = T \, dS - P \, dV + \left(\frac{\partial U}{\partial n_A}\right)_{S,V,n_B} dn_A + \left(\frac{\partial U}{\partial n_B}\right)_{S,V,n_A} dn_B \tag{12.22}$$

On comparing this equation with Eq. 12.21, we find that the chemical potential can be defined by the relation

$$\mu_A = \left(\frac{\partial U}{\partial n_A}\right)_{S,V,n_B}, \qquad \mu_B = \left(\frac{\partial U}{\partial n_B}\right)_{S,V,n_A} \tag{12.23}$$

We can also relate the chemical potential to the partial molal Gibbs function. We proceed as follows.

$$G = U + PV - TS$$
$$dG = dU + P\,dV + V\,dP - T\,dS - S\,dT$$

Substituting Eq. 12.21 into this relation, we have

$$dG = -S\,dT + V\,dP + \mu_A\,dn_A + \mu_B\,dn_B \tag{12.24}$$

This equation suggests that we write an expression for G in the following form.

$$G = f(T, P, n_A, n_B)$$

Proceeding as we did for a similar expression for internal energy, Eq. 12.22, we have

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_A,n_B} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_A,n_B} dP + \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T,P,n_A} dn_B$$
$$= -S\,dT + V\,dP + \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T,P,n_A} dn_B$$

When this equation is compared with Eq. 12.24, it follows that

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B}, \qquad \mu_B = \left(\frac{\partial G}{\partial n_B}\right)_{T,P,n_A}$$

Because partial molal properties are defined at constant temperature and pressure, the quantities $(\partial G/\partial n_A)_{T,P,n_B}$ and $(\partial G/\partial n_B)_{T,P,n_A}$ are the partial molal Gibbs functions for the two components. That is, the chemical potential is equal to the partial molal Gibbs function.

$$\mu_A = \overline{G}_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B}, \qquad \mu_B = \overline{G}_B = \left(\frac{\partial G}{\partial n_B}\right)_{T,P,n_A} \tag{12.25}$$

Although μ can also be defined in terms of other properties, such as in Eq. 12.23, this expression is not the partial molal internal energy, since the pressure and temperature are not constant in this partial derivative. The partial molal Gibbs function is an extremely important property in the thermodynamic analysis of chemical reactions, for at constant temperature and pressure (the conditions under which many chemical reactions occur) it is a measure of the chemical potential or the driving force that tends to make a chemical reaction take place.

12.4 THE CLAPEYRON EQUATION

The Clapeyron equation is an important relation concerning the saturation pressure and temperature, the change of enthalpy associated with a change of phase, and the specific volumes of the two phases. In particular, it is an example of how a change in a property that cannot be measured directly, for example, the enthalpy, can be determined from measurements of pressure, temperature, and specific vol-

ume. It can be derived in a number of ways. Here we proceed by considering one of the Maxwell relations, Eq. 12.13.

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

Consider, for example, the change of state from saturated liquid to saturated vapor of a pure substance. This is a constant-temperature process, and therefore Eq. 12.13 can be integrated between the saturated-liquid and saturated-vapor states. We also note that when saturated states are involved, pressure and temperature are independent of volume. Therefore,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{s_g - s_f}{v_g - v_f} = \frac{s_{fg}}{v_{fg}} = \frac{h_{fg}}{Tv_{fg}} \tag{12.26}$$

The significance of this equation is that $(dP/dT)_{\text{sat}}$ is the slope of the vapor-pressure curve. Thus, h_{fg} at a given temperature can be determined from the slope of the vapor–pressure curve and the specific volume of saturated liquid and saturated vapor at the given temperature.

There are several different changes of phase that can occur at constant temperature and constant pressure. If we designate the two phases with superscripts $''$ and $'$, we can write the Clapeyron equation for the general case.

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{s'' - s'}{v'' - v'}$$

We also note that $T(s'' - s') = h'' - h'$. Therefore,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h'' - h'}{T(v'' - v')} \tag{12.27}$$

If the phase designated $''$ is vapor, then at low pressure the equation is usually simplified by assuming that $v'' \gg v'$ and that $v'' = RT/P$. The relation then becomes

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_g - h'}{T(RT/P)}$$

$$\left(\frac{dP}{P}\right)_{\text{sat}} = \frac{h_g - h'}{R}\left(\frac{dT}{T^2}\right)_{\text{sat}} \tag{12.28}$$

EXAMPLE 12.2

Determine the saturation pressure of water vapor at $-60°C$ using data available in the steam tables.

System: Water.

Solution

Table 6 of the steam tables (Table A.1.5) does not give saturation pressures for temperatures less than $-40°C$. However, we do notice that h_{ig} is relatively constant in this range and, therefore, we proceed to use Eq. 12.28 and integrate between

the limits $-40°C$ and $-60°C$.

$$\int_1^2 \frac{dP}{P} = \int_1^2 \frac{h_{ig}}{R}\frac{dT}{T^2} = \frac{h_{ig}}{R}\int_1^2 \frac{dT}{T^2}$$

$$\ln \frac{P_2}{P_1} = \frac{h_{ig}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Let

$$P_2 = 0.0129 \text{ kPa}, \qquad T_2 = 233.2 \text{ K} \qquad T_1 = 213.2 \text{ K}$$

Then

$$\ln \frac{P_2}{P_1} = \frac{2838.9}{0.46152}\left(\frac{233.2 - 213.2}{233.2 \times 213.2}\right) = 2.4744$$

$$P_1 = 0.001\,09 \text{ kPa}$$

12.5 SOME THERMODYNAMIC RELATIONS CONCERNING ENTHALPY, INTERNAL ENERGY, AND ENTROPY

Let us first derive two equations, one for C_p and the other for C_v. We have defined C_p as

$$C_p \equiv \left(\frac{\partial h}{\partial T}\right)_p$$

We have also noted that for a pure substance

$$T\,ds = dh - v\,dP$$

Therefore,

$$C_p = \left(\frac{\partial h}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p \tag{12.29}$$

Similarly, from the definition of C_v,

$$C_v \equiv \left(\frac{\partial u}{\partial T}\right)_v$$

and the relation

$$T\,ds = du + P\,dv,$$

it follows that

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v \tag{12.30}$$

We will now derive a general relation for the change of enthaply of a pure substance. We first note that for a pure substance

$$h = h(T, P)$$

Therefore,

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

From the relation

$$T\,ds = dh - v\,dP$$

it follows that

$$\left(\frac{\partial h}{\partial P}\right)_T = v + T\left(\frac{\partial s}{\partial P}\right)_T$$

Substituting the Maxwell relation, Eq. 12.14 gives

$$\left(\frac{\partial h}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P \tag{12.31}$$

On substituting this equation and Eq. 12.29, we have

$$dh = C_p\,dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP \tag{12.32}$$

Along an isobar we have

$$dh_P = C_p\,dT_P$$

and along an isotherm,

$$dh_T = \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP_T \tag{12.33}$$

The significance of Eq. 12.32 is that it can be integrated to give the change in enthalpy associated with a change of state:

$$h_2 - h_1 = \int_1^2 C_p\,dT + \int_1^2 \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP \tag{12.34}$$

The information needed to integrate the first term is a constant-pressure specific heat along one (and only one) isobar. The integration of the second integral requires that an equation of state giving the relation between P, v, and T be known. Furthermore, it is advantageous to have this equation of state explicit in v, for then the derivation $(\partial v/\partial T)_P$ is readily evaluated.

This matter can be further illustrated by referring to Fig. 12.3. Suppose we wish to know the change of enthaply between states 1 and 2. We might determine this change along path 1–x–2, which consists of one isotherm, 1–x, and one isobar, x–2. Thus, we could integrate Eq. 12.34:

$$h_2 - h_1 = \int_{T_1}^{T_2} C_p\,dT + \int_{P_1}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

Since $T_1 = T_x$ and $P_2 = P_x$, this can be written

$$h_2 - h_1 = \int_{T_x}^{T_2} C_p\,dT + \int_{P_1}^{P_x} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

The second term in this equation gives the change in enthalpy along the isotherm 1–x and the first term the change in enthalpy along the isobar x–2. When these terms are added together, the result is the net change in enthalpy between 1 and 2. Therefore, the constant-pressure specific heat must be known along the isobar passing through 2 and x. The change in enthalpy can also be found by following path 1–y–2, in which case the constant-pressure specific heat must be known along 1–y isobar. If the constant-pressure specific heat is known at another pressure, say the isobar passing through m–n, the change in enthalpy can be found by following path 1–m–n–2. This involves calculating the change of enthalpy along two isotherms—1–m and n–2.

Let us now derive a similar relation for the change of internal energy. All the steps in this derivation are given, but without detailed comment. The starting point is to write $u = u(T, v)$, whereas for enthalpy the starting point is $h = h(T, P)$.

$$u = f(T, v)$$

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$T\,ds = du + P\,dv$$

Therefore,

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P \tag{12.35}$$

Substituting the Maxwell relation, Eq. 12.13, we have

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$$

Therefore,

$$du = C_v\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv \tag{12.36}$$

Along an isometric this reduces to

$$du_v = C_v\,dT_v$$

and along an isotherm we have

$$du_T = \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv_T \tag{12.37}$$

In a manner similar to that outlined earlier for changes in enthalpy, the change of internal energy for a given change of state for a pure substance can be determined from Eq. 12.36 if the constant-volume specific heat is known along one isometric and an equation of state explicit in P [to obtain the derivative $(\partial P/\partial T)_v$] is available in the region involved. A diagram similar to Fig. 12.3 could be drawn, with the isobars replaced with isometrics, and the same general conclusions would be released.

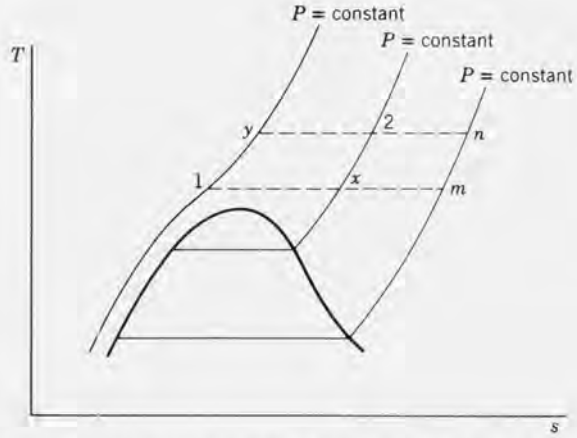


FIGURE 12.3 Sketch showing various paths by which a given change of state can take place.

To summarize, we have derived Eqs. 12.32 and 12.36:

$$dh = C_p\,dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]dP$$

$$du = C_v\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv$$

The first of these equations concerns the change of enthalpy and the constant-pressure specific heat and is particularly suited to an equation of state explicit in v. The second equation concerns the change of internal energy and the constant-volume specific heat and is particularly suited to an equation of state explicit in P. If the first of these equations is used to determine the change of enthalpy, the internal energy is readily found by noting that

$$u_2 - u_1 = h_2 - h_1 - (P_2v_2 - P_1v_1)$$

If the second equation is used to find changes of internal energy, the change of enthalpy is readily found from this same relation. Which of these two equations is used to determine changes in internal energy and enthalpy will depend on the information available for specific heat and an equation of state (or other P–v–T data).

Two parallel expressions can be found for the change of entropy.

$$s = s(T, P)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$

Substituting Eqs. 12.29 and 12.14, we have

$$ds = C_p\frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_P dP \tag{12.38}$$

$$s_2 - s_1 = \int_1^2 C_p\frac{dT}{T} - \int_1^2 \left(\frac{\partial v}{\partial T}\right)_P dP \tag{12.39}$$

Along an isobar we have

$$(s_2 - s_1)_P = \int_1^2 C_p \frac{dT_P}{T}$$

and along an isotherm,

$$(s_2 - s_1)_T = -\int_1^2 \left(\frac{\partial v}{\partial T}\right)_P dP$$

Note from Eq. 12.39 that if a constant-pressure specific heat is known along one isobar and an equation of state explicit in v is available, the change of entropy can be evaluated. This is analogous to the expression for the change of enthalpy given in Eq. 12.32.

The second equation for the change of entropy can be found as follows.

$$s = s(T, v)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

Substituting Eqs. 12.30 and 12.13 gives

$$ds = C_v \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_v dv \tag{12.40}$$

$$s_2 - s_1 = \int_1^2 C_v \frac{dT}{T} + \int_1^2 \left(\frac{\partial P}{\partial T}\right)_v dv \tag{12.41}$$

This expression for change of entropy concerns the change of entropy along an isometric where the constant-volume specific heat is known and along an isotherm where an equation of state explicit in P is known. Thus, it is analogous to the expression for change of internal energy given in Eq. 12.36.

It should also be noted that it follows directly from Eq. 12.32 that the enthalpy of an ideal gas is a function of only the temperature. From Eq. 12.32,

$$dh = C_p\, dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

For an ideal gas, for which the equation of state is $Pv = RT$, it follows that

$$T\left(\frac{\partial v}{\partial T}\right)_P = T\left(\frac{R}{P}\right) = v$$

Therefore,

$$\left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] = 0$$

and for an ideal gas

$$dh = C_p\, dT$$

Let us also apply Eq. 12.38,

$$ds = C_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_P dP$$

to an ideal gas. For an ideal gas we have

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

and

$$ds = C_p \frac{dT}{T} - R\frac{dP}{P}$$

This equation was derived as Eq. 8.21 by an alternate procedure, in a discussion of ideal-gas behavior.

EXAMPLE 12.3

Over a certain range of pressures and temperatures, the equation of state of a certain substance is given with reasonable accuracy by the relation

$$\frac{Pv}{RT} = 1 - C'\frac{P}{T^4}$$

or

$$v = \frac{RT}{P} - \frac{C}{T^3}$$

where C and C' are constants.

Derive an expression for the change of enthalpy and one for the change of entropy of this substance in an isothermal process.

System: Gas.

Solution

Since the equation of state is explicit in v, Eq. 12.33 is particularly relevant to the change in enthalpy. On integrating this equation, we have

$$(h_2 - h_1)_T = \int_1^2 \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP_T$$

From the equation of state,

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} + \frac{3C}{T^4}$$

Therefore,

$$(h_2 - h_1)_T = \int_1^2 \left[v - T\left(\frac{R}{P} + \frac{3C}{T^4}\right)\right] dP_T$$

$$= \int_1^2 \left[\frac{RT}{P} - \frac{C}{T^3} - \frac{RT}{P} - \frac{3C}{T^3}\right] dP_T$$

$$(h_2 - h_1)_T = \int_1^2 -\frac{4C}{T^3} dP_T = -\frac{4C}{T^3}(P_2 - P_1)_T$$

For the change in entropy we use Eq. 12.39, which is particularly relevant for an equation of state explicit in v.

$$(s_2 - s_1)_T = -\int_1^2 \left(\frac{\partial v}{\partial T}\right)_P dP_T = -\int_1^2 \left(\frac{R}{P} + \frac{3C}{T^4}\right) dP_T$$

$$(s_2 - s_1)_T = -R \ln\left(\frac{P_2}{P_1}\right)_T - \frac{3C}{T^4}(P_2 - P_1)_T$$

12.6 SOME THERMODYNAMIC RELATIONS CONCERNING SPECIFIC HEAT

Some important relations concerning specific heats can also be developed. We have noted that the specific heat of an ideal gas is a function of the temperature only. For real gases the specific heat varies with pressure as well as temperature, and frequently we are interested in the variation of specific heat with pressure or volume. These relations can be derived as follows. Consider Eq. 12.38:

$$ds = \left(\frac{C_p}{T}\right) dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

Since this equation is of the general form $dz = M\,dx + N\,dy$, we can proceed as follows to find a relation that gives the variation of the constant-pressure specific heat with pressure at constant temperature.

$$\left[\frac{\partial (C_p/T)}{\partial P}\right]_T = -\left[\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right)_P\right]_P$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P \tag{12.42}$$

The variation of the constant-volume specific heat with volume as the temperature remains constant can be found in a similar manner. Consider Eq. 12.40:

$$ds = \left(\frac{C_v}{T}\right) dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

Since this is of the form $dz = M\,dx + N\,dy$,

$$\left[\frac{\partial (C_v/T)}{\partial v}\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_v\right]_v$$

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v \tag{12.43}$$

The important thing to note about Eqs. 12.42 and 12.43 is that the variation of the constant-volume and constant-pressure specific heats at constant temperature can be found from the equation of state.

EXAMPLE 12.4

Determine the variation of C_p with pressure at constant temperature for a substance such as the one in Example 12.3 over the range in which the equation of state is given by the relation

$$v = \frac{RT}{P} - \frac{C}{T^3}$$

System: Gas.

Solution

Using Eq. 12.42, we have

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} + \frac{3C}{T^4}$$

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_P = -\frac{12C}{T^5}$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(-\frac{12C}{T^5}\right) = \frac{12C}{T^4}$$

A final interesting and useful relation involving the difference between C_p and C_v can be derived by equating Eqs. 12.38 and 12.40.

$$C_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_P dP = C_v \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$dT = \frac{T(\partial P/\partial T)_v}{C_p - C_v} dv + \frac{T(\partial v/\partial T)_P}{C_p - C_v} dP$$

But

$$T = f(v, P)$$

$$dT = \left(\frac{\partial T}{\partial v}\right)_P dv + \left(\frac{\partial T}{\partial P}\right)_v dP$$

Therefore,

$$\left(\frac{\partial T}{\partial v}\right)_P = \frac{T(\partial P/\partial T)_v}{C_p - C_v}$$

and

$$\left(\frac{\partial T}{\partial P}\right)_v = \frac{T(\partial v/\partial T)_P}{C_p - C_v}$$

When these equations are solved for $C_p - C_v$, they yield the same result.

$$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v \tag{12.44}$$

But from Eq. 12.2,

$$\left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial v}\right)_T$$

Therefore,

$$C_p - C_v = -T\left(\frac{\partial v}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial v}\right)_T \tag{12.45}$$

We draw several conclusions from this equation.

1. For liquids and solids, $(\partial v/\partial T)_P$ is usually relatively small, and, therefore, for these phases the difference between the constant-pressure and the constant-volume specific heats is small. For this reason many tables simply give the specific heat of a solid or a liquid without designating that it is at constant volume or pressure. Further, $C_p = C_v$ exactly when $(\partial v/\partial T)_P = 0$, as is true at the point of maximum density of water.
2. Because $C_p \to C_v$ as $T \to 0$, we therefore conclude that the constant-pressure and constant-volume specific heats are equal at absolute zero.
3. The difference between C_p and C_v is always positive because $(\partial v/\partial T)_P^2$ is always positive and $(\partial P/\partial v)_T$ is negative for all known substances.
4. For an ideal gas,

$$\left(\frac{\partial v}{\partial T}\right)_P^2 = \frac{R^2}{P^2} \qquad \text{and} \qquad \left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{v^2}$$

Therefore,

$$C_p - C_v = -T\left(\frac{R}{P}\right)^2 \left(-\frac{RT}{v^2}\right) = R$$

This relationship was derived by another procedure whereby we arrived at Eq. 5.27.

12.7 VOLUME EXPANSIVITY AND ISOTHERMAL AND ADIABATIC COMPRESSIBILITY

The student has most likely encountered the coefficient of linear expansion in his or her studies of the strength of materials. This coefficient indicates how the length of a solid body is influenced by a change in temperature while the pressure remains constant. In terms of the notation of partial derivatives, the *coefficient of linear expansion*, δ_T, is defined as

$$\delta_T = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_P \tag{12.46}$$

A similar coefficient can be defined for changes in volume. Such a coefficient is applicable to liquids and gases as well as to solids. This coefficient of volume expansion, α, also called the volume expansivity, is an indication of the change in volume as temperature changes while the pressure remains constant. The definition of *volume expansivity* is

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \tag{12.47}$$

The isothermal compressibility, β_T, is an indication of the change in volume as pressure changes while the temperature remains constant. The definition of *isothermal compressibility* is

$$\beta_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \tag{12.48}$$

The reciprocal of the isothermal compressibility is called the *isothermal bulk modulus*, B_T.

$$B_T \equiv -v\left(\frac{\partial P}{\partial v}\right)_T \tag{12.49}$$

The *adiabatic compressibility*, β_s, is an indication of the change in volume as pressure changes while the entropy remains constant; it is defined as

$$\beta_s \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_s \tag{12.50}$$

The *adiabatic bulk modulus*, B_s, is the reciprocal of the adiabatic compressibility.

$$B_s \equiv -v\left(\frac{\partial P}{\partial v}\right)_s \tag{12.51}$$

Both the volume expansivity and isothermal compressibility are thermodynamic properties of a substance, and for a simple compressible substance are functions of two independent properties. Values of these properties are found in the standard handbooks of physical properties. The following examples give an indication of the use and significance of the volume expansivity and isothermal compressibility.

EXAMPLE 12.5

Show that $C_p - C_v$ can be expressed in terms of the volume expansivity α, the specific volume v, the temperature T, and the isothermal compressibility β_T by the relation

$$C_p - C_v = \frac{\alpha^2 v T}{\beta_T}$$

System: Pure substance.

Solution

From Eq. 12.45

$$C_p - C_v = -T\left(\frac{\partial v}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial v}\right)_T$$

$$\alpha \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P, \qquad \left(\frac{\partial v}{\partial T}\right)^2 = \alpha^2 v^2$$

$$\beta_T \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T, \qquad \left(\frac{\partial P}{\partial v}\right)_T = -\frac{1}{\beta_T v}$$

Therefore,

$$C_p - C_v = -T(\alpha^2 v^2)\left(-\frac{1}{\beta_T v}\right) = \frac{\alpha^2 v T}{\beta_T}$$

EXAMPLE 12.6

The pressure on a block of copper having a mass of 1 kg is increased in a reversible process from 0.1 to 100 MPa while the temperature is held constant at 15°C. Determine the work done on the copper during this process, the change in entropy per kilogram of copper, the heat transfer, the change of internal energy per kilogram, and $C_p - C_v$ for this change of state.

Over the range of pressure and temperature in this problem, the following data can be used:

Volume expansivity $= \alpha = 5.0 \times 10^{-5}\ \mathrm{K}^{-1}$

Isothermal compressibility $= \beta_T = 8.6 \times 10^{-12}\ \mathrm{m}^2/\mathrm{N}$

Specific volume $= 0.000\,114\ \mathrm{m}^3/\mathrm{kg}$

System: Copper block.

States: Initial and final states known.

Process: Constant temperature.

Analysis: The work done during the isothermal compression is

$$w = \int P\, dv_T$$

The isothermal compressibility has been defined as

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

$$v\beta_T\, dP_T = -dv_T$$

Therefore, for this isothermal process,

$$w = -\int_1^2 v\beta_T P\, dP_T$$

Since v and β_T remain essentially constant, this is readily integrated:

$$w = -\frac{v\beta_T}{2}(P_2^2 - P_1^2)$$

The change of entropy can be found by considering the Maxwell relation, Eq. 12.14, and the definition of volume expansivity.

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P = -\frac{v}{v}\left(\frac{\partial v}{\partial T}\right)_P = -v\alpha$$

$$ds_T = -v\alpha\, dP_T$$

This equation can be readily integrated, if we assume that v and α remain constant:

$$(s_2 - s_1)_T = -v\alpha(P_2 - P_1)_T$$

The heat transfer for this reversible isothermal process is

$$q = T(s_2 - s_1)$$

The change in internal energy follows directly from the first law.

$$u_2 - u_1 = q - w$$

From Example 12.5,

$$C_p - C_v = \frac{\alpha^2 vT}{\beta_T}$$

Solution

$$w = -\frac{v\beta_T}{2}(P_2^2 - P_1^2)$$

$$= -\frac{0.000\,114 \times 8.6 \times 10^{-12}}{2}(100^2 - 0.1^2) \times 10^{12}$$

$$= -4.9 \text{ J/kg}$$

$$(s_2 - s_1)_T = -v\alpha(P_2 - P_1)_T$$

$$= -0.000\,114 \times 5.0 \times 10^{-5}(100 - 0.1) \times 10^6$$

$$= -0.5694 \text{ J/kg K}$$

$$q = T(s_2 - s_1) = -288.2 \times 0.5694 = -164.1 \text{ J/kg}$$

$$u_2 - u_1 = q - w = -164.1 - (-4.9) = -159.2 \text{ J/kg}$$

$$C_p - C_v = (5.0 \times 10^{-5})^2 \times \frac{0.000\,114 \times 288.2}{8.6 \times 10^{-12}}$$

$$= 9.55 \text{ J/kg K}$$

This is consistent with the earlier observation that $C_p - C_v$ is relatively small for solids.

12.8 DEVELOPING TABLES OF THERMODYNAMIC PROPERTIES FROM EXPERIMENTAL DATA

There are many ways in which tables of thermodynamic properties can be developed from experimental data. The purpose of this section is to convey some general principles and concepts by considering only the liquid and vapor phases.

Let us assume that the following data for a pure substance have been obtained in the laboratory.

1. Vapor-pressure data. That is, saturation pressures and temperatures have been measured over a wide range.
2. Pressure, specific volume, and temperature data in the vapor region. These data are usually obtained by determining the mass of the substance in a closed vessel (which means a fixed specific volume) and then measuring the pressure as the temperature is varied. This is done for a large number of specific volumes.
3. Density of the saturated liquid and the critical pressure and temperature.
4. Zero-pressure specific heat for the vapor. This might be obtained either calorimetrically or from spectroscopic data.

From these data a complete set of thermodynamic tables for the saturated liquid, saturated vapor, and superheated vapor can be calculated. The first step is to determine an equation for the vapor-pressure curve that accurately fits the data. It may be necessary to use one equation for one portion of the vapor-pressure curve and a different equation for another portion of the curve.

One form of equation that has been used is

$$\ln P_{\text{sat}} = A + \frac{B}{T} + C \ln T + DT$$

Once an equation that accurately represents the data has been found, the saturation pressure for any given temperature can be found by solving this equation. Thus, the saturation pressures in Table 1 of the steam tables would be determined for the given temperatures. The second step is to determine an equation of state for the vapor region that accurately represents the P–v–T data. The equation of state may take many possible forms. The equation of state that is selected must accurately represent the data and be of such a form that the differentiations required can be performed. That is, sometimes it may be desirable to have an equation of state explicit in v, but on other occasions an equation of state that is explicit in P may be more desirable.

Once an equation of state has been determined, the specific volume of superheated vapor at given pressures and temperatures can be determined by solving the equation and tabulating the results as in the superheat tables for steam, ammonia, and R-12 or R-22. The specific volume of saturated vapor at a given temperature may be found by determining the saturation pressure from the vapor-pressure curve and substituting this saturation pressure and temperature into the equation of state.

The procedure for determining enthalpy and entropy is best explained with the help of Fig. 12.4. Let us assume that the enthalpy and the entropy of saturated

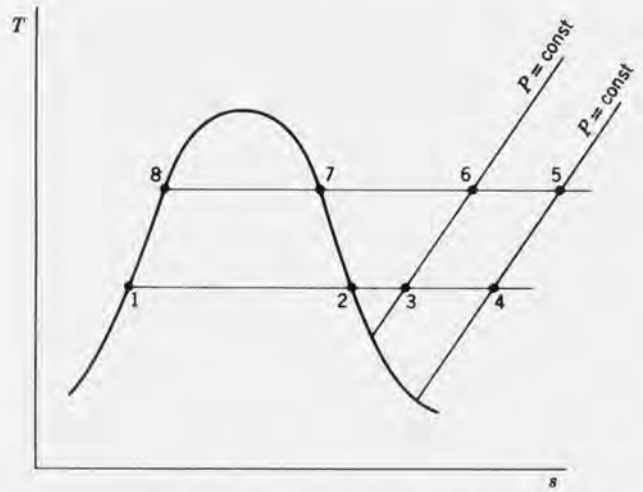


FIGURE 12.4 Sketch showing procedure for developing a table of thermodynamic properties from experimental data.

liquid in state 1 are zero. The enthalpy of saturated vapor in state 2 can be found from the Clapeyron equation.

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{T(v_g - v_f)}$$

The left side of this equation is found by differentiating the vapor-pressure curve. The specific volume of the saturated vapor is found by the procedure outlined in the last paragraph, and it is assumed that the specific volume of the saturated liquid has been measured. Thus, the enthalpy of evaporation, h_{fg}, can be found for this particular temperature, and the enthalpy at state 2 is equal to the enthalpy of evaporation (since the enthalpy in state 1 is assumed to be zero). The entropy at state 2 is readily found, since

$$s_{fg} = \frac{h_{fg}}{T}$$

From state 2 we proceed along this isotherm into the superheated vapor region. The specific volume at state 3 is found from the equation of state at this pressure. The enthalpy and entropy are determined by integrating Eqs. 12.33 and 12.39:

$$h_3 - h_2 = \int_2^3 \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dP_T$$

$$s_3 - s_2 = \int_2^3 -\left(\frac{\partial v}{\partial T}\right)_P dP_T$$

The properties at state 4 are found in exactly the same manner. Pressure P_4 is sufficiently low that the real superheated vapor behaves essentially as an ideal gas (perhaps 10 kPa). Thus, we use this constant-pressure line to make all temperature changes for our calculations, as, for example, to state 5. Since the specific heat C_{p0}

is known as a function of temperature, the enthalpy and entropy at state 5 are found by integrating the ideal-gas relations

$$(h_5 - h_4)_P = \int_4^5 C_{p0}\, dT_P$$

$$(s_5 - s_4)_P = \int_4^5 C_{p0} \frac{dT_P}{T}$$

The properties at states 6 and 7 are found from those at 5 in the same manner as those at states 3 and 4 were found from 2 (the saturation pressure P_7 is calculated from the vapor-pressure equation). Finally, the enthalpy and entropy for saturated liquid at state 8 are found from the properties at state 7 by applying the Clapeyron equation.

Thus, values for the pressure, temperature, specific volume, enthalpy, entropy, and internal energy of saturated liquid, saturated vapor, and superheated vapor can be tabulated for the entire region for which experimental data were obtained. The accuracy of such a table depends both on the accuracy of the experimental data and on the degree to which the equation for the vapor pressure and the equation of state represent the experimental data.

12.9 *P–v–T* BEHAVIOR OF REAL GASES

For real gases we use the compressibility factor, Z, which is defined in Eq. 3.6 as

$$Z = \frac{Pv}{RT}$$

The compressibility factor has the value of unity for an ideal gas. That is, as $P \to 0$, $Z \to 1$.

A plot of lines of constant temperature on a Z–P diagram is one effective way of showing P–v–T behavior for a real gas. Figure 12.5 shows such a diagram for nitrogen. Note that as the pressure approaches zero, Z approaches unity for all isotherms, which is consistent with our observations regarding ideal gases. At pressures less than the critical pressure, both saturated-liquid and saturated-vapor states can be shown on a Z–P diagram.

The behavior of the critical isotherm on a P–v diagram in the vicinity of the critical point is particularly important in a study of real gases. Consider the P–v plot for a pure substance shown in Fig. 12.6.

From a careful study of experimental data, it is evident that at least the first two derivatives are zero at the critical point. This means that the critical isotherm goes through a horizontal point of inflection at the critical point.

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 \qquad \text{at critical point}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0 \qquad \text{at critical point}$$

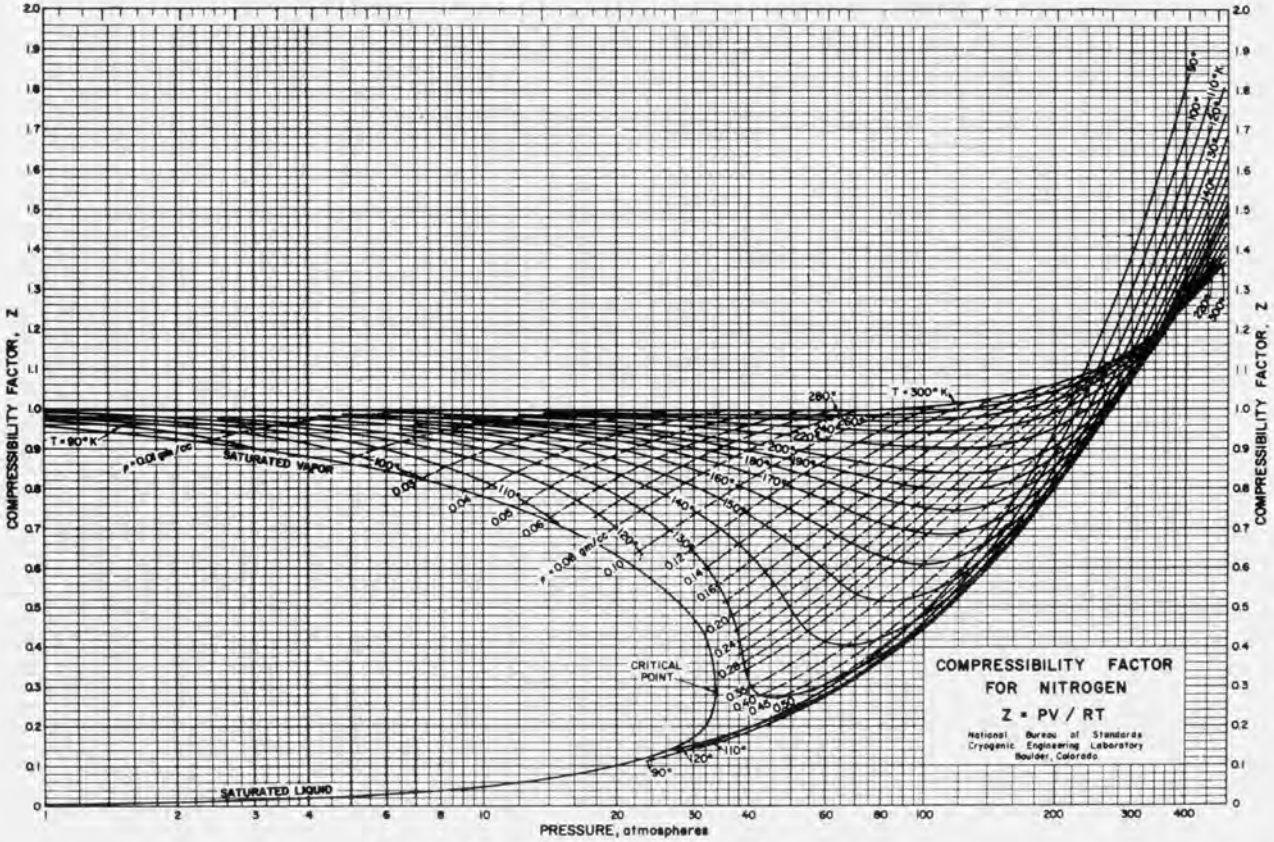


FIGURE 12.5 Compressibility diagram for nitrogen.

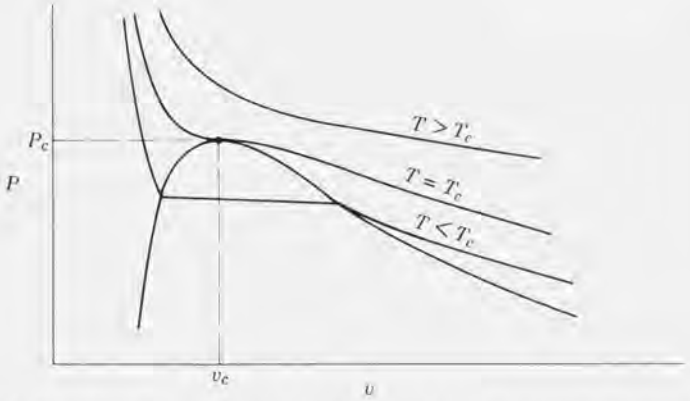


FIGURE 12.6 Plot of isotherms in the region of the critical point on pressure-volume coordinates for a typical pure substance.

One of the most important characteristics of the P–v–T behavior of real gases concerns the concept of reduced pressure, reduced temperature, and reduced specific volume. These terms are defined as follows:

$$\text{Reduced pressure} = P_r = \frac{P}{P_c} \qquad P_c = \text{Critical pressure}$$

$$\text{Reduced temperature} = T_r = \frac{T}{T_c} \qquad T_c = \text{Critical temperature}$$

$$\text{Reduced specific volume} = v_r = \frac{v}{v_c} \qquad v_c = \text{Critical specific volume}$$

These equations state that the reduced property for a given state is the value of this property in this state divided by the value of this same property at the critical point.

If lines of constant T_r are plotted on a Z versus P_r diagram, a plot such as that in Fig. A.7 is obtained. The striking fact is that when such Z versus P_r diagrams are prepared for a number of different substances, all of them very nearly coincide, especially when the substances have simple, essentially spherical molecules. Correlations for substances with more complicated molecules are reasonably close, except near or at saturation or at high density. Thus, Figure A.7 is actually a generalized diagram for simple molecules, which means that it represents the average behavior for a number of different simple substances; we use the superscript 0 to denote the compressibility factor for simple fluids. When such a diagram is used for a particular substance, the results will generally be somewhat in error. On the other hand, if P–v–T information is required for a substance in a region where no experimental measurements have been made, this generalized compressibility diagram will give reasonably accurate results. We need know only the critical pressure and critical temperature to use this basic generalized chart.

A third parameter is often introduced to improve the accuracy of correlation of the generalized compressibility factor. One such parameter is termed the acentric

factor ω, which is intended to account for molecular shape, geometric complexity, and polarity. The acentric factor ω adds a correction factor to the simple-fluid compressibility correlation represented by Fig. A.7. It is observed that simple fluids have a reduced saturation pressure of about 0.1 at a reduced temperature of 0.7. Therefore, the acentric factor for any molecule is defined in terms of its reduced saturation pressure at the reduced temperature of 0.7 as

$$\omega = -\frac{\ln P_{r\,\text{at}\,T_r=0.7}^{\text{sat}}}{2.302\,585} - 1.0 \tag{12.52}$$

The compressibility factor Z for any molecule can now be represented in terms of the simple-fluid value $Z^{(0)}$ plus a first-order correction term in the form

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{12.53}$$

In this text, both the simple-fluid and correction term compressibilities are calculated from a generalized analytical equation of state called the Lee–Kesler equation, which is an extension of the Benedict–Webb–Rubin equation, Eq. 3.7. Both equations are discussed in some detail in the next section. The Lee–Kesler equation and the generalized results are presented in Tables A.14. Use of these generalized tables is illustrated by the following example.

EXAMPLE 12.7

1. Volume unknown. Calculate the specific volume of propane at a pressure of 7 MPa and a temperature of 150°C. Compare this with the specific volume given by the ideal-gas equation of state.

System: Propane.

State: P, T known.

Model: Generalized compressibility tables, Table A.14.

Solution

For propane

$$T_c = 369.8\ \text{K}, \qquad P_c = 4.25\ \text{MPa}, \qquad \omega = 0.153$$
$$R = 0.188\,55\ \text{kJ/kg K}$$
$$T_r = \frac{423.2}{369.8} = 1.144, \qquad P_r = \frac{7}{4.25} = 1.647$$

From the compressibility tables,

$$Z = 0.5233 + 0.153 \times 0.1774 = 0.5504$$
$$v = \frac{ZRT}{P} = \frac{0.5504 \times 0.188\,55 \times 423.2}{7000} = 0.006\,27\ \text{m}^3/\text{kg}$$

The ideal-gas equation would give the value

$$v = \frac{0.188\,55 \times 423.2}{7000} = 0.0114\ \text{m}^3/\text{kg}$$

2. Pressure unknown. What pressure is required for propane to have a specific volume of 0.006 27 m^3/kg at a temperature of 150°C?

State: T, v known.

Solution

$$T_r = \frac{423.2}{369.8} = 1.144$$

$$P_r = \frac{P}{P_c} = \frac{ZRT}{vP_c} = Z \times \frac{0.188\,55 \times 423.2}{0.006\,27 \times 4250} = 2.994Z$$

By trial and error P_r is found to be 1.647 at the point where $T_r = 1.144$. Therefore,

$$P = P_r P_c = 1.647 \times 4250 = 7000 \text{ kPa} = 7 \text{ MPa}$$

3. Temperature unknown. What will the temperature of propane be when it has a specific volume of 0.006 27 m^3/kg and a pressure of 7 MPa?

State: P, v known.

Solution

$$P_r = \frac{7}{4.25} = 1.647$$

$$T_r = \frac{T}{T_c} = \frac{Pv}{ZRT_c} = \frac{7000 \times 0.006\,27}{Z \times 0.188\,55 \times 369.8} = \frac{0.6295}{Z}$$

By trial and error the reduced temperature at which this expression is satisfied for the reduced pressure of 1.647 is found to be 1.144. Therefore,

$$T_r = 1.144$$

$$T = T_r \times T_c = 1.144 \times 369.8 = 423.2 \text{ K}$$

To gain additional insight into the behavior of gases at low density, let us examine the low-pressure portion of the generalized compressibility chart in greater detail. This behavior is as shown in Fig. 12.7. The isotherms are essentially straight lines in this region, and their slope is of particular importance. Note that the slope increases as T_r increases until a maximum value is reached at a T_r of about 5, and then the slope decreases toward the $Z = 1$ line for higher temperatures. The single temperature, about 2.5 times the critical temperature, for which

$$\lim_{P \to 0} \left(\frac{\partial Z}{\partial P} \right)_T = 0$$

is defined as the Boyle temperature of the substance. This is the only temperature at which a gas really behaves exactly as an ideal gas at low, but finite pressures, since all other isotherms go to zero pressure on Fig. 12.7 with a nonzero slope.

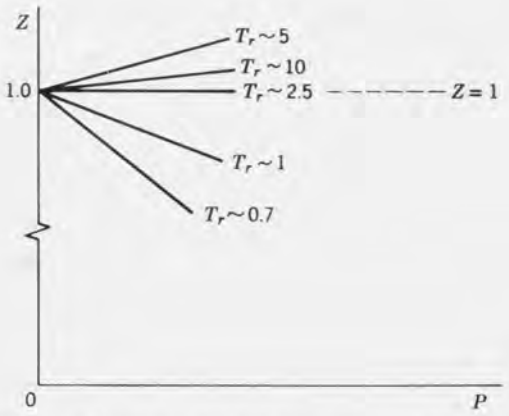


FIGURE 12.7 Low-pressure region of compressibility chart.

The Joule–Thomson coefficient, defined in connection with the throttling process, can be expressed in terms of P–v–T behavior as

$$\mu_J = \left(\frac{\partial T}{\partial P}\right)_h = \frac{T\left(\frac{\partial v}{\partial T}\right)_P - v}{C_p} = \frac{RT^2}{PC_p}\left(\frac{\partial Z}{\partial T}\right)_P \tag{12.54}$$

From Eq. 12.54 and Fig. 12.7 it is evident that at low pressure μ_J is zero only at one temperature, T_r about 5, and is positive at lower temperatures and negative at higher temperatures. By examining higher density P–v–T data, we can determine the locus of points at which μ_J is zero, which is called the Joule–Thomson inversion curve. The result is as shown in Fig. 12.8. Inside the dome μ_J is positive, which means that a substance cools upon being throttled to a lower pressure. Outside the dome μ_J is negative, and the temperature increases during a throttling process.

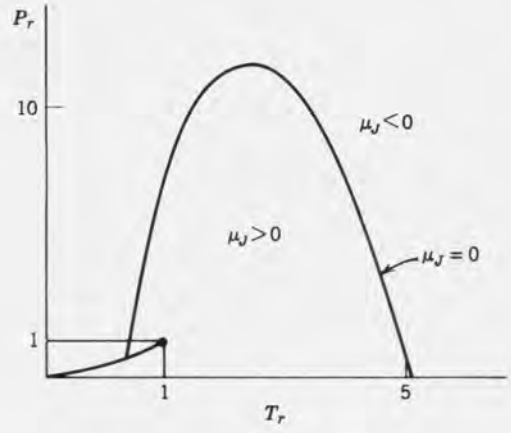


FIGURE 12.8 Joule–Thomson inversion curve.

12.10 EQUATIONS OF STATE

An accurate equation of state, which is an analytical representation of P–v–T behavior, is often desirable from a computational standpoint. Many different equations of state have been developed. Most of these equations are accurate only to some density less than the critical density, although a few are reasonably accurate to approximately 2.5 times the critical density. All equations of state fail badly when the density exceeds the maximum density for which the equation was developed.

Three broad classifications of equations of state can be identified—generalized, empirical, and theoretical.

The best known of the generalized equations of state is also the oldest—the van der Waals equation—which was presented in 1873 as a semitheoretical improvement over the ideal-gas equation. The van der Waals equation of state is

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \tag{12.55}$$

The constant b corrects for the volume occupied by the molecules, and the term a/v^2 corrects for the intermolecular forces of attraction. As might be expected for a generalized equation, the constants a and b are evaluated from the general behavior of gases. In particular, these constants are evaluated by noting that the critical isotherm passes through a point of inflection at the critical point, and that the slope is zero at this point. Thus, for the van der Waals equation of state, we have

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v - b)^2} + \frac{2a}{v^3} \tag{12.56}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2RT}{(v - b)^3} - \frac{6a}{v^4} \tag{12.57}$$

Since both of these derivatives are equal to zero at the critical point, we can write

$$\begin{aligned} -\frac{RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} &= 0 \\ \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} &= 0 \\ P_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2} & \end{aligned} \tag{12.58}$$

Solving these three equations, we find

$$\begin{aligned} v_c &= 3b \\ a &= \frac{27}{64}\frac{R^2 T_c^2}{P_c} \\ b &= \frac{RT_c}{8P_c} \end{aligned} \tag{12.59}$$

The compressibility factor at the critical point for the van der Waals equation is

$$Z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8}$$

which is higher than the actual value for essentially all substances.

The van der Waals equation can be written in terms of the compressibility factor, the reduced pressure, and the reduced temperature as follows:

$$Z^3 - \left(\frac{P_r}{8T_r} + 1\right)Z^2 + \left(\frac{27P_r}{64T_r^2}\right)Z - \frac{27P_r^2}{512T_r^3} = 0 \tag{12.60}$$

It is significant that this is of the same form as the simple generalized compressibility chart—$Z = f(P_r, T_r)$—although the functional relation may be quite different from that of the generalized chart. This concept that different substances will have the same compressibility factor at the same reduced pressure and reduced temperature is another way of expressing the rule of corresponding states.

A simple equation of state that is considerably more accurate than the van der Waals equation is that proposed by Redlich and Kwong in 1949,

$$P = \frac{\overline{R}T}{\bar{v} - b} - \frac{a}{\bar{v}(\bar{v} + b)T^{1/2}} \tag{12.61}$$

with

$$a = 0.427\,48\,\frac{\overline{R}^2 T_c^{5/2}}{P_c} \tag{12.62}$$

$$b = 0.086\,64\,\frac{\overline{R}T_c}{P_c} \tag{12.63}$$

The numerical values in the constants have been determined by a procedure similar to that followed in the van der Waals equation. Because of its simplicity, this equation cannot be expected to be sufficiently accurate for use in the calculation of precision tables of thermodynamic properties. It has, however, been used frequently and with reasonably good success for mixture calculations and phase equilibrium correlations. A number of modified versions of this equation have also been utilized in recent years.

One of the best-known empirical equations of state is the Benedict–Webb–Rubin equation, often termed the BWR equation. First proposed in 1940, it has since then been very widely used in its original version and in modified versions. The original form of this equation, given in Chapter 3, is

$$P = \frac{RT}{v} + \frac{RTB_0 - A_0 - C_0/T^2}{v^2} + \frac{RTb - a}{v^3} + \frac{a\alpha}{v^6} + \frac{c}{v^3T^2}\left(1 + \frac{\gamma}{v^2}\right)e^{-\gamma/v^2} \tag{12.64}$$

with eight empirical constants. The values of the constants are given for a number of substances in Table 3.3.

One particularly interesting modification of the BWR equation of state is the Lee–Kesler equation, which was proposed in 1975. This equation has twelve constants and is written in terms of generalized properties as

$$
\begin{aligned}
Z = \frac{P_r v'_r}{T_r} &= 1 + \frac{B}{v'_r} + \frac{C}{v'^2_r} + \frac{D}{v'^5_r} + \frac{c_4}{T_r^3 v'^2_r}\left(\beta + \frac{\gamma}{v'^2_r}\right)\exp\left(-\frac{\gamma}{v'^2_r}\right) \\
B &= b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \\
C &= c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \\
D &= d_1 + \frac{d_2}{T_r}
\end{aligned}
\tag{12.65}
$$

in which the variable v'_r is not the true reduced specific volume, but is instead defined as

$$
v'_r = \frac{v}{RT_c/P_c} \tag{12.66}
$$

Two sets of empirical constants are given for this equation in Table A.14. The first set of constants is based on observed generalized behavior of simple fluids and therefore yields, from Eq. 12.65, the corresponding compressibility factor $Z^{(0)}$. The second set of constants is for a relatively complicated reference fluid, octane, which yields, again from Eq. 12.65, a compressibility factor $Z^{(r)}$. The correction factor $Z^{(1)}$ of Eq. 12.53 is now assumed to be a linear weighted average value, such that

$$
\begin{aligned}
Z &= Z^{(0)} + \frac{\omega}{\omega^{(r)}}\left[Z^{(r)} - Z^{(0)}\right] = Z^{(0)} + \omega Z^{(1)} \\
\omega^{(r)} &= 0.3978, \qquad Z^{(1)} = \frac{Z^{(r)} - Z^{(0)}}{\omega^{(r)}}
\end{aligned}
\tag{12.67}
$$

Values for $Z^{(0)}$ and $Z^{(1)}$ as calculated using the generalized empirical equation of state 12.65 are then the values listed in Table A.14. Values for $Z^{(0)}$ are given in the simple-fluid compressibility chart, Fig. A.7.

We now approach the equation of state problem from a theoretical point of view. The theoretical equation of state, which is derived from kinetic theory or statistical thermodynamics, is written here in the form of a power series in reciprocal volume,

$$
Z = \frac{P\bar{v}}{RT} = 1 + \frac{B(T)}{\bar{v}} + \frac{C(T)}{\bar{v}^2} + \frac{D(T)}{\bar{v}^3} + \cdots \tag{12.68}
$$

where $B(T)$, $C(T)$, and $D(T)$ are temperature-dependent and are called virial coefficients. $B(T)$ is termed the second virial coefficient and is due to binary interactions on the molecular level. The general temperature dependence of the second virial coefficient is as shown for nitrogen in Fig. 12.9.

It can be demonstrated that the single temperature at which $B(T) = 0$, as shown in Fig. 12.9, is the Boyle temperature, which was defined in connection with the

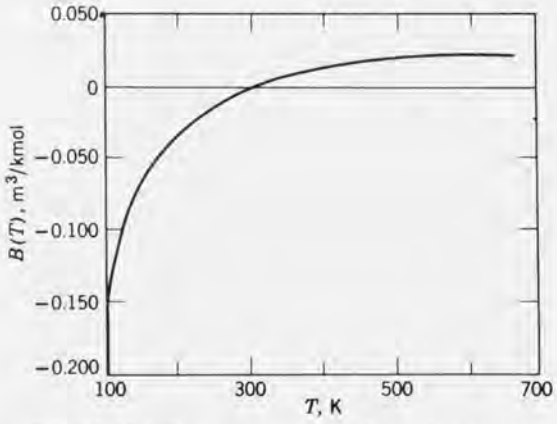


FIGURE 12.9 The second virial coefficient for nitrogen.

discussion of low-density gas behavior, Fig. 12.7. The second virial coefficient can be viewed as the first-order correction for nonideality of the gas, and consequently it is of considerable importance and interest. In fact, the low-density behavior of the isotherms shown in Fig. 12.7 is directly attributable to the second virial coefficient. This is of additional interest, since the virial coefficients can be expressed in terms of intermolecular forces from statistical mechanics and evaluated on the selection of an empirical potential function model. The best known of these functions is the Lennard-Jones (6–12) potential. This function has two force constants, ϵ/k and b_0, values of which are listed for various substances in Table A.13. The expression for $B(T)$ can be put into dimensionless form in terms of the parameter

$$T^* = \frac{T}{\epsilon/k} \tag{12.69}$$

and evaluated for the dimensionless second virial coefficient $B^*(T^*)$, defined from the relation

$$B^*(T^*) = \frac{B(T)}{b_0} \tag{12.70}$$

Values of the dimensionless parameter $B^*(T^*)$, as calculated using the Lennard–Jones (6–12) potential, are also given in Table A.13.1.

EXAMPLE 12.8

Use the virial equation of state to determine the error in specific volume if carbon dioxide is assumed to be an ideal gas at 300 K, 1-MPa pressure.

System: Carbon dioxide.

State: P, T known.

Model: Virial equation with second virial coefficient; compare with the ideal-gas model.

Solution

From Eq. 12.68 at low density,

$$Z = \frac{P\bar{v}}{\bar{R}T} = 1 + \frac{B(T)}{\bar{v}}$$

For carbon dioxide, from Table A.13.2,

$$\epsilon/k = 186 \text{ K}, \qquad b_0 = 0.118 \text{ m}^3/\text{kmol}$$

Therefore,

$$T^* = \frac{T}{\epsilon/k} = \frac{300}{186} = 1.612$$

From Table A.13.1

$$B^*(T^*) = -1.0365$$

Using Eq. 12.70, we have

$$B(T) = b_0 B^*(T^*) = 0.118(-1.0365) = -0.122 \text{ m}^3/\text{kmol}$$

Substituting and solving for $\bar{v}$ gives

$$\frac{1000\bar{v}}{8.3144 \times 300} = 1 - \frac{0.122}{\bar{v}}$$

$$\bar{v} = 2.366 \text{ m}^3/\text{kmol}$$

For an ideal gas,

$$\bar{v} = \frac{\bar{R}T}{P} = \frac{8.3144 \times 300}{1000} = 2.494 \text{ m}^3/\text{kmol}$$

which is in error by 5.4 percent.

12.11 THE GENERALIZED TABLE/CHART FOR CHANGES OF ENTHALPY AT CONSTANT TEMPERATURE

In Section 12.5, Eq. 12.34 was derived for the change of enthalpy at constant temperature,

$$(h_2 - h_1)_T = \int_1^2 \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dP_T$$

This equation is appropriately used when a volume-explicit equation of state is known. Otherwise, it is more convenient to calculate the isothermal change in internal energy from Eq. 12.37,

$$(u_2 - u_1)_T = \int_1^2 \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right] dv_T$$

and then calculate the change in enthalpy from its definition as

$$(h_2 - h_1) = (u_2 - u_1) + (P_2 v_2 - P_1 v_1)$$
$$= (u_2 - u_1) + RT(Z_2 - Z_1)$$

To determine the change in enthalpy behavior consistent with the generalized tables of Table A.14 (and as represented in chart form in Fig. A.7), we follow the second of these approaches, since the Lee–Kesler generalized equation of state, Eq. 12.65, is a pressure-explicit form in terms of specific volume and temperature. Equation 12.65 is expressed in terms of the compressibility factor Z, so we write

$$P = \frac{ZRT}{v}, \qquad \left(\frac{\partial P}{\partial T}\right)_v = \frac{ZR}{v} + \frac{RT}{v}\left(\frac{\partial Z}{\partial T}\right)_v$$

Therefore, substituting into Eq. 12.37, we have

$$du = \frac{RT^2}{v}\left(\frac{\partial Z}{\partial T}\right)_v dv$$

But

$$\frac{dv}{v} = \frac{dv_r'}{v_r'}, \qquad \frac{dT}{T} = \frac{dT_r}{T_r}$$

so that, in terms of reduced variables,

$$\frac{1}{RT_c}du = \frac{T_r^2}{v_r'}\left(\frac{\partial Z}{\partial T_r}\right)_{v_r'} dv_r'$$

This expression is now integrated at constant temperature from any given state (P_r, v_r') to the ideal-gas limit $(P_r^* \to 0, v_r'^* \to \infty)$ (the superscript * will always denote an ideal-gas state or property), causing an internal energy change or departure from the ideal-gas value at the given state,

$$\frac{u^* - u}{RT_c} = \int_{v_r'}^{\infty} \frac{T_r^2}{v_r'}\left(\frac{\partial Z}{\partial T_r}\right)_{v_r'} dv_r' \tag{12.71}$$

The integral on the right-hand side of Eq. 12.71 can be evaluated from the Lee–Kesler equation, Eq. 12.65. The corresponding enthalpy departure at the given state (P_r, v_r') is then found from integrating Eq. 12.71 to be

$$\frac{h^* - h}{RT_c} = \frac{u^* - u}{RT_c} + T_r(1 - Z) \tag{12.72}$$

Following the same procedure as for the compressibility factor, we can evaluate Eq. 12.72 with the set of Lee–Kesler simple-fluid constants to give a simple-fluid enthalpy departure. The values for the enthalpy departure are listed in Table A.14 and are shown graphically in Fig. A.8. Following the same procedure and using the reference fluid constants, we obtain values for the reference fluid enthalpy departure. The overall enthalpy departure at a given state is then the simple-fluid value plus a correction term,

$$\frac{h^* - h}{RT_c} = \left(\frac{h^* - h}{RT_c}\right)^{(0)} + \omega\left(\frac{h^* - h}{RT_c}\right)^{(1)} \tag{12.73}$$

The correction term (1) is taken as the linear weighted average of the (0) and (r) enthalpy departure values, as was done for the compressibility factor in Eq. 12.67. These correction terms are also listed in Table A.14, to give more accurate representations for enthalpy calculations. This procedure is illustrated in the following example.

EXAMPLE 12.9

Nitrogen is throttled from 20 MPa, −70°C, to 2 MPa in an adiabatic, steady-state, steady-flow process. Determine the final temperature of the nitrogen.

Control volume: Throttling valve.
Inlet state: P_1, T_1 known; state fixed.
Exit state: P_2 known.
Process: SSSF, throttling process.
Diagram: Figure 12.10.
Model: Generalized tables, Table A.14.
Analysis:

First law: $$h_1 = h_2$$

Solution

Using values from Table A.6, we have

$$P_1 = 20 \text{ MPa}, \qquad P_{r1} = \frac{20}{3.39} = 5.9$$

$$T_1 = 203.2 \text{ K}, \qquad T_{r1} = \frac{203.2}{126.2} = 1.61$$

$$P_2 = 2 \text{ MPa}, \qquad P_{r2} = \frac{2}{3.39} = 0.59$$

$$\omega = 0.039$$

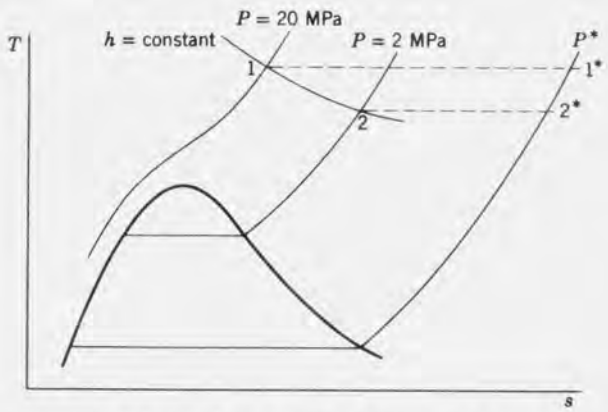


FIGURE 12.10 Sketch for Example 12.9.

From the generalized tables, Table A.14, for the change in enthalpy at constant temperature, we have

$$\frac{h_1^* - h_1}{RT_c} = 2.0314 + 0.039 \times 0.0176 = 2.0321$$

$$h_1^* - h_1 = 2.0321 \times 0.2968 \times 126.2 = 76.1 \text{ kJ/kg}$$

It is now necessary to assume a final temperture and to check whether the net change in enthalpy for the process is zero. Let us assume that $T_2 = 148$ K. Then the change in enthalpy between 1* and 2* can be found from the zero-pressure, specific-heat data.

$$h_1^* - h_2^* = C_{p0}(T_1^* - T_2^*) = 1.0416(203.2 - 148) = +57.5 \text{ kJ/kg}$$

(The variation in C_{p0} with temperature can be taken into account when necessary.)

We now find the enthalpy change between 2* and 2.

$$T_{r2} = \frac{148}{126.2} = 1.173, \qquad P_{r2} = 0.59$$

Therefore, from the enthalpy departure table, Table A.14, at this state

$$\frac{h_2^* - h_2}{RT_c} = 0.4901 + 0.039 \times 0.2601 = 0.5002$$

$$h_2^* - h_2 = 0.5002 \times 0.2968 \times 126.2 = 18.7 \text{ kJ/kg}$$

We now check to see whether the net change in enthalpy for the process is zero.

$$\begin{aligned} h_1 - h_2 = 0 &= -(h_1^* - h_1) + (h_1^* - h_2^*) + (h_2^* - h_2) \\ &= -76.1 + 57.5 + 18.7 = 0.1 \approx 0 \end{aligned}$$

It essentially checks. We conclude that the final temperature is approximately 148 K. It is interesting that the thermodynamic tables for nitrgoen, Table A.5, give essentially this same value for the final temperature.

12.12 THE GENERALIZED TABLE/CHART FOR CHANGES OF ENTROPY AT CONSTANT TEMPERATURE

In this section we wish to develop a generalized table or chart giving entropy departures from ideal gas values at a given temperature and pressure, in a manner similar to that followed for enthalpy in the previous section. Once again, we have two alternatives. From Eq. 12.38, at constant temperature,

$$ds_T = -\left(\frac{\partial v}{\partial T}\right)_P dP_T$$

which is convenient for use with a volume-explicit equation of state. The Lee–Kesler expression, Eq. 12.65, is, however, a pressure-explicit equation. It is therefore more appropriate to use Eq. 12.40, which is, along an isotherm,

$$ds_T = \left(\frac{\partial P}{\partial T}\right)_v dv_T$$

In the Lee–Kesler form, in terms of reduced properties, this equation becomes

$$\frac{ds}{R} = \left(\frac{\partial P_r}{\partial T_r}\right)_{v'_r} dv'_r$$

When this expression is integrated from a given state (P_r, v'_r) to the ideal-gas limit ($P_r^* \to 0$, $v_r'^* \to \infty$), there is a problem because ideal-gas entropy is a function of pressure and approaches infinity as the pressure approaches zero. We can eliminate this problem with a two-step procedure. First, the integral is taken only to a certain finite P_r^*, $v_r'^*$, which gives the entropy change

$$\frac{s^*_{P^*} - s_P}{R} = \int_{v'_r}^{v'^*_r} \left(\frac{\partial P_r}{\partial T_r}\right)_{v'_r} dv'_r \tag{12.74}$$

This integration by itself is not entirely acceptable, because it contains the entropy at some arbitrary, low reference pressure. A value for the reference pressure would have to be specified. Let us now repeat the integration over the same change of state, except this time for a hypothetical ideal gas. The entropy change for this integration is

$$\frac{s^*_{P^*} - s^*_P}{R} = +\ln \frac{P}{P^*} \tag{12.75}$$

If we now subtract Eq. 12.75 from Eq. 12.74, the result is the difference in entropy of a hypothetical ideal gas at a given state (T_r, P_r) and that of the real substance at the same state, or

$$\frac{s^*_P - s_P}{R} = -\ln \frac{P}{P^*} + \int_{v'_r}^{v'^*_r \to \infty} \left(\frac{\partial P_r}{\partial T_r}\right)_{v'_r} dv'_r \tag{12.76}$$

Here the values associated with the arbitrary reference state P_r^*, $v_r'^*$, cancel out of the right-hand side of the equation. (The first term of the integral includes the term $+\ln(P/P^*)$, which cancels the other term. The three different states associated with the development of Eq. 12.76 are shown in Fig. 12.11.

The same procedure that was given in Section 12.11 for enthalpy departure values is followed for generalized entropy departure values. The Lee–Kesler simple-

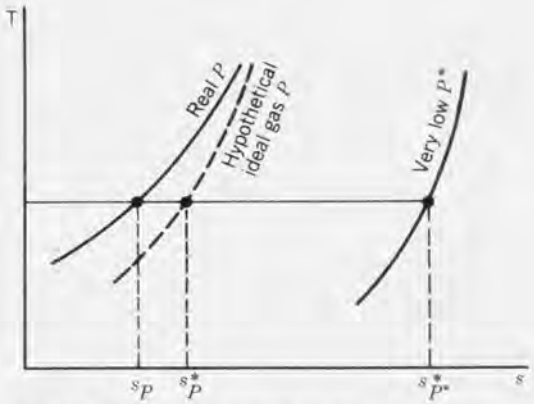


FIGURE 12.11 Real and ideal gas states and entropies.

fluid constants are used in evaluating the integral of Eq. 12.76 and yield a simple-fluid entropy departure. The values for the entropy departure are listed in Table A.14 and shown graphically in Fig. A.9. The procedure using the reference fluid constants gives a set of values for the reference fluid entropy departure. The overall entropy departure at a given state is then the simple-fluid value plus a correction term,

$$\frac{s_P^* - s_P}{R} = \left(\frac{s_P^* - s_P}{R}\right)^{(0)} + \omega\left(\frac{s_P^* - s_P}{R}\right)^{(1)} \tag{12.77}$$

The correction term (1) is once again taken as the linear weighted average of the (0) and (*r*) entropy departure values, as was done for the compressibility factor and the enthalpy departure values. These correction terms are also listed in Table A.14 to give more accurate representations for entropy departure values than do the simple-fluid correlations alone.

EXAMPLE 12.10

Nitrogen at 8 MPa, 150 K, is throttled to 0.5 MPa. After the gas passes through a short length of pipe, its temperature is measured and found to be 125 K. Determine the heat transfer and the change of entropy using the generalized charts. Compare these results with those obtained by using the nitrogen tables.

Control volume: Throttle and pipe.

Inlet state: P_1, T_1 known; state fixed.

Exit state: P_2, T_2 known; state fixed.

Process: SSSF.

Diagram: Figure 12.12.

Model: Generalized tables, results to be compared with those obtained with nitrogen tables.

Analysis: There is no work done, and we neglect changes in kinetic and potential energies. Therefore, per kilogram,

First law: $$q + h_1 = h_2$$

$$q = h_2 - h_1 = -(h_2^* - h_2) + (h_2^* - h_1^*) + (h_1^* - h_1)$$

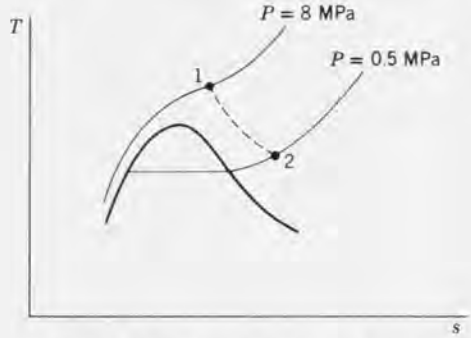


FIGURE 12.12 Sketch for Example 12.10.

Solution

Using values from Table A.6, $\omega = 0.039$, we have

$$P_{r1} = \frac{8}{3.39} = 2.36, \qquad T_{r1} = \frac{150}{126.2} = 1.189$$

$$P_{r2} = \frac{0.5}{3.39} = 0.147, \qquad T_{r2} = \frac{125}{126.2} = 0.99$$

From Table A.14,

$$\frac{h_1^* - h_1}{RT_c} = 2.5085 + 0.039 \times 0.5767 = 2.5310$$

$$h_1^* - h_1 = 2.531 \times 0.2968 \times 126.2 = 94.8 \text{ kJ/kg}$$

$$\frac{h_2^* - h_2}{RT_c} = 0.1562 + 0.039 \times 0.1443 = 0.1618$$

$$h_2^* - h_2 = 0.1618 \times 0.2968 \times 126.2 = 6.1 \text{ kJ/kg}$$

Assuming a constant specific heat for the ideal gas, we have

$$h_2^* - h_1^* = C_{p0}(T_2 - T_1) = 1.0416(125 - 150) = -26.0 \text{ kJ/kg}$$

$$q = -6.1 - 26.0 + 94.8 = 62.7 \text{ kJ/kg}$$

From the nitrogen tables, Table A.5, we can find the change of enthalpy directly.

$$q = h_2 - h_1 = 123.77 - 61.92 = 61.85 \text{ kJ/kg}$$

To calculate the change of entropy using the generalized charts, we proceed as follows:

$$s_2 - s_1 = -(s_{P_2,T_2}^* - s_2) + (s_{P_2,T_2}^* - s_{P_1,T_1}^*) + (s_{P_1,T_1}^* - s_1)$$

From Table A.14

$$\frac{s_{P_1,T_1}^* - s_{P_1,T_1}}{R} = 1.5905 + 0.039 \times 0.6590 = 1.6162$$

$$s_{P_1,T_1}^* - s_{P_1,T_1} = 1.6162 \times 0.2968 = 0.4797 \text{ kJ/kg K}$$

$$\frac{s_{P_2,T_2}^* - s_{P_2,T_2}}{R} = 0.1064 + 0.039 \times 0.1341 = 0.1117$$

$$s_{P_2,T_2}^* - s_{P_2,T_2} = 0.1117 \times 0.2968 = 0.0332 \text{ kJ/kg K}$$

Assuming a constant specific heat for the ideal gas, we have

$$s_{P_2,T_2}^* - s_{P_1,T_1}^* = C_{p0} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$= 1.0416 \ln \frac{125}{150} - 0.2968 \ln \frac{0.5}{8}$$

$$= 0.6330 \text{ kJ/kg K}$$

$$s_2 - s_1 = -0.0332 + 0.6330 + 0.4797$$
$$= 1.0795 \text{ kJ/kg K}$$

From the nitrogen tables, Table A.5,

$$s_2 - s_1 = 5.4282 - 4.3522 = 1.0760 \text{ kJ/kg K}$$

12.13 FUGACITY AND THE GENERALIZED FUGACITY TABLE/CHART

At this point a new thermodynamic property, fugacity, f, is introduced. Fugacity is particularly important when considering mixtures and equilibrium, which is discussed in Chapter 14. A generalized fugacity table and chart can be developed, however. For this reason fugacity is introduced here.

Fugacity is essentially a pseudopressure. When fugacity is substituted for pressure, we can, in effect use the same equations for real gases that we normally use for ideal gases. The concept of fugacity is introduced as follows. Consider the relation

$$dg = -s\,dT + v\,dP$$

At constant temperature

$$dg_T = v\,dP_T \tag{12.78}$$

For an ideal gas this last equation can be written

$$dg_T = \frac{RT}{P}\,dP_T = RT\,d(\ln P)_T \tag{12.79}$$

and for a real gas, with the equation of state $Pv = ZRT$, this equation becomes

$$dg_T = ZRT\frac{dP_T}{P} = ZRT\,d(\ln P)_T \tag{12.80}$$

Fugacity, f, is defined as

$$dg_T = RT\,d(\ln f)_T \tag{12.81}$$

with the requirement that

$$\lim_{P \to 0}\left(\frac{f}{P}\right) = 1 \tag{12.82}$$

Therefore, as $P \to 0, f \to 0$.

Let us consider the change in the Gibbs function of a real gas during an isothermal process at temperature T that changes pressure from very low P^* (where ideal-gas behavior can be assumed), to a higher pressure P. Let the Gibbs function at this low pressure be designated g^*. The value of the Gibbs function at this

temperature T and at the pressure P can be found in terms of the fugacity at P and T and g^*. This is evident if we integrate Eq. 12.81 from the very low pressure P^* to the pressure P,

$$\int_{g^*}^{g} dg_T = \int_{f^*}^{f} RT(d \ln f)_T$$

$$g_P = g^*_{P^*} + RT \ln \frac{f}{P^*} \tag{12.83}$$

Let us repeat this integration of Eq. 12.81 at constant temperature from pressure P^* to P, except now for a hypothetical ideal gas. The expression is

$$g^*_P = g^*_{P^*} + RT \ln \frac{P}{P^*} \tag{12.84}$$

Subtracting Eq. 12.84 from Eq. 12.83 gives

$$g_P - g^*_P = RT \ln \frac{f}{P} \tag{12.85}$$

Using the definition of the Gibbs function, we have

$$g_P - g^*_P = (h_P - h^*_P) - T(s_P - s^*_P) \tag{12.86}$$

Substituting Eq. 12.85 and rearranging terms, we obtain the following expression for the fugacity coefficient:

$$\ln \frac{f}{P} = -\frac{1}{T_r} \frac{h^*_P - h_P}{RT_c} + \frac{s^*_P - s_P}{R} \tag{12.87}$$

The two terms on the right-hand side of this equation are the enthalpy departure and the entropy departure, which were considered in Sections 12.11 and 12.12. Therefore, we can make up a generalized table and chart for the fugacity coefficient in the same manner as has already been done for the enthalpy and entropy properties. The expression is

$$\ln \frac{f}{P} = \ln \left(\frac{f}{P} \right)^{(0)} + \omega \ln \left(\frac{f}{P} \right)^{(1)} \tag{12.88}$$

The simple-fluid term (0) is listed in Table A.14 and shown graphically in Fig. A.10. The correction term (1) is listed in Table A.14.

Another development related to fugacity is often very useful, particularly when pressure is an independent variable. Comparing Eqs. 12.78 and 12.81 at a given temperature, we note that

$$d \ln f_T = \frac{v}{RT} dP_T = \frac{Z}{P} dP_T$$

If we subtract the identity

$$d \ln P_T = \frac{dP_T}{P}$$

from this expression, we obtain

$$d \ln\left(\frac{f}{P}\right)_T = (Z - 1)\frac{dP_T}{P} = (Z - 1)d \ln P_T$$

This expression can now be integrated along the isotherm from very low pressure $P^* \to 0$ to pressure P, which gives for the fugacity coefficient at P

$$\ln \frac{f}{P} = \int_0^P (Z - 1)d \ln P_T \tag{12.89}$$

EXAMPLE 12.11

Calculate the work of compression and the heat transfer per kilogram when ethane is compressed reversibly and isothermally from 0.1 to 7 MPa at a temperature of 45°C in a steady-state, steady-flow process.

Control volume: Compressor.

Inlet state: P_1, T known; state fixed.

Exit state: P_2, T known; state fixed.

Process: SSSF, isothermal and reversible.

Diagram: Figure 12.13.

Model: Generalized tables.

Analysis:

First law: $q + h_1 + \text{KE}_1 + \text{PE}_1 = h_2 + \text{KE}_2 + \text{PE}_2 + w$

Since the process is reversible and isothermal,

$$q = T(s_2 - s_1) = T_2 s_2 - T_1 s_1$$

Therefore,

$$-w = h_2 - h_1 - (T_2 s_2 - T_1 s_1) + \Delta\text{KE} + \Delta\text{PE}$$
$$-w = g_2 - g_1 + \Delta\text{KE} + \Delta\text{PE}$$

We assume that the changes in kinetic and potential energy are negligible.

$$-w = g_2 - g_1 = RT \ln (f_2/f_1)$$

Solution

The fugacity in state 1 and state 2 can be found from the generalized fugacity table in Table A.14.

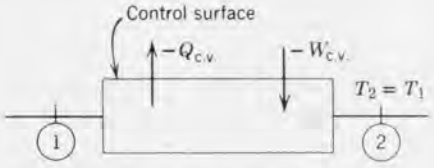


FIGURE 12.13 Sketch for Example 12.11.

For ethane,

$$P_c = 4.88 \text{ MPa}, \qquad T_c = 305.4 \text{ K}, \qquad \omega = 0.099$$

Therefore,

$$P_{r_1} = \frac{0.1}{4.88} = 0.0205, \qquad P_{r_2} = \frac{7.0}{4.88} = 1.434$$

$$T_{r_1} = T_{r_2} = \frac{318.2}{305.4} = 1.042$$

From the generalized enthalpy departure table, Table A.14,

$$\frac{h_1^* - h_1}{RT_c} = 0.0191 + 0.099 \times 0.0157 = 0.0206$$

$$h_1^* - h_1 = 0.0206 \times 0.2765 \times 305.4 = 1.7 \text{ kJ/kg}$$

$$\frac{h_2^* - h_2}{RT_c} = 3.0614 + 0.099 \times 1.6048 = 3.2203$$

$$h_2^* - h_2 = 3.2203 \times 0.2765 \times 305.4 = 271.9 \text{ kJ/kg}$$

Since $h_2^* - h_1^* = 0$,

$$h_2 - h_1 = -271.9 + 0 + 1.7 = -270.2 \text{ kJ/kg}$$

From the generalized fugacity table,

$$\ln\left(\frac{f}{P}\right)_1 = -0.0060 + 0.099(-0.0007) = -0.0061$$

$$f_1 = 0.9939 \times 0.1 = 0.099 \text{ MPa}$$

$$\ln\left(\frac{f}{P}\right)_2 = -0.5494 + 0.099(0.0053) = -0.5489$$

$$f_2 = 0.5776 \times 7 = 4.043 \text{ MPa}$$

Therefore,

$$-w = g_2 - g_1 = RT \ln \frac{f_2}{f_1}$$

$$= 0.2765 \times 318.2 \ln \frac{4.043}{0.099} = 326.4 \text{ kJ/kg}$$

$$g_2 - g_1 = (h_2 - h_1) - T(s_2 - s_1) = (h_2 - h_1) - q$$

$$q = -270.2 - 326.4 = -596.6 \text{ kJ/kg}$$

12.14 EQUATIONS OF STATE AND PSEUDOCRITICAL STATE FOR MIXTURES

Frequently it is desirable to have an equation of state for a mixture of gases. The question is how an equation of state for a mixture can be developed from the

equations of state for the pure components. For example, suppose the equations of state of the components are available in a given form with given constants for each component. How can these constants be combined to provide an equation of state that accurately represents the P–v–T behavior of the mixture?

An extensive discussion of this question is beyond the scope of this text. Instead, we simply note that various empirical combining rules have been proposed for the different equations of state and compared with experimental data for mixtures. As an example, for both the van der Waals equation, Eq. 12.55, and the Redlich–Kwong equation, Eq. 12.61, the two pure substance constants a and b are commonly combined according to the relations

$$a_{\text{mix}} = \left(\sum_i y_i a_i^{1/2} \right)^2, \qquad b_{\text{mix}} = \sum_i y_i b_i \tag{12.90}$$

When limited P–v–T data are available, the generalized compressibility table or chart can often be used with considerable accuracy. The mixture may be treated as a pseudopure substance, for which a set of critical constants are determined by some empirical combinations of the pure-substance constants. For the Lee–Kesler equation, Eq. 12.65, which represents generalized compressibility behavior in this text, the following procedure is recommended. For the pseudocritical specific volume and temperature,

$$\bar{v}_{c\,\text{mix}} = \sum_j \sum_k y_j y_k \bar{v}_{c_{jk}} \tag{12.91}$$

$$(\bar{v}_c T_c)_{\text{mix}} = \sum_j \sum_k y_j y_k \bar{v}_{c_{jk}} T_{c_{jk}} \tag{12.92}$$

In these expressions the interaction parameters are

$$\bar{v}_{c_{jk}} = \tfrac{1}{8}(\bar{v}_{c_j}^{1/3} + \bar{v}_{c_k}^{1/3})^3, \qquad T_{c_{jk}} = (T_{c_j} T_{c_k})^{1/2} \tag{12.93}$$

Once these values have been determined, the pseudocritical pressure can then be found from the expressions

$$\omega_{\text{mix}} = \sum_j y_j \omega_j \tag{12.94}$$

$$Z_{c\,\text{mix}} = 0.2905 - 0.085\omega_{\text{mix}} \tag{12.95}$$

and

$$P_{c\,\text{mix}} = Z_{c\,\text{mix}} \bar{R} T_{c\,\text{mix}} / \bar{v}_{c\,\text{mix}} \tag{12.96}$$

These pseudocritical properties have been found to give reasonably good correlations with properties of mixtures for a wide variety of gas mixtures and compostions.

EXAMPLE 12.12

A mixture of 59.39 percent CO_2 and 40.61 percent CH_4 (mole basis) is maintained at 310.94 K, 86.19 bar, at which condition the specific volume has been measured as 0.2205 m^3/kmol. Calculate the percent deviation if the specific volume had been calculated by (a) the Lee–Kesler equation and (b) the van der Waals equation of state.

System: Gas mixture.
State: P, v, T known.
Model: (a) the Lee–Kesler equation, (b) the van der Waals equation.

Solution

(a) For convenience, let

$$CO_2 = A, \qquad CH_4 = B.$$

Then

$$T_{c_A} = 304.1 \text{ K}, \qquad \bar{v}_{c_A} = 0.0939 \text{ m}^3/\text{kmol}$$
$$T_{c_B} = 190.4 \text{ K}, \qquad \bar{v}_{c_B} = 0.0992 \text{ m}^3/\text{kmol}$$

The two intersection parameters are found from the expressions in Eq. 12.93,

$$\bar{v}_{c_{AB}} = \tfrac{1}{8}(0.0939^{1/3} + 0.0992^{1/3})^3 = 0.0965 \text{ m}^3/\text{kmol}$$
$$T_{c_{AB}} = (304.1 \times 190.4)^{1/2} = 240.6 \text{ K}$$

From Eq. 12.91,

$$\begin{aligned}\bar{v}_{c\,\text{mix}} &= y_A^2\bar{v}_{c_A} + 2y_Ay_B\bar{v}_{c_{AB}} + y_B^2\bar{v}_{c_B} \\ &= (0.5939)^2(0.0939) + 2(0.5939)(0.4061)(0.0965) + (0.4061)^2(0.0992) \\ &= 0.0960 \text{ m}^3/\text{kmol}\end{aligned}$$

From Eq. 12.92,

$$\begin{aligned}0.0960 \times T_{c\,\text{mix}} &= y_A^2\bar{v}_{c_A}T_{c_A} + 2y_Ay_B\bar{v}_{c_{AB}}T_{c_{AB}} + y_B^2\bar{v}_{c_B}T_{c_B} \\ &= (0.5939)^2(0.0939)(304.1) + 2(0.5939)(0.4061)(0.0965)(240.6) \\ &\quad + (0.4061)^2(0.0992)(190.4) \\ T_{c\,\text{mix}} &= 254.0 \text{ K}\end{aligned}$$

Using Eqs. 12.94 through 12.96, we have

$$\omega_{\text{mix}} = 0.5939(0.239) + 0.4061(0.011) = 0.146$$
$$Z_{c\,\text{mix}} = 0.2905 - 0.085(0.146) = 0.278$$
$$P_{c\,\text{mix}} = 0.278 \times 8.3144 \times \frac{254}{0.0960}$$
$$= 6116 \text{ kPa} = 6.116 \text{ MPa}$$

Therefore, the pseudoreduced properties of the mixture are

$$T_{r\,\text{mix}} = \frac{T}{T_{c\,\text{mix}}} = \frac{310.94}{254.0} = 1.224$$
$$P_{r\,\text{mix}} = \frac{P}{P_{c\,\text{mix}}} = \frac{8.619}{6.116} = 1.409$$

From the generalized tables, Table A.14,

$$Z_{\text{mix}} = 0.7107 + 0.146 \times 0.1318 = 0.7299$$

$$\bar{v} = \frac{Z_{\text{mix}}\bar{R}T}{P} = \frac{0.7299 \times 8.3144 \times 310.94}{8619}$$

$$= 0.2189 \text{ m}^3/\text{kmol}$$

The percent deviation from the experimental value is

$$\text{Percent deviation} = \frac{0.2205 - 0.2189}{0.2205} \times 100 = 0.7 \text{ percent}$$

(b) For the van der Waals equation, the pure-substance constants are

$$a_A = \frac{27\bar{R}^2 T_{c_A}^2}{64 P_{c_A}} = 365.445 \frac{\text{kPa m}^6}{\text{kmol}^2}$$

$$b_A = \frac{\bar{R}T_{c_A}}{8P_{c_A}} = 0.042\,83 \text{ m}^3/\text{kmol}$$

and

$$a_B = \frac{27\bar{R}^2 T_{c_B}^2}{64 P_{c_B}} = 229.838 \frac{\text{kPa m}^6}{\text{kmol}^2}$$

$$b_B = \frac{\bar{R}T_{c_B}}{8P_{c_B}} = 0.043\,02 \text{ m}^3/\text{kmol}$$

Therefore, for the mixture, from Eq. 12.79,

$$a_{\text{mix}} = \left(y_A\sqrt{a_A} + y_B\sqrt{a_B}\right)^2$$

$$= \left(0.5939\sqrt{365.445} + 0.4061\sqrt{229.838}\right)^2$$

$$= 306.600 \frac{\text{kPa m}^6}{\text{kmol}^2}$$

$$b_{\text{mix}} = y_A b_A + y_B b_B$$

$$= (0.5939 \times 0.042\,83 + 0.4061 \times 0.043\,02)$$

$$= 0.042\,91 \text{ m}^3/\text{kmol}$$

The equation of state for the mixture of this composition is

$$P = \frac{\bar{R}T}{\bar{v} - b_{\text{mix}}} - \frac{a_{\text{mix}}}{\bar{v}^2}$$

$$8619 = \frac{8.3144 \times 310.94}{\bar{v} - 0.042\,91} - \frac{306.600}{\bar{v}^2}$$

Solving for $\bar{v}$ by trial and error, we have

$$\bar{v} = 0.2063 \text{ m}^3/\text{kmol}$$

$$\text{Percent deviation} = \frac{0.2205 - 0.2063}{0.2205} \times 100 = 6.4 \text{ percent}$$

As a point of interest, from the ideal-gas law, $\bar{v} = 0.300$ m^3/kmol, which is a deviation of 36 percent from the measured value. Moreover, if we use the Redlich–Kwong equation of state and follow the same procedure as for the van der Waals equation, the calculated specific volume of the mixture is 0.2127 m^3/kmol, which is in error by 3.5 percent.

We must be careful not to draw too general a conclusion from the results of this example. We have calculated percent deviation in v at only a single point for only one mixture. We do note, however, that the various methods give quite different results. From a more general study of these models for a number of mixtures, we find that our results are fairly typical, at least qualitatively. The Lee–Kesler equation is very useful because it is fairly accurate yet relatively simple. The van der Waals equation is too simplified an expression to represent accurately P–v–T behavior except at moderate densities, but it is useful for demonstrating the procedures followed with more complex analytical equations of state. The Redlich–Kwong equation is considerably better and is still relatively simple to use.

The more sophisticated generalized behavior models and empirical equations of state will represent mixture P–v–T behavior to within about 1 percent over a wide range of density, but they are of course more difficult to use than the methods considered in Example 12.12. The generalized models have the advantage of being easier to use, and they are suitable for hand computations. Calculations with the complex empirical equations of state become very involved, but they have the advantage of expressing the P–v–T composition relations in analytical form, which is of great value when using a digital computer for such calculations.

The theoretical virial equation of state, Eq. 12.68, can be applied to mixtures, in which case the virial coefficients are dependent on composition as well as on temperature. For a mixture of A and B, the second virial coefficient becomes

$$B(T, y) = y_A^2 B_A(T) + 2y_A y_B B_{AB}(T) + y_B^2 B_B(T) \tag{12.97}$$

in which the interaction coefficient $B_{AB}(T)$ is due to forces between unlike molecules. For the Lennard–Jones (6-12) potential, this interaction can be found from the parameters

$$\begin{aligned} \epsilon_{AB} &= (\epsilon_A \epsilon_B)^{1/2} \\ b_{0AB} &= \tfrac{1}{8}(b_{0A}^{1/3} + b_{0B}^{1/3})^3 \end{aligned} \tag{12.98}$$

and the values in Table A.13.

PROBLEMS

12.1 Calculate the values h_{fg} and s_{fg} for nitrogen at 70 K and at 110 K from the Clapeyron equation, using the necessary pressure and specific volume values from Table A.5.1SI.

12.2 Using thermodynamic data for water from Tables A.1.1SI and A.1.5SI, estimate the freezing temperature of liquid water at a pressure of 30 MPa.

12.2E Using thermodynamic data for water from Tables A.1.1E and A.1.5E, estimate the freezing temperature of liquid water at a pressure of 5000 lbf/in.^{2}.

12.3 At standard atmospheric pressure, 101.3 kPa, helium boils at 4.22 K, and the latent heat of vaporization is 83.3 kJ/kmol. We wish to estimate how low a temperature can be obtained by pumping a vacuum over liquid helium, which will cause the liquid helium to boil at a lower pressure and temperature. Determine what pressures would be necessary to produce a temperature of 1 K and one of 0.5 K. What do you think is the lowest temperature that could be obtained by pumping a vacuum over liquid helium?

12.4 A transfer line for liquid oxygen is designed with a double-walled pipe, as shown in Fig. 12.14. At ambient temperature, the annular space in the line is filled with carbon dioxide gas at slightly above ambient pressure. When liquid oxygen at 100 K flows through the transfer line, most of the carbon dioxide in the annular space will freeze on the inner wall, and the pressure in this space will be equal to the sublimation pressure of carbon dioxide at 100 K. There are no thermodynamic tables available for this low a temperature, but it is known that at $-90°C$ the sublimation pressure is 38.1 kPa and the enthalpy of sublimation is 574.5 kJ/kg. Estimate the carbon dioxide pressure in the annular space when liquid oxygen is flowing through the transfer line.

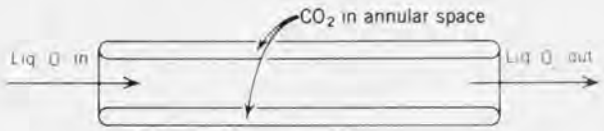


FIGURE 12.14 Sketch for Problem 12.4.

12.5 An experiment is to be conducted at $-100°C$ using R-22 as the bath liquid in a rigid closed tank (with a small amount of vapor at the top).

(a) What is the pressure inside the tank?

(b) When the experiment is completed, the tank will be allowed to warm to room temperature, 20°C. If the pressure inside is not to exceed 1.0 MPa at this time, what is the maximum percent liquid (by volume) that can be used in the tank during the experiment at $-100°C$?

12.6 A particular pollutant in combustion products takes the form of very small solid particles. To analyze and evaluate the problem, we need to know the sublimation pressure of this substance at various temperatures. Suppose that the only thermodynamic data available are as follows: normal (101.3 kPa) boiling-point temperature and enthalpy of vaporization h_{fg}; and normal melting-point temperature and enthalpy of fusion h_{if}. Develop a procedure for estimating the sublimation pressure as a function of temperature based on this information.

12.7 Consider a Carnot-cycle heat engine in which the working fluid changes from saturated liquid to saturated vapor at temperature T (and pressure P) during the heat addition process. The heat rejection occurs at $T - \Delta T$ (and $P - \Delta P$). Using a first- and second-law analysis, by assuming that the four processes in the cycle

are system processes with work done at the moving boundary, show that the Clapeyron equation, Eq. 12.26, results at the limit as $\Delta T \to dT$.

12.8 Repeat Problem 12.7, but assume that the four processes are steady-state, steady-flow processes with shaft work.

12.9 Derive expressions for $(\partial h/\partial v)_T$ and for $(\partial h/\partial T)_v$ that do not contain the properties h, u, or s.

12.10 Derive expressions for $(\partial T/\partial v)_u$ and for $(\partial h/\partial s)_v$ that do not contain the properties h, u, or s.

12.11 Develop an expression for the relation between temperature and pressure in an isentropic process that includes only the P–v–T behavior and the specific heat of the substance.

12.12 We wish to determine the average value (over a range of pressure) of the isothermal compressibility of liquid water at 0°C, and also at 100 and 300°C, using data from the compressed-liquid table, Table A.1.4SI. Does the isothermal compressibility vary significantly with pressure at a given temperature?

12.12E We wish to determine the average value (over a range of pressure) of the isothermal compressibility of liquid water at 32 F, and also at 200 and 500 F, using data from the compressed-liquid table, Table A.1.4E. Does the isothermal compressibility vary significantly with pressure at a given temperature?

12.13 It can be shown that the velocity of sound c in a fluid is given by the expression

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_s$$

The adiabatic compressibility of liquid ethanol at 20°C is 940 $\mu m^2/N$. Calculate the velocity of sound at this temperature.

12.14 A cylinder fitted with a piston contains liquid methanol at 20°C, 100 kPa. The volume is 10 L. The piston is moved, compressing the methanol to 20 MPa at constant temperature. Calculate the work required for this process. The isothermal compressibility of liquid methanol at this temperature is 1220 $\mu m^2/N$.

12.15 Suppose that the following data are available for a given pure substance:

A liquid–vapor vapor–pressure curve.
An equation of state (vapor) of the form $P = fn(T, v)$.
Specific volume of saturated liquid.
Critical pressure and temperature.
Constant-volume specific heat (vapor) at one specific volume.

Outline the procedure that you would follow to develop a table of thermodynamic properties comparable to Tables 1, 2, and 3 of the steam tables.

12.16 A 200-L rigid tank contains propane at 9 MPa, 280°C. The propane is then allowed to cool to 50°C as heat is transferred with the surroundings. Determine the quality at the final state and the mass of liquid in the tank, using the generalized compressibility tables, Table A.14 (or chart, Fig. A.7). Assume that the propane behaves as a "simple" fluid.

12.17 Repeat Problem 12.16 using Table A.14 and include the acentric factor correction term in the compressibility factor.

12.18 A rigid tank contains 5 kg of ethylene at 3 MPa, 30°C. This system is cooled until the ethylene reaches the saturated-vapor curve. What is the final temperature?

12.18E A rigid tank contains 5 lbm of ethylene at 450 lbf/in.^{2}, 90 F. This system is cooled until the ethylene reaches the saturated-vapor curve. What is the final temperature?

12.19 A cylinder fitted with a piston contains 5 kg of butane gas at 500 K, 5 MPa. The butane expands in a reversible polytropic process with polytropic exponent $n = 1.05$ until the final pressure is 3 MPa. Determine

(a) The final temperature of the butane.
(b) The work done during the process.

12.20 Show that the two expressions for the Joule–Thomson coefficient μ_J given by Eq. 12.54 are valid.

12.21 Two uninsulated tanks of equal volume are connected by a valve. One tank contains a gas at moderate pressure P_1, and the other tank is evacuated. The valve is opened and remains open for a long time. Is the final pressure P_2 greater than, equal to, or less than one-half of P_1?

12.22 Develop expressions for isothermal changes in enthalpy and in entropy for each of the following equations of state:

(a) The van der Waals equation.
(b) The Redlich–Kwong equation.
(c) The Benedict–Webb–Rubin equation.

12.23 Determine the Boyle temperature as predicted by an equation of state, using

(a) The van der Waals equation.
(b) The Redlich–Kwong equation.

12.24 Consider a straight line connecting the point $P = 0$, $Z = 1$ to the critical point $P = P_c$, $Z = Z_c$ on a Z versus P compressibility diagram. This straight line will be tangent to one particular isotherm at low pressure. Determine what value of reduced temperature is predicted by an equation of state, using

(a) The van der Waals equation.
(b) The Redlich–Kwong equation.

12.25 Determine the low-pressure Joule–Thomson inversion temperature

$$\lim_{P \to 0} \mu_J = 0$$

as predicted by an equation of state, using

(a) The van der Waals equation.
(b) The Redlich–Kwong equation.

12.26 One early attempt to improve on the van der Waals equation of state was an expression of the form

$$P = \frac{RT}{v - b} - \frac{a}{v^2 T}$$

(a) Solve for the constants a, b, and v_c using the same procedure as for the van der Waals equation.

(b) Repeat Problems 12.23, 12.24, and 12.25 using this equation of state.

12.27 Boil-off vapor from a liquid argon storage facility is collected and stored in a 100-L rigid tank at 120 K, 500 kPa. Use the virial equation of state to determine the mass of argon inside the tank at this state. Explain why one of two possible answers cannot be correct.

12.28 Calculate the difference in internal energy of the ideal-gas value and the real-gas value for carbon dioxide at the state 20°C, 1 MPa, as determined using the virial equation of state.

12.28E Calculate the difference in internal energy of the ideal-gas value and the real-gas value for carbon dioxide at the state 70 F, 150 lbf/in.^{2}, as determined using the virial equation of state.

12.29 Repeat Problem 12.28 for the corresponding difference in entropy values.

12.30 Refrigerant-123, dichlorotrifluoroethane, which is currently under development as a potential replacement for environmentally hazardous refrigerants, undergoes an isothermal SSSF process in which the R-123 enters the heat exchanger as saturated liquid at 40°C and exits at 100 kPa. Calculate the heat transfer per kilogram of R-123, using the generalized tables, Table A.14.

12.31 Calculate the heat transfer during the process described in Problem 12.19.

12.32 Saturated vapor R-22 at 30°C is throttled to 200 kPa in a SSSF process. Calculate the exit temperature, using

(a) The generalized tables, Table A.14.

(b) The R-22 tables, Table A.4.

12.33 A 250-L tank contains propane at 30°C, 90 percent quality. The tank is heated to 300°C. Calculate the heat transfer during this process.

12.33E A 10-ft^3 tank contains propane at 90 F, 90 percent quality. The tank is heated to 600 F. Calculate the heat transfer during this process.

12.34 Nitrogen gas is to be injected into an oil field at very high pressure as part of an enhanced oil recovery process. The nitrogen enters a compressor from storage at 17 MPa, 15°C, and is compressed to 34 MPa in a compressor having an isentropic efficiency of 85 percent. Determine the required work per kilogram of nitrogen and the compressor exit temperature.

12.35 How much less work would be required if the compression process of Problem 12.34 is achieved in two stages, of equal pressure ratios, with intercooling back to 15°C between the stages?

12.36 A 200-L rigid tank contains propane at 400 K, 3.5 MPa. A valve is opened, and propane flows out until half the initial mass has escaped, at which point the valve is closed. During this process the mass remaining inside the tank expands according to the relation $Pv^{1.4}$ = constant. Calculate the heat transfer to the tank during the process.

12.37 The refrigerant R-152a, difluoroethane, is under study as a possible replacement for other refrigerants. Several tanks are to be filled with R-152a for testing in

another location. The procedure is as follows. A 10-L evacuated tank is connected to a line flowing saturated-vapor R-152a at 40°C. The valve is then opened, and the fluid flows in rapidly, so that the process is essentially adiabatic. The valve is to be closed when the pressure reaches a certain value P_2, and the tank will then be disconnected from the line. After a period of time, the temperature inside the tank will return to ambient temperature, 25°C, through heat transfer with the surroundings. At this time, the pressure inside the tank must be 500 kPa. What is the pressure P_2 at which the valve should be closed during the filling process? The ideal-gas constant-pressure specific heat of R-152a is 0.996 kJ/kg K.

12.38 An evacuated 100-L rigid tank is connected to a line flowing R-142b gas, chlorodifluoroethane, at 2 MPa, 100°C. The valve is opened, allowing the gas to flow into the tank for a period of time. The valve is then closed. Eventually, the tank cools to ambient temperature, 20°C, at which point it contains 50 percent liquid, 50 percent vapor, by volume. Calculate the heat transfer for this process. The ideal-gas constant-pressure specific heat of R-142b is 0.787 kJ/kg K.

12.39 An insulated vertical cylinder is fitted with a piston restrained by a spring and held by a pin, as shown in Fig. 12.15. The cylinder cross-sectional area is 0.2 m^2, the initial volume is 0.1 m^3, and the cylinder contains carbon dioxide at 2.5 MPa, 0°C. Ambient pressure above the piston plus gravitational force per area on the piston is 250 kPa. The spring is linear (force proportional to distance) with a spring constant of 600 kN/m, and the spring force would be zero at a cylinder volume of 0.05 m^3. The pin is pulled from the piston. What is the final pressure inside the cylinder?

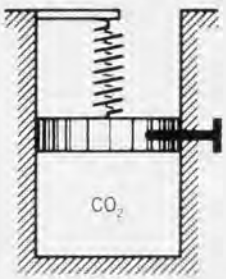


FIGURE 12.15 *Sketch for Problems 12.39 and 12.39E.*

12.39E An insulated vertical cylinder is fitted with a piston restrained by a spring and held by a pin, as shown in Fig. 12.15. The cylinder cross-sectional area is 2 ft^2, the initial volume is 3.5 ft^3, and the cylinder contains carbon dioxide at 350 $lbf/in.^2$, 35 F. Ambient pressure above the piston plus gravitational force per area on the piston is 35 $lbf/in.^2$. The spring is linear (force proportional to distance) with a spring constant of 3500 lbf/in., and the spring force would be zero at a cylinder volume of 1.5 ft^3. The pin is pulled from the piston. What is the final pressure inside the cylinder?

12.40 A 10-m^3 storage tank contains methane at low temperature. The pressure inside is 700 kPa, and the tank contains 25 percent liquid and 75 percent vapor, on a volume basis. The tank warms very slowly because heat is transferred from the ambient.

(a) What is the temperature inside the storage tank when the pressure reaches 10 MPa?

(b) Calculate the heat transferred during this process, using the generalized tables or charts.

(c) Repeat parts a and b, using the methane tables, Table A.6. Discuss the differences in the results.

12.41 Carbon dioxide enters a nozzle at 15 MPa, 400 K, at a velocity of 10 m/s. The cross-sectional area at the nozzle entrance is 2000 mm^2. At the nozzle exit, the area is 200 mm^2 and the pressure is 5 MPa. There is heat rejection at the rate of 200 kW from the nozzle to the surroundings. What is the exit velocity of the carbon dioxide?

12.42 A system consisting of 10 kg of butane gas initially at 80°C, 500 kPa, is compressed in a reversible isothermal process to one-fifth of its initial volume. What is the heat transfer during the process?

12.43 Carbon dioxide gas enters a turbine at 5 MPa, 100°C, and exits at 1-MPa pressure. If the isentropic efficiency of the turbine is 75 percent, determine

(a) The exit temperature.
(b) The second-law efficiency for this process.

12.43E Carbon dioxide gas enters a turbine at 50 atm, 200 F, and exits at 10-atm pressure. If the isentropic efficiency of the turbine is 75 percent, determine

(a) The exit temperature.
(b) The second-law efficiency for this process.

12.44 A 4-m^3 uninsulated storage tank, which is initially evacuated, is connected to a line flowing ethane gas at 10 MPa, 100°C. The valve is opened, and ethane flows into the tank for a period of time, after which the valve is closed. Eventually, the tank cools to ambient temperature, 0°C, at which time it contains one-fourth liquid and three-fourths vapor, by volume. For the overall process, calculate

(a) The heat transfer from the tank.
(b) The net change of entropy.

12.45 An insulated, hollow steel sphere has an inside diameter of 1 m and a wall thickness of 4 mm. The sphere contains saturated-vapor ethane at ambient temperature, 300 K. A valve on the top of the sphere is opened, and ethane flows out rapidly until the pressure reaches 500 kPa, at which point the valve is closed. During this process the ethane remaining inside the sphere may be assumed to undergo a reversible, adiabatic expansion. Now, after sitting for a period of time, the sphere and its contents come to a uniform temperature. Assuming no heat transfer with the surroundings, determine the final state of the ethane inside the sphere.

12.46 The environmentally safe refrigerant R-142b (see Problem 12.38) is to be evaluated for possible use as the working fluid in a portable, closed-cycle power plant, as shown schematically in Fig. 12.16. The air-cooled condenser temperature is fixed at 50°C, and the maximum cycle temperature is fixed at 180°C, because of concerns about thermal stability. The isentropic efficiency of the expansion engine is estimated to be 80 percent, and the minimum allowable quality of the fluid exiting the expansion engine is 90 percent.

(a) Calculate the heat transfer from the condenser, assuming saturated liquid at the exit.

(b) Determine the maximum cycle pressure, based on the specifications listed.

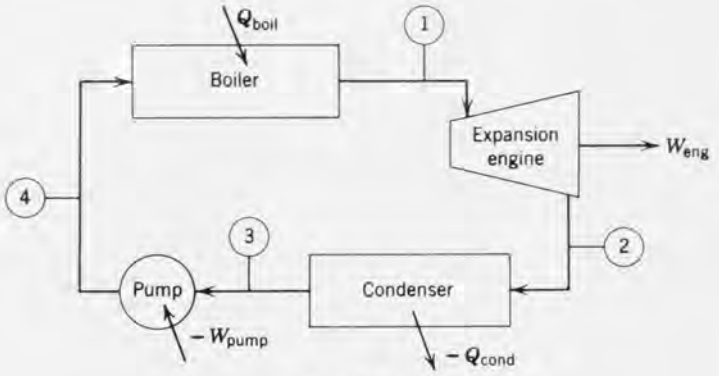


FIGURE 12.16 Sketch for Problem 12.46.

12.47 One kilogram per second of water enters a solar collector at 40°C and exits at 90°C, as shown in Fig. 12.17. The hot water is sprayed into a direct-contact heat exchanger (no mixing of the two fluids) used to boil liquid butane. Pure saturated-vapor butane exits at the top at 80°C and is fed to the turbine. If the butane condenser temperature is 30°C and the turbine and pump isentropic efficiencies are each 80 percent, determine the net power output of the cycle.

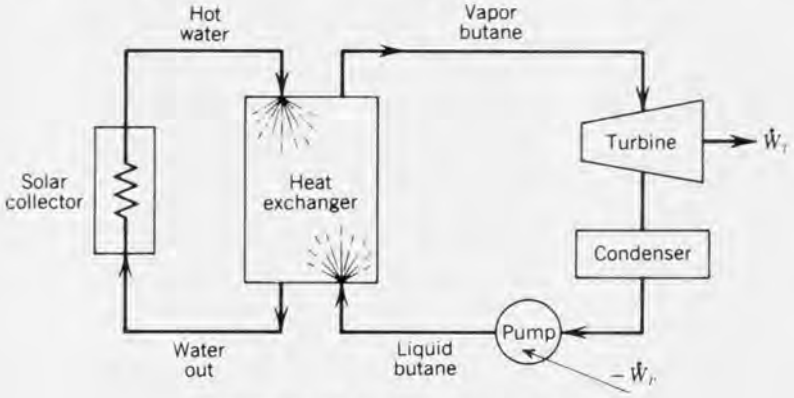


FIGURE 12.17 Sketch for Problem 12.47.

12.48 The environmentally safe refrigerant R-152a (see Problem 12.37) is to be evaluated for possible use as the working fluid for a heat pump system that will heat winter households in two different climates. In the colder climate the cycle evaporator temperature is −20°C, and in the more moderate climate the evaporator temperature is 0°C. In both climates the cycle condenser temperature is 30°C. For purposes of this study, all processes are assumed to be ideal.

(a) Determine the cycle coefficient of performance for the two cases.

(b) Compare the results of part a with the cycle performance calculated using R-12 as the working fluid.

12.49 Consider the following reference state condition. The entropy of real saturated-liquid methane at −100°C is taken as 100 kJ/kmol K, and the entropy of hypothetical ideal-gas ethane at −100°C, 1 MPa, is taken as 200 kJ/kmol K. Calculate the entropy per kilomole of a real-gas mixture of 50 percent methane, 50 percent

ethane (mole basis) at 20°C, 4 MPa, in terms of the specified reference state values. Use Table A.14 with pseudocritical constants for the behavior of the real-gas mixture.

12.50 Consider a gas mixture of 50 percent nitrogen and 50 percent argon, on a mole basis, contained in a 1-L volume at 180 K, 2 MPa. Calculate the mass of this mixture, using the virial equation of state, and determine the percent error if ideal-gas behavior is assumed.

12.50E Consider a gas mixture of 50 percent nitrogen and 50 percent argon, on a mole basis, contained in a 1-ft^3 volume at 320 R, 20 atm. Calculate the mass of this mixture, using the virial equation of state, and determine the percent error if ideal-gas behavior is assumed.

12.51 Consider the gas mixture described in Problem 12.50. Calculate the mass of this mixture, using pseudocritical constants and the generalized tables, Table A.14. Also, calculate the mass using the Redlich–Kwong equation of state to represent the behavior of the mixture.

12.52 It is frequently necessary to have available a gas mixture of a certain composition (for example, for calibrating gas analysis instruments). Such a mixture is prepared for storage by initially charging one of the components into a tank at some given pressure, so that when the second component is added until a final specified pressure is reached, the mixture composition will be of the desired proportions. We wish to prepare a gas mixture of 80 percent ethylene and 20 percent carbon dioxide (mole basis) at 10 MPa, 25°C, in a 50-L uninsulated, rigid tank. The tank is initially to contain CO_2 at 25°C and some pressure P_1. The valve to a line flowing C_2H_4 at 25°C, 10 MPa, is opened slightly and remains open until the tank reaches 10 MPa, at which point the temperature can be assumed to be 25°C. Assume that the gas mixture so prepared can be represented by the generalized tables or charts.

(a) Given the desired final state, what is the initial pressure of the carbon dioxide, P_1?

(b) Determine the heat transfer and the net entropy change for the process of charging ethylene into the tank.

12.53 One technique for preparing a gas mixture of a desired composition was described in Problem 12.52. Another is the following. Two 25-L uninsulated tanks are located in a room at ambient temperature, 25°C. One tank contains ethylene gas at 10 MPa, and the other contains carbon dioxide at pressure P_1. The valve connecting the tanks is opened, and after a long time the two tanks contain a homogeneous gas mixture with a composition of 80 percent ethylene and 20 percent carbon dioxide (mole basis). Assume that the gas mixture can be represented by the generalized tables or charts.

(a) What is the initial pressure of the carbon dioxide, P_1?

(b) What is the final pressure of the gas mixture?

(c) Determine the heat transfer and the net entropy change for this mixing process.

12.53E One technique for preparing a gas mixture of a desired composition was described in Problem 12.52. Another is the following. Two 1-ft^3 uninsulated tanks are located in a room at ambient temperature, 75 F. One tank contains ethylene gas at 1500 lbf/in.^{2}, and the other contains carbon dioxide at pressure P_1. The valve connecting the tanks is opened, and after a long time the two tanks contain a homo-

geneous gas mixture with a composition of 80 percent ethylene and 20 percent carbon dioxide (mole basis). Assume that the gas mixture can be represented by the generalized tables or charts.

(a) What is the initial pressure of the carbon dioxide, P_1?

(b) What is the final pressure of the gas mixture?

(c) Determine the heat transfer and the net entropy change for this mixing process.

12.54 A 100-L insulated vessel contains a mixture of 70 mole percent methane and 30 mole percent butane at 310 K, 6 MPa. A valve on the vessel is opened, giving access to a semipermeable membrane that allows methane but not butane to flow out. This valve is closed when the pressure inside the vessel reaches 3 MPa.

(a) Determine the final state inside the vessel.

(b) Using a logical reference state and reference values, calculate the entropy of the contents of the vessel at the initial state, before the valve is opened.

12.55 A gas mixture, 80 percent ethylene and 20 percent propane on a mole basis, enters a SSSF device at 30°C, 3.5 MPa, at the rate of 4 L/s. Two separate streams leave the device; one is pure ethylene gas at 30°C, 2.8 MPa, and the other is pure liquid propane at 65°C, 3.5 MPa. Determine the minimum power input, in kilowatts, required to operate this device.

COMPUTER PROBLEMS

12.1C Write a program to solve the following problem. We wish to obtain a plot of pressure versus specific volume at various temperatures (all on a generalized reduced basis) as predicted by the van der Waals equation of state. Temperatures less than the critical temperature should be included in the results.

12.2C Write a program to solve the following problem. For one of the substances listed in Table 3.3, calculate enthalpy changes along several isotherms at various integral pressures, using the Benedict–Webb–Rubin equation of state.

12.3C Write a program to solve the following problem. We wish to curve-fit a polynomial in reduced temperature T^* to values of the reduced second virial coefficient $B^*(T^*)$ given in Table A.13.1 over a specific range of reduced temperatures. For one of the substances listed in Table A.13.2, plot Z versus P at low pressures for various isotherms.

12.4C Extend the program of Problem 12.3C to include the calculation of isothermal enthalpy and entropy changes. For one of the substances listed in Table A.13.2, plot these changes versus P at low pressures for various isotherms.

12.5C Write a program to plot out the entire Joule–Thomson inversion locus as shown in Figure 12.8, using both the van der Waals equation of state and the Redlich–Kwong equation of state.

12.6C Write a program to calculate the enthalpy and entropy changes between two arbitrary gas-phase states, using the Redlich–Kwong equation of state to represent the real-gas behavior and an ideal-gas specific-heat equation from either Table A.10 (Problem 5.1C) or from the result of Problem 5.2C. Input parameters should

include the specific-heat information, the critical pressure and temperature, and the two independent properties specifying each of the two states.

12.7C Supercritical fluid chromatography is a new experimental technique for analyzing compositions of mixtures. It utilizes a carrier fluid, often carbon dioxide, in the dense fluid region just above the critical temperature. Write a program to express the fluid density as a function of reduced temperature and pressure and acentric factor, in the region of 1.0 to 1.2 reduced temperature and 2 to 8 reduced pressure. The relation should be an expression curve-fitted to values consistent with the generalized compressibility tables, Table A.14.

12.8C Write a program that will generate a set of Lee–Kesler pseudocritical constants for a gas mixture, given the critical constants of the (variable number of) mixture components and the mixture composition.

12.9C Extend the programs developed in Problems 12.3C and 12.4C to include binary gas mixture calculations. Input parameters should include the Lennard–Jones force constants of the components and the composition, in addition to the thermodynamic state variables.

12.10C Extend the program developed in Problem 12.6C to include binary gas mixture calculations using the Redlich–Kwong equation of state. Input parameters should include the critical pressure and temperature of the components and the composition, in addition to the thermodynamic state variables.

13
CHEMICAL REACTIONS

Many thermodynamic problems concern chemical reactions. Among the most familiar of these is the combustion of hydrocarbon fuels, for this process is utilized in most of our power-generating devices. However, we can all think of a host of other processes in which chemical reactions take place, including those that occur in the human body.

It is our purpose in this chapter to consider a first- and second-law analysis of systems undergoing a chemical reaction. In many respects, this chapter is simply an extension of our previous consideration of the first and second laws. However, a number of new terms are introduced, and it will also be necessary to introduce the third law of thermodynamics.

In this chapter the combustion process is considered in detail. There are two reasons for this emphasis. The first reason is that the combustion process is of great significance in many problems and devices with which the engineer is concerned. The second reason is that the combustion process provides an excellent vehicle for teaching the basic principles of the thermodynamics of chemical reactions. The student should keep both of these objectives in mind as the study of this chapter progresses.

Chemical equilibrium will be considered in Chapter 14 and, therefore, the matter of dissociation will be deferred until then.

13.1 FUELS

A thermodynamics textbook is not the place for a detailed treatment of fuels. However, some knowledge of them is a prerequisite to considering combustion, and this section is therefore devoted to a brief discussion of some of the hydrocarbon fuels. Most fuels fall into one of three categories—coal, liquid hydrocarbons, or gaseous hydrocarbons.

Coal consists of the remains of vegetation deposits of past geologic ages, after subjection to biochemical actions, high pressure, temperature, and submersion. The characteristics of coal vary considerably with location, and even within a given mine there is some variation in composition.

The analysis of a sample of coal is given on one of two bases; the proximate analysis specifies, on a mass basis, the relative amounts of moisture, volatile matter, fixed carbon and ash; the ultimate analysis specifies, on a mass basis, the relative amounts of carbon, sulfur, hydrogen, nitrogen, oxygen, and ash. The ultimate analysis may be given on an "as received" basis or on a dry basis. If on a dry basis,

TABLE 13.1 Characteristics of Some of the Hydrocarbon Families

Family	Formula	Structure	Saturated
Paraffin	C_nH_{2n+2}	Chain	Yes
Olefin	C_nH_{2n}	Chain	No
Diolefin	C_nH_{2n-2}	Chain	No
Naphthene	C_nH_{2n}	Ring	Yes
Aromatic			
Benzene	C_nH_{2n-6}	Ring	No
Naphthalene	C_nH_{2n-12}	Ring	No

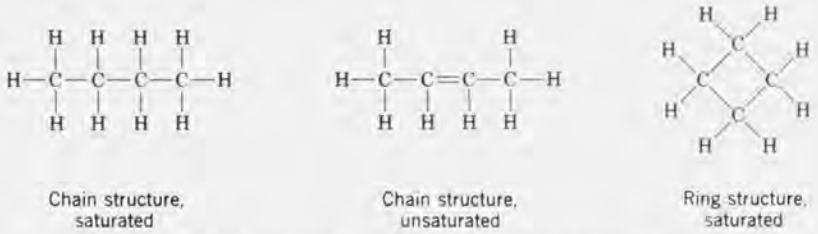
the ultimate analysis does not include the moisture as determined by the proximate analysis.

There are also a number of other properties of coal that are important in its evaluation for a given use. Some of these properties are the fusibility of the ash, the grindability or ease of pulverization, the weathering characteristics, and size.

Most liquid and gaseous hydrocarbon fuels are a mixture of many different hydrocarbons. For example, gasoline consists primarily of a mixture of about 40 hydrocarbons, with many others present in very small quantities. In a discussion of hydrocarbon fuels, therefore, brief consideration should be given to the most important families of hydrocarbons, which are summarized in Table 13.1.

Three concepts should be defined. The first pertains to the structure of the molecule. The important types are the ring and chain structures; the difference between the two is illustrated in Fig. 13.1. The same figure illustrates the definition of saturated and unsaturated hydrocarbons. An unsaturated hydrocarbon has two or more adjacent carbon atoms joined by a double or triple bond, whereas in a saturated hydrocarbon all the carbon atoms are joined to another by a single bond. Isomer is the third concept to be defined. Two hydrocarbons with the same number of carbon and hydrogen atoms and different structures are called isomers. Thus, there are several different octanes (C_8H_{18}), each having 8 carbon atoms and 18 hydrogen atoms, but each with a different structure.

The various hydrocarbon families are identified by a common suffix. The compounds making up the paraffin family all end in "-ane" (as propane and octane). Similarly, the compounds making up the olefin family end in "-ylene" or "-ene"



Chain structure, saturated

Chain structure, unsaturated

Ring structure, saturated

FIGURE 13.1 Molecular structure of some hydrocarbon fuels.

(as propene and octene), and the diolefin family ends in "-diene" (as butadiene). The naphthene family has the same chemical formula as the olefin family, but it has a ring rather than a chain structure. The hydrocarbons in the naphthene family are named by adding the prefix "cyclo-" (as cyclopentane).

The aromatic family includes the benzene series (C_nH_{2n-6}) and the naphthalene series (C_nH_{2n-12}). The benzene series has a ring structure and is unsaturated.

Alcohols are sometimes used as a fuel in internal-combustion engines. The characteristic feature of the alcohol family is that one of the hydrogen atoms is replaced by an OH radical. Thus, methyl alcohol, also called methanol, is CH_3OH.

Most liquid hydrocarbon fuels are mixtures of hydrocarbons that are derived from crude oil through distillation and cracking processes. Thus, from a given crude oil, a variety of different fuels can be produced, some of the common ones being gasoline, kerosene, diesel fuel, and fuel oil. Within each of these classifications there is a wide variety of grades, and each is made up of a large number of different hydrocarbons. The important distinction between these fuels is the distillation curve, Fig. 13.2. The distillation curve is obtained by slowly heating a sample of fuel so that it vaporizes. The vapor is then condensed and the amount of condensate measured. The more volatile hydrocarbons are vaporized first, and thus the temperature of the nonvaporized fraction increases during the process. The distillation curve, which is a plot of the temperature of the nonvaporized fraction versus the amount of vapor condensed, is an indication of the volatility of the fuel.

For the combustion of liquid fuels, it is convenient to express the composition in terms of a single hydrocarbon, even though it is a mixture of many hydrocarbons. Thus, gasoline is usually considered to be octane, C_8H_{18}, and diesel fuel is considered to be dodecane, $C_{12}H_{26}$. The composition of a hydrocarbon fuel may also be given in terms of percentage of carbon and hydrogen.

The two primary sources of gaseous hydrocarbon fuels are natural gas wells and certain chemical manufacturing processes. Table 13.2 gives the composition

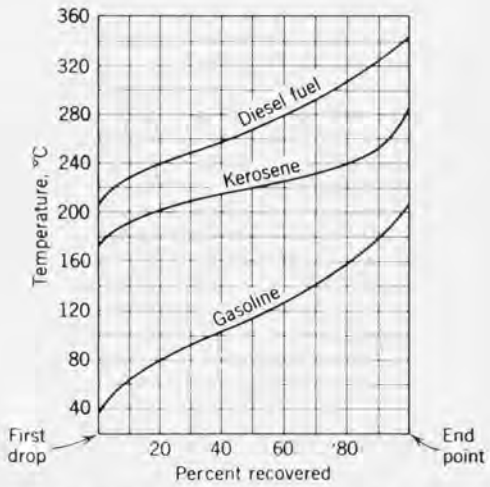


FIGURE 13.2 Typical distillation curves of some hydrocarbon fuels.

TABLE 13.2 *Volumetric Analyses of Some Typical Gaseous Fuels*

Constituent	Various Natural Gases				Producer Gas from Bituminous Coal	Carbureted Water Gas	Coke-Oven Gas
	A	B	C	D			
Methane	93.9	60.1	67.4	54.3	3.0	10.2	32.1
Ethane	3.6	14.8	16.8	16.3			
Propane	1.2	13.4	15.8	16.2			
Butanes plus[a]	1.3	4.2		7.4			
Ethene						6.1	3.5
Benzene						2.8	0.5
Hydrogen					14.0	40.5	46.5
Nitrogen		7.5		5.8	50.9	2.9	8.1
Oxygen					0.6	0.5	0.8
Carbon monoxide					27.0	34.0	6.3
Carbon dioxide					4.5	3.0	2.2

[a] This includes butane and all heavier hydrocarbons.

of a number of gaseous fuels. The major constituent of natural gas is methane, which distinguishes it from manufactured gas.

At the present time, considerable effort is being devoted to developing more economical processes for producing gaseous and liquid hydrocarbon fuels from coal, and also from oil shale and tar sands deposits. Several alternative techniques have been demonstrated to be feasible, and these resources promise to provide an increasing proportion of our fuel supply in future years.

13.2 THE COMBUSTION PROCESS

The combustion process consists of the oxidation of constituents in the fuel that are capable of being oxidized, and can therefore be represented by a chemical equation. During a combustion process the mass of each element remains the same. Thus, writing chemical equations and solving problems concerning quantities of the various constituents basically involves the conservation of mass of each element. A brief review of this subject, particularly as it applies to the combustion process, is presented in this chapter.

Consider first the reaction of carbon with oxygen.

$$\underset{\text{Reactants}}{C + O_2} \rightarrow \underset{\text{Products}}{CO_2}$$

This equation states that 1 kmol of carbon reacts with 1 kmol of oxygen to form 1 kmol of carbon dioxide. This also means that 12 kg of carbon react with 32 kg of oxygen to form 44 kg of carbon dioxide. All the initial substances that undergo

the combustion process are called the reactants, and the substances that result from the combustion process are called the products.

When a hydrocarbon fuel is burned, both the carbon and the hydrogen are oxidized. Consider the combustion of methane as an example.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{13.1}$$

Here the products of combustion include both carbon dioxide and water. The water may be in the vapor, liquid, or solid phases, depending on the temperature and pressure of the products of combustion.

It should be pointed out that in the combustion process many intermediate products are formed during the chemical reaction. In this book we are concerned with the initial and final products and not with the intermediate products, but this aspect is very important in a detailed consideration of combustion.

In most combustion processes the oxygen is supplied as air rather than as pure oxygen. The composition of air on a molal basis is approximately 21 percent oxygen, 78 percent nitrogen, and 1 percent argon. We assume that the nitrogen and the argon do not undergo chemical reaction (except for dissociation, which will be considered in Chapter 14). They do leave at the same temperature as the other products, however, and therefore undergo a change of state if the products are at a temperature other than the original air temperature. It should be pointed out that at the high temperatures achieved in internal-combustion engines, there is actually some reaction between the nitrogen and oxygen, which is the source of the oxides of nitrogen in the engine exhaust and the air pollution problem associated with them.

In combustion calculations concerning air, the argon is usually neglected, and the air is considered to be composed of 21 percent oxygen and 79 percent nitrogen by volume. When this assumption is made, the nitrogen is sometimes referred to as atmospheric nitrogen. Atmospheric nitrogen has a molecular weight of 28.16 (which takes the argon into account) compared to 28.013 for pure nitrogen. This distinction will not be made in this text, and we will consider the 79 percent nitrogen to be pure nitrogen.

The assumption that air is 21.0 percent oxygen and 79.0 percent nitrogen by volume leads us to the conclusion that for each mole of oxygen, there are $79.0/21.0 = 3.76$ moles of nitrogen. Therefore, when the oxygen for the combustion of methane is supplied as air, the reaction can be written

$$CH_4 + 2O_2 + 2(3.76)N_2 \rightarrow CO_2 + 2H_2O + 7.52N_2 \tag{13.2}$$

The minimum amount of air that supplies sufficient oxygen for the complete combustion of all the carbon, hydrogen, and any other elements in the fuel that may oxidize is called the theoretical air. When complete combustion is achieved with theoretical air, the products contain no oxygen. In practice, complete combustion is not likely to be achieved unless the amount of air supplied is somewhat greater than the theoretical amount. The amount of air actually supplied is expressed in terms of percent theoretical air. Thus, 150 percent theoretical air means that the air actually supplied is 1.5 times the theoretical air. The complete combustion of methane with 150 percent theoretical air is written

$$CH_4 + 2(1.5)O_2 + 2(3.76)(1.5)N_2 \rightarrow CO_2 + 2H_2O + O_2 + 11.28N_2 \tag{13.3}$$

The amount of air actually supplied may also be expressed in terms of percent excess air. The excess air is the amount of air supplied over and above the theoretical air. Thus, 150 percent theoretical air is equivalent to 50 percent excess air. The terms theoretical air and excess air are both in current usage.

Two important parameters applied to combustion processes are the air–fuel ratio (designated AF) and its reciprocal, the fuel–air ratio (designated FA). The air–fuel ratio is usually expressed on a mass basis, but a mole basis is also used at times. The theoretical air–fuel ratio is the ratio of the mass (or moles) of theoretical air to the mass (or moles) of fuel.

When the amount of air supplied is less than the theoretical air required, the combustion is incomplete. If there is only a slight deficiency of air, some of the carbon usually unites with the oxygen to form carbon monoxide (CO) instead of carbon dioxide (CO_2). If the air supplied is considerably less than the theoretical air, there may also be some hydrocarbons in the products of combustion.

Even when some excess air is supplied, small amounts of carbon monoxide may be present. The exact amount depends on a number of factors, such as the mixing and turbulence during combustion. Thus, the combustion of methane with 110 percent theoretical air might be

$$CH_4 + 2(1.1)O_2 + 2(1.1)3.76N_2 \rightarrow$$
$$+0.95CO_2 + 0.05CO + 2H_2O + 0.225O_2 + 8.27N_2 \quad (13.4)$$

The material covered so far in this section is illustrated by the following examples.

EXAMPLE 13.1

Calculate the theoretical air–fuel ratio for the combustion of octane, C_8H_{18}.

Solution

The combustion equation is

$$C_8H_{18} + 12.5O_2 + 12.5(3.76)N_2 \rightarrow 8CO_2 + 9H_2O + 47.0N_2$$

The air–fuel ratio on a mole basis is

$$AF = \frac{12.5 + 47.0}{1} = 59.5 \text{ kmol air/kmol fuel}$$

The theoretical air–fuel ratio on a mass basis is found by introducing the molecular weight of the air and fuel.

$$AF = \frac{59.5(28.97)}{114.2} = 15.0 \text{ kg air/kg fuel}$$

EXAMPLE 13.2

Determine the molal analysis of the products of combustion when octane, C_8H_{18}, is burned with 200 percent theoretical air. In addition, determine the dew point of the products if the pressure is 0.1 MPa.

Solution

The equation for the combustion of octane with 200 percent theoretical air is

$$C_8H_{18} + 12.5(2)O_2 + 12.5(2)(3.76)N_2 \rightarrow 8CO_2 + 9H_2O + 12.5O_2 + 94.0N_2$$

The total kilomoles of product are $8 + 9 + 12.5 + 94.0 = 123.5$

The molal analysis of products is

$$\begin{aligned} CO_2 &= 8/123.5 &&= 6.47 \text{ percent} \\ H_2O &= 9/123.5 &&= 7.29 \\ O_2 &= 12.5/123.5 &&= 10.12 \\ N_2 &= 94/123.5 &&= 76.12 \\ & & & \overline{100.00} \text{ percent} \end{aligned}$$

The partial pressure of the water is $100(0.0729) = 7.29$ kPa.

The saturation temperature corresponding to this pressure is 39.7°C, which is also the dew-point temperature.

The water condensed from the products of combustion usually contains some dissolved gases and may therefore be quite corrosive. For this reason the products of combustion are often kept above the dew point until discharged to the atmosphere.

EXAMPLE 13.3

Producer gas from bituminous coal (see Table 13.2) is burned with 20 percent excess air. Calculate the air–fuel ratio on a volumetric basis and on a mass basis.

Solution

To calculate the theoretical air requirement, write the combustion equation for the combustible substances in 1 kmol of fuel.

$$\begin{aligned} 0.14H_2 + 0.070O_2 &\rightarrow 0.14H_2O \\ 0.27CO + 0.135O_2 &\rightarrow 0.27CO_2 \\ 0.03CH_4 + 0.06O_2 &\rightarrow 0.03CO_2 + 0.06H_2O \\ \overline{0.265} &= \text{kmol oxygen required/kmol fuel} \\ -\ \overline{0.006} &= \text{oxygen in fuel/kmol fuel} \\ \overline{0.259} &= \text{kmol oxygen required from air/kmol fuel} \end{aligned}$$

Therefore, the complete combustion equation for 1 kmol of fuel is

$$\overbrace{0.14H_2 + 0.27CO + 0.03CH_4 + 0.006O_2 + 0.509N_2 + 0.045CO_2}^{\text{fuel}}$$

$$\overbrace{+ 0.259O_2 + 0.259(3.76)N_2}^{\text{air}} \rightarrow 0.20H_2O + 0.345CO_2 + 1.482N_2$$

$$\left(\frac{\text{kmol air}}{\text{kmol fuel}}\right)_{\text{theo}} = 0.259 \times \frac{1}{0.21} = 1.233$$

If the air and fuel are at the same pressure and temperature, this value also represents the ratio of the volume of air to the volume of fuel.

For 20 percent excess air,

$$\frac{\text{kmol air}}{\text{kmol fuel}} = 1.233 \times 1.200 = 1.48$$

The air–fuel ratio on a mass basis is

$$AF = \frac{1.48(28.97)}{0.14(2) + 0.27(28) + 0.03(16) + 0.006(32) + 0.509(28) + 0.045(44)}$$

$$= \frac{1.48(28.97)}{24.74} = 1.73 \text{ kg air/kg fuel}$$

An analysis of the products of combustion affords a very simple method for calculating the actual amount of air supplied in a combustion process. There are various experimental methods by which such an analysis can be made. Some yield results on a "dry" basis, that is, the fractional analysis of all the components except water vapor. Other experimental procedures give results that include the water vapor. In this presentation we are not concerned with the experimental devices and procedures, but rather with the use of such information in a thermodynamic analysis of the chemical reaction. The following examples illustrate how an analysis of the products can be used to determine the chemical reaction and the composition of the fuel.

The basic principle in using the analysis of the products of combustion to obtain the actual fuel–air ratio is conservation of the mass of each of the elements. Thus, in changing from reactants to products, we can make a carbon balance, hydrogen balance, oxygen balance, and nitrogen balance (plus any other elements that may be involved). Furthermore, we recognize that there is a definite ratio between the amounts of some of these elements. Thus, the ratio between the nitrogen and oxygen supplied in the air is fixed, as well as the ratio between carbon and hydrogen if the composition of a hydrocarbon fuel is known.

EXAMPLE 13.4

Methane (CH_4) is burned with atmospheric air. The analysis of the products on a dry basis, percent by volume, is

Product	*Percent by Volume*
CO_2	10.00
O_2	2.37
CO	0.53
N_2	87.10

Calculate the air–fuel ratio and the percentage of theoretical air, and determine the combustion equation.

Solution

The solution consists of writing the combustion equation for 100 kmol of dry products, introducing letter coefficients for the unknown quantities, and then solving for them.

From the analysis of the products, the following equation can be written, keeping in mind that this analysis is on a dry basis.

$$a\text{CH}_4 + b\text{O}_2 + c\text{N}_2 \rightarrow 10.0\text{CO}_2 + 0.53\text{CO} + 2.37\text{O}_2 + d\text{H}_2\text{O} + 87.1\text{N}_2$$

A balance for each of the elements will enable us to solve for all the unknown coefficients.

Nitrogen balance: $c = 87.1$. Since all the nitrogen comes from the air,

$$\frac{c}{b} = 3.76, \qquad b = \frac{87.1}{3.76} = 23.16$$

Carbon balance: $a = 10.00 + 0.53 = 10.53$.

Hydrogen balance: $d = 2a = 21.06$.

Oxygen balance: All the unknown coefficients have been solved for, and therefore the oxygen balance provides a check on the accuracy. Thus, b can also be determined by an oxygen balance.

$$b = 10.00 + \frac{0.53}{2} + 2.37 + \frac{21.06}{2} = 23.16$$

Substituting these values for a, b, c, and d, we have

$$10.53\text{CH}_4 + 23.16\text{O}_2 + 87.1\text{N}_2 \rightarrow 10.0\text{CO}_2 + 0.53\text{CO} + 2.37\text{O}_2 + 21.06\text{H}_2\text{O} + 87.1\text{N}_2$$

Dividing through by 10.53 yields the combustion equation per kilomole of fuel.

$$\text{CH}_4 + 2.2\text{O}_2 + 8.27\text{N}_2 \rightarrow 0.95\text{CO}_2 + 0.05\text{CO} + 2\text{H}_2\text{O} + 0.225\text{O}_2 + 8.27\text{N}_2$$

The air–fuel ratio on a mole basis is

$$2.2 + 8.27 = 10.47 \text{ kmol air/kmol fuel}$$

The air–fuel ratio on a mass basis is found by introducing the molecular weights.

$$AF = \frac{10.47 \times 28.97}{16.0} = 18.97 \text{ kg air/kg fuel}$$

The theoretical air–fuel ratio is found by writing the combustion equation for theoretical air.

$$\text{CH}_4 + 2\text{O}_2 + 2(3.76)\text{N}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 7.52\text{N}_2$$

$$AF_{\text{theo}} = \frac{(2 + 7.52)28.97}{16.0} = 17.23 \text{ kg air/kg fuel}$$

The percentage of theoretical air is

$$\frac{18.97}{17.23} = 110 \text{ percent}$$

EXAMPLE 13.5

Coal from Jenkin, Kentucky, has the following ultimate analysis on a dry basis, percent by mass:

Component	*Percent by Mass*
sulfur	0.6
hydrogen	5.7
carbon	79.2
oxygen	10.0
nitrogen	1.5
ash	3.0

This coal is to be burned with 30 percent excess air. Calculate the air–fuel ratio on a mass basis.

Solution

One approach to this problem is to write the combustion equation for each of the combustible elements per 100 kg of fuel. The molal composition per 100 kg of fuel is found first.

$$\text{kmol S/100 kg fuel} = \frac{0.6}{32} = 0.02$$

$$\text{kmol } H_2\text{/100 kg fuel} = \frac{5.7}{2} = 2.85$$

$$\text{kmol C/100 kg fuel} = \frac{79.2}{12} = 6.60$$

$$\text{kmol } O_2\text{/100 kg fuel} = \frac{10}{32} = 0.31$$

$$\text{kmol } N_2\text{/100 kg fuel} = \frac{1.5}{28} = 0.05$$

The combustion equations for the combustible elements are now written, enabling us to find the theoretical oxygen required.

$$\begin{aligned} 0.02S &+ 0.02O_2 \rightarrow 0.02SO_2 \\ 2.85H_2 &+ 1.42O_2 \rightarrow 2.85H_2O \\ 6.60C &+ 6.60O_2 \rightarrow 6.60CO_2 \end{aligned}$$

8.04 kmol O_2 required/100 kg fuel
− 0.31 kmol O_2 in fuel/100 kg fuel
7.73 kmol O_2 from air/100 kg fuel

$$AF_{\text{theo}} = \frac{[7.73 + 7.73(3.76)]28.97}{100} = 10.63 \text{ kg air/kg fuel}$$

For 30 percent excess air, the air–fuel ratio is

$$AF = 1.3 \times 10.63 = 13.82 \text{ kg air/kg fuel}$$

13.3 ENTHALPY OF FORMATION

In the first twelve chapters of this book, the problems always concerned a fixed chemical composition and never a change of composition through a chemical reaction. Therefore, in dealing with a thermodynamic property, we used tables of thermodynamic properties for the given substance, and in each of these tables the thermodynamic properties were given relative to some arbitrary base. In the steam tables, for example, the internal energy of saturated liquid at 0.01°C is assumed to be zero. This procedure is quite adequate when there is no change in composition, because we are concerned with the changes in the properties of a given substance. The properties at the condition of the reference state cancel out in the calculation. When dealing with the matter of reference states in Section 12.14, we noted that for a given substance (perhaps a component of a mixture), we are free to choose a reference state condition, for example, a hypothetical ideal gas, as long as we then carry out a consistent calculation from this state and condition to the real desired state. We also noted that we are free to choose a reference state value, as long as there is no subsequent inconsistency in the calculation of the change in a property because of a chemical reaction with a resulting change in the amount of a given substance. Now that we are to include the possibility of a chemical reaction, it will become necessary to choose these reference state values on a common and consistent basis. We will use as our reference state a temperature of 25°C, a pressure of 0.1 MPa, and a hypothetical ideal-gas condition for the substances that are gases.

Consider the simple SSSF combustion process shown in Fig. 13.3. This idealized reaction involves the combustion of solid carbon with gaseous oxygen (ideal gas), each of which enters the control volume at the reference state, 25°C and 0.1 MPa. The carbon dioxide (ideal gas) formed by the reaction leaves the chamber at the reference state, 25°C and 0.1 MPa. If the heat transfer could be accurately measured, it would be found to be −393 522 kJ/kmol of carbon dioxide formed. The chemical

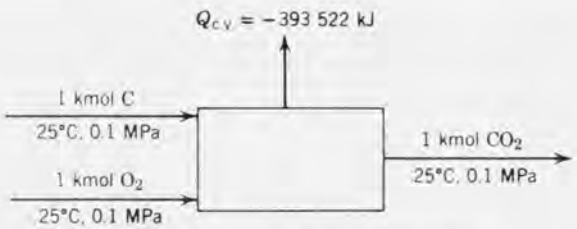


FIGURE 13.3 Example of combustion process.

reaction can be written

$$C + O_2 \rightarrow CO_2$$

Applying the first law to this process, we have

$$Q_{c.v.} + H_R = H_P \tag{13.5}$$

where the subscripts R and P refer to the reactants and products, respectively. We will find it convenient to also write the first law for such a process in the form

$$Q_{c.v.} + \sum_R n_i \bar{h}_i = \sum_P n_e \bar{h}_e \tag{13.6}$$

where the summations refer, respectively, to all the reactants or all the products.

Thus, a measurement of the heat transfer would give us the difference between the enthalpy of the products and the reactants, where each is at the reference state condition. Suppose, however, that we assign the value of zero to the enthalpy of all the elements at the reference state. Then the enthalpy of the reactants is zero, and

$$Q_{c.v.} = H_P = -393\,522 \text{ kJ/kmol}$$

The enthalpy of (hypothetical) ideal-gas carbon dioxide at 25°C, 0.1-MPa pressure (with reference to this arbitrary base in which the enthalpy of the elements is chosen to be zero), is called the enthalpy of formation. We designate this by the symbol $\bar{h}_f^\circ$. Thus, for carbon dioxide

$$\bar{h}_f^\circ = -393\,522 \text{ kJ/kmol}$$

The enthalpy of carbon dioxide in any other state, relative to this base in which the enthalpy of the elements is zero, is found by adding the change of enthalpy between ideal gas at 25°C, 0.1 MPa, and the given state to the enthalpy of formation. That is, the enthalpy at any temperature and pressure, $\bar{h}_{T,P}$, is

$$\bar{h}_{T,P} = (\bar{h}_f^\circ)_{298,\,0.1\text{ MPa}} + (\Delta\bar{h})_{298,\,0.1\text{ MPa} \rightarrow T,P} \tag{13.7}$$

where the term $(\Delta\bar{h})_{298,\,0.1\text{ MPa} \rightarrow T,P}$ represents the difference in enthalpy between any given state and the enthalpy of ideal gas at 298.15 K, 0.1 MPa. For convenience, we usually drop the subscripts in the examples that follow.

The procedure that we have demonstrated for carbon dioxide can be applied to any compound. Table A.15 gives values of the enthalpy of formation for a number of substances in the units kJ/kmol.

Three observations should be made regarding the enthalpy of formation.

1. We have demonstrated the concept of enthalpy of formation in terms of the measurement of the heat transfer in an idealized chemical reaction in which a compound is formed from the elements. Actually, the enthalpy of formation is usually found by applying statistical thermodynamics and using observed spectroscopic data.
2. The justification of this procedure of arbitrarily assigning the value of zero to the enthalpy of the elements at 25°C, 0.1 MPa, rests on the fact that in the absence of nuclear reactions, the mass of each element is conserved in a chemical

reaction. There are no conflicts or ambiguities with this choice of reference state, and it proves to be very convenient in studying chemical reactions from a thermodynamic point of view.

3. In certain cases an element or compound can exist in more than one state at 25°C, 0.1 MPa. Carbon, for example, can be in the form either of graphite or of diamond. It is essential that the state to which a given value relates be clearly identified. Thus, in Table A.15, the enthalpy of formation of graphite is given the value of zero, and the enthalpy of each substance that contains carbon is given the value relative to this base. Another example is that oxygen may exist in the monatomic or diatomic form, and also as ozone, O_3. The value chosen as zero is for the form that is chemically stable at the reference state, which for oxygen is the diatomic form. Then each of the other forms must have an enthalpy of formation consistent with the chemical reaction and heat transfer for the reaction that produces that form of oxygen.

It will be noted from Table A.15 that two values are given for the enthalpy of formation for water; one is for liquid water and the other for gaseous (hypothetical ideal gas) water. Both values are given at the reference state of 25°C, 0.1 MPa. It is convenient to use the hypothetical ideal-gas reference in conjunction with the ideal-gas table property changes given in Table A.12 and to use the real-liquid reference in connection with real-water property changes as given in the steam tables, Table A.1. The real-liquid reference state properties are obtained from those at the hypothetical ideal-gas reference by following the procedure of calculation described in Section 12.14. The same procedure can be followed for other substances that have a saturation pressure less than 0.1 MPa at the reference temperature of 25°C.

Frequently, students are bothered by the minus sign when the enthalpy of formation is negative. For example, the enthalpy of formation of carbon dioxide is negative. This is quite evident because the heat transfer is negative during the steady-flow chemical reaction, and the enthalpy of the carbon dioxide must be less than the sum of enthalpy of the carbon and oxygen initially, both of which are assigned the value of zero. This is quite analogous to the situation we would have in the steam tables if we let the enthalpy of saturated vapor be zero at 0.1-MPa pressure, for then the enthalpy of the liquid would be negative, and we would simply use the negative value for the enthalpy of the liquid when solving problems.

13.4 FIRST-LAW ANALYSIS OF REACTING SYSTEMS

The significance of the enthalpy of formation is that it is most convenient in performing a first-law analysis of a reacting system, for the enthalpies of different substances can be added or subtracted, since they are all given relative to the same base.

In such problems we write the first law for a steady-state, steady-flow process in the form

$$Q_{\text{c.v.}} + H_R = W_{\text{c.v.}} + H_P$$

or

$$Q_{c.v.} + \sum_R n_i \bar{h}_i = W_{c.v.} + \sum_P n_e \bar{h}_e$$

where R and P refer to the reactants and products, respectively. In each problem it is necessary to choose one parameter as the basis of the solution. Usually this is taken as 1 kmol of fuel.

EXAMPLE 13.6

Consider the following reaction, which occurs in a steady-state, steady-flow process.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(l)$$

The reactants and products are each at a total pressure of 0.1 MPa and temperature of 25°C. Determine the heat transfer per kilomole of fuel entering the combustion chamber.

Control volume: Combustion chamber.
Inlet state: P and T known; state fixed.
Exit state: P and T known; state fixed.
Process: SSSF.
Model: Three gases ideal gases; real-liquid water.
Analysis:

First law: $$Q_{c.v.} + \sum_R n_i \bar{h}_i = \sum_P n_e \bar{h}_e$$

Solution

Using values from Table A.15, we have

$$\sum_R n_i \bar{h}_i = (\bar{h}_f^\circ)_{CH_4} = -74\,873 \text{ kJ}$$

$$\sum_P n_e \bar{h}_e = (\bar{h}_f^\circ)_{CO_2} + 2(\bar{h}_f^\circ)_{H_2O(l)}$$

$$= -393\,522 + 2(-285\,830) = -965\,182 \text{ kJ}$$

$$Q_{c.v.} = -965\,182 - (-74\,873) = -890\,309 \text{ kJ}$$

In most instances, however, the substances that comprise the reactants and products in a chemical reaction are not at a temperature of 25°C and a pressure of 0.1 MPa (the state at which the enthalpy of formation is given). Therefore, the change of enthalpy between 25°C and 0.1 MPa and the given state must be known. For a solid or liquid, this change of enthalpy can usually be found from a table of thermodynamic properties or from specific heat data. For gases, this change of enthalpy can usually be found by one of the following procedures.

1. Assume ideal-gas behavior between 25°C, 0.1 MPa, and the given state. The enthalpy is a function of the temperature only and can be found by an equa-

tion of C_{p0} or from tabulated values of enthalpy as a function of temperature (which assumes ideal-gas behavior). Table A.10 gives an equation for $\overline{C}_{p0}$ for a number of substances, and Table A.12 gives values of $\overline{h}^\circ - \overline{h}^\circ_{298}$ (that is, the $\Delta\overline{h}$ of Eq. 13.7) in kilojoules per kilomole. (The symbol $\overline{h}^\circ_{298}$ refers to 25°C or 298.15 K. For simplicity this is designated $\overline{h}^\circ_{298}$.) The superscript ° designates that this is the enthalpy at 0.1-MPa pressure, based on ideal-gas behavior, that is, the standard-state enthalpy.

2. If a table of thermodynamic properties is available, $\Delta\overline{h}$ can be found directly from these tables. This is necessary when the deviation from ideal-gas behavior is significant.
3. If the deviation from ideal-gas behavior is significant, but no tables of thermodynamic properties are available, the value for $\Delta\overline{h}$ can be found from the generalized charts and the values for $\overline{C}_{p0}$ or $\Delta\overline{h}$ at 0.1-MPa pressure as just indicated.

Thus, in general, for applying the first law to a steady-state, steady-flow process involving a chemical reaction and negligible changes in kinetic and potential energy, we can write

$$Q_{c.v.} + \sum_R n_i(\overline{h}^\circ_f + \Delta\overline{h})_i = W_{c.v.} + \sum_P n_e(\overline{h}^\circ_f + \Delta\overline{h})_e \tag{13.8}$$

EXAMPLE 13.7

Calculate the enthalpy of water (on a kilomole basis) at 3.5 MPa, 300°C, relative to the base of 0.1 MPa and 25°C, using the following procedures.

1. Assume the steam to be an ideal gas with the value of $\overline{C}_{p0}$ as given in Table A.10.
2. Assume the steam to be an ideal gas with the value for $\Delta\overline{h}$ as given in Table A.12.
3. Refer to the steam tables.
4. Use the ideal-gas result from step 2 and the generalized charts/tables.

Solution

For each of these procedures, we can write

$$\overline{h}_{T,P} = (\overline{h}^\circ_f + \Delta\overline{h})$$

The only difference is in how we calculate $\Delta\overline{h}$. From Table A.15 we note that

$$(\overline{h}^\circ_f)_{H_2O(g)} = -241\,826 \text{ kJ/kmol}$$

1. Using the specific-heat equation for $H_2O(g)$ from Table A.10, we have

$$\overline{C}_{p0} = 143.05 - 183.54\theta^{0.25} + 82.751\theta^{0.5} - 3.6989\theta \text{ kJ/kmol K}$$

where

$$\theta = T/100$$

Therefore,

$$\Delta\bar{h} = \int_{298.15}^{573.15} \bar{C}_{p0}(T)\, dT$$

$$= \int_{2.9815}^{5.7315} \bar{C}_{p0}(\theta)100\, d\theta$$

$$= 9517 \text{ kJ/kmol}$$

$$\bar{h}_{T,P} = -241\,826 + 9517 = -232\,309 \text{ kJ/kmol}$$

2. Using Table A.12 for $H_2O(g)$, we have

$$\Delta\bar{h} = 9494 \text{ kJ/kmol}$$

$$\bar{h}_{T,P} = -241\,826 + 9494 = -232\,332 \text{ kJ/kmol}$$

3. Using the steam tables, choose either the liquid reference state or the gaseous reference state. For the liquid,

$$\Delta\bar{h} = 18.015(2977.5 - 105.0) = 51\,748 \text{ kJ/kmol}$$

$$\bar{h}_{T,P} = -285\,830 + 51\,748 = -234\,082 \text{ kJ/kmol}$$

For the gas,

$$\Delta\bar{h} = 18.015(2977.5 - 2547.2) = 7752 \text{ kJ/kmol}$$

$$\bar{h}_{T,P} = -241\,826 + 7752 = -234\,074 \text{ kJ/kmol}$$

The very small difference results from using the enthalpy of saturated vapor at 25°C (which is almost but not exactly an ideal gas) in calculating the Δh.

4. When using the generalized charts/tables, we apply the notation introduced in Chapter 12,

$$\bar{h}_{T,P} = \bar{h}_f^\circ - (\bar{h}_2^* - \bar{h}_2) + (\bar{h}_2^* - \bar{h}_1^*) + (\bar{h}_1^* - \bar{h}_1)$$

where subscript 2 refers to the state at 3.5 MPa, 300°C, and subscript 1 refers to the state at 0.1 MPa, 25°C. From step 2 $\bar{h}_2^* - \bar{h}_1^* = 9494$ kJ/kmol and

$$\bar{h}_1^* - \bar{h}_1 = 0 \qquad \text{(ideal-gas reference)}$$

$$P_{r2} = \frac{3.5}{22.12} = 0.158, \qquad T_{r2} = \frac{573.2}{647.3} = 0.886, \qquad \omega = 0.344$$

From the generalized enthalpy charts/tables,

$$\frac{\bar{h}_2^* - \bar{h}_2}{\bar{R}T_c} = 0.2113 + 0.344(0.2525) = 0.2981$$

$$\bar{h}_2^* - \bar{h}_2 = 0.2981 \times 8.3144 \times 647.3 = 1604 \text{ kJ/kmol}$$

$$\bar{h}_{T,P} = -241\,826 - 1604 + 9494 = -233\,936 \text{ kJ/kmol}$$

The particular approach used for a given problem will depend on the data available for the given substance.

EXAMPLE 13.8

A small gas turbine uses $C_8H_{18}(l)$ for fuel and 400 percent theoretical air. The air and fuel enter at 25°C, and the products of combustion leave at 900 K. The output

of the engine and the fuel consumption are measured and it is found that the specific fuel consumption is 0.25 kg/s of fuel per megawatt output. Determine the heat transfer from the engine per kilomole of fuel. Assume complete combustion.

Control volume: Gas-turbine engine.

Inlet states: T known for fuel and air.

Exit state: T known for combustion products.

Process: SSSF.

Model: All gases ideal gases, Table A.12; liquid octane, Table A.15.

Analysis: The combustion equation is

$$C_8H_{18}(l) + 4(12.5)O_2 + 4(12.5)(3.76)N_2 \rightarrow 8CO_2 + 9H_2O + 37.5O_2 + 188.0N_2$$

First law: $$Q_{c.v.} + \sum_R n_i(\bar{h}_f^\circ + \Delta\bar{h})_i = W_{c.v.} + \sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h})_e$$

Solution

Since the air is composed of elements and enters at 25°C, the enthalpy of the reactants is equal to that of the fuel,

$$\sum_R n_i(\bar{h}_f^\circ + \Delta\bar{h})_i = (\bar{h}_f^\circ)_{C_8H_{18}(l)} = -250\,105 \text{ kJ/kmol fuel}$$

Considering the products, we have

$$\begin{aligned}\sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h})_e &= n_{CO_2}(\bar{h}_f^\circ + \Delta\bar{h})_{CO_2} + n_{H_2O}(\bar{h}_f^\circ + \Delta\bar{h})_{H_2O} \\ &\quad + n_{O_2}(\Delta\bar{h})_{O_2} + n_{N_2}(\Delta\bar{h})_{N_2} \\ &= 8(-393\,522 + 28\,030) + 9(-241\,826 + 21\,892) \\ &\quad + 37.5(19\,249) + 188(18\,222) \\ &= -755\,769 \text{ kJ/kmol fuel}\end{aligned}$$

$$W_{c.v.} = \frac{1000 \text{ kJ/s}}{0.25 \text{ kg/s}} \times \frac{114.23 \text{ kg}}{\text{kmol}} = 456\,920 \text{ kJ/kmol fuel}$$

Therefore, from the first law,

$$\begin{aligned}Q_{c.v.} &= -755\,769 + 456\,920 - (-250\,105) \\ &= -48\,744 \text{ kJ/kmol fuel}\end{aligned}$$

EXAMPLE 13.9

A mixture of 1 kmol of gaseous ethene and 3 kmol of oxygen at 25°C react in a constant-volume bomb. Heat is transferred until the products cool to 600 K. Determine the amount of heat transfer from the reactants.

System: Constant-volume bomb.

Initial state: T known.

Final state: T known.

Process: Constant volume.

Model: Ideal-gas mixtures, Tables A.12, A.15.

Analysis: The chemical reaction is

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O(g)$$

First law: $Q + U_R = U_P$

$$Q + \sum_R n(\bar{h}_f^\circ + \Delta\bar{h} - \bar{R}T) = \sum_P n(\bar{h}_f^\circ + \Delta\bar{h} - \bar{R}T)$$

Solution

Using values from Tables A.12 and A.15, gives

$$\sum_R n(\bar{h}_f^\circ + \Delta\bar{h} - \bar{R}T) = (\bar{h}_f^\circ - \bar{R}T)_{C_2H_4} - n_{O_2}(\bar{R}T)_{O_2} = (\bar{h}_f^\circ)_{C_2H_4} - 4\bar{R}T$$

$$= 52\,467 - 4 \times 8.3144 \times 298.2 = 42\,550 \text{ kJ}$$

$$\sum_P n(\bar{h}_f^\circ + \Delta\bar{h} - \bar{R}T) = 2[(\bar{h}_f^\circ)_{CO_2} + \Delta\bar{h}_{CO_2}] + 2[(\bar{h}_f^\circ)_{H_2O(g)} + \Delta\bar{h}_{H_2O(g)}] - 4\bar{R}T$$

$$= 2(-393\,522 + 12\,899) + 2(-241\,826 + 10\,463) - 4 \times 8.3144 \times 600$$

$$= -1\,243\,927 \text{ kJ}$$

Therefore,

$$Q = -1\,243\,927 - 42\,550 = -1\,286\,477 \text{ kJ}$$

For a real-gas mixture, a pseudocritical method, such as that discussed in Section 12.14, can be used to evaluate the nonideal-gas contribution to enthalpy at the temperature and pressure of the mixture, and this value can be added to the enthalpy of the ideal-gas mixture at that temperaure.

13.5 ADIABATIC FLAME TEMPERATURE

Consider a given combustion process that takes place adiabatically and with no work or changes in kinetic or potential energy. For such a process the temperature of the products is referred to as the adiabatic flame temperature. With the assumptions of no work and no changes in kinetic or potential energy, this is the maximum temperature that can be achieved for the given reactants because any heat transfer from the reacting substances and any incomplete combustion would tend to lower the temperature of the products.

For a given fuel and given pressure and temperature of the reactants, a stoichiometric mixture gives the maximum achievable adiabatic flame temperature. The adiabatic flame temperature can be controlled by the amount of excess air that is used. This is important, for example, in gas turbines, where the maximum permissible temperature is determined by metallurgical considerations in the turbine, and close control of the temperature of the products is essential.

Example 13.10 shows how the adiabatic flame temperature may be found. The dissociation that takes place in the combustion products, which has a significant effect on the adiabatic flame temperature, will be considered in the next chapter.

EXAMPLE 13.10

Liquid octane at 25°C is burned with 400 percent theoretical air at 25°C in a steady-flow process. Determine the adiabatic flame temperature.

Control volume: Combustion chamber.

Inlet states: T known for fuel and air.

Process: SSSF.

Model: All gases ideal gases, Table A.12; liquid octane, Table A.15.

Analysis: The reaction is

$$C_8H_{18}(l) + 4(12.5)O_2 + 4(12.5)(3.76)N_2 \rightarrow 8CO_2 + 9H_2O(g) + 37.5O_2 + 188.0N_2$$

First law: Since the process is adiabatic,

$$H_R = H_P$$

$$\sum_R n_i(\bar{h}_f^\circ + \Delta\bar{h})_i = \sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h})_e$$

where $\Delta\bar{h}_e$ refers to the change in enthalpy for each constituent in the products at the adiabatic flame temperature.

Solution

From Tables A.12 and A.15,

$$H_R = \sum_R n_i(\bar{h}_f^\circ + \Delta\bar{h})_i = (\bar{h}_f^\circ)_{C_8H_{18}(l)} = -250\,105 \text{ kJ/kmol fuel}$$

$$H_P = \sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h})_e$$

$$= 8(-393\,522 + \Delta\bar{h}_{CO_2}) + 9(-241\,826 + \Delta\bar{h}_{H_2O}) + 37.5\Delta\bar{h}_{O_2} + 188.0\Delta\bar{h}_{N_2}$$

By trial-and-error solution, a temperature of the products is found that satisfies this equation. Assume that

$$T_P = 900 \text{ K}$$

$$H_P = \sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h})_e$$

$$= 8(-393\,522 + 28\,030) + 9(-241\,826 + 21\,892)$$
$$+ 37.5(19\,249) + 188(18\,222)$$
$$= -755\,769 \text{ kJ/kmol fuel}$$

Assume that

$$T_P = 1000 \text{ K}$$

$$H_P = \sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h})_e$$

$$= 8(-393\,522 + 33\,400) + 9(-241\,826 + 25\,956)$$
$$+ 37.5(22\,710) + 188(21\,461)$$
$$= 62\,487 \text{ kJ/kmol fuel}$$

Since $H_P = H_R = -250\,105$ kJ, we find by linear interpolation that the adiabatic flame temperature is 961.8 K. Because the ideal-gas enthalpy is not really a linear function of temperature, the true answer will be slightly different from this value.

13.6 ENTHALPY AND INTERNAL ENERGY OF COMBUSTION; HEAT OF REACTION

The enthalpy of combustion, h_{RP}, is defined as the difference between the enthalpy of the products and the enthalpy of the reactants when complete combustion occurs at a given temperature and pressure. That is,

$$\bar{h}_{RP} = H_P - H_R$$
$$\bar{h}_{RP} = \sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h})_e - \sum_R n_i(\bar{h}_f^\circ + \Delta\bar{h})_i \tag{13.9}$$

The usual parameter for expressing the enthalpy of combustion is a unit mass of fuel, such as a kilogram (h_{RP}) or a kilomole ($\bar{h}_{RP}$) of fuel.

The tabulated values of the enthalpy of combustion of fuels are usually given for a temperature of 25°C and a pressure of 0.1 MPa. The enthalpy of combustion for a number of hydrocarbon fuels at this temperature and pressure, which we designate h_{RP_0}, is given in Table 13.3.

The internal energy of combustion is defined in a similar manner,

$$\bar{u}_{RP} = U_P - U_R$$
$$= \sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h} - P\bar{v})_e - \sum_R n_i(\bar{h}_f^\circ + \Delta\bar{h} - P\bar{v})_i \tag{13.10}$$

When all the gaseous constituents can be considered as ideal gases, and the volume of the liquid and solid constituents is negligible compared to the value of the gaseous constituents, this relation for $\bar{u}_{RP}$ reduces to

$$\bar{u}_{RP} = \bar{h}_{RP} - \bar{R}T(n_{\text{gaseous products}} - n_{\text{gaseous reactants}}) \tag{13.11}$$

Frequently the term "heating value" or "heat of reaction" is used. This term represents the heat transferred from the chamber during combustion or reaction at constant temperature. For a constant-pressure or steady-flow process, we conclude from the first law of thermodynamics that it is equal to the negative of the enthalpy of combustion. For this reason this heat transfer is sometimes designated the constant-pressure heating value for combustion processes.

For a constant-volume process, the heat transfer is equal to the negative of the internal energy of combustion. This is sometimes designated the constant-volume heating value for combustion.

When the term heating value is used, the terms "higher" and "lower" designate whether the water in the products is liquid or vapor. The higher heating value is the heat transfer with liquid water in the products, and the lower heating value is the heat transfer with vapor water in the products.

TABLE 13.3 Enthalpy of Combustion of Some Hydrocarbons at 25°C

		Liquid water in Products (Negative of Higher Heating Value)		Vapor Water in Products (Negative of Lower Heating Value)	
Hydrocarbon	Formula	Liquid Hydrocarbon, kJ/kg fuel	Gaseous Hydrocarbon, kJ/kg fuel	Liquid Hydrocarbon, kJ/kg fuel	Gaseous Hydrocarbon, kJ/kg fuel
Paraffin Family					
Methane	CH_4		−55 496		−50 010
Ethane	C_2H_6		−51 875		−47 484
Propane	C_3H_8	−49 973	−50 343	−45 982	−46 352
Butane	C_4H_{10}	−49 130	−49 500	−45 344	−45 714
Pentane	C_5H_{12}	−48 643	−49 011	−44 983	−45 351
Hexane	C_6H_{14}	−48 308	−48 676	−44 733	−45 101
Heptane	C_7H_{16}	−48 071	−48 436	−44 557	−44 922
Octane	C_8H_{18}	−47 893	−48 256	−44 425	−44 788
Decane	$C_{10}H_{22}$	−47 641	−48 000	−44 239	−44 598
Dodecane	$C_{12}H_{26}$	−47 470	−47 828	−44 109	−44 467
Olefin Family					
Ethene	C_2H_4		−50 296		−47 158
Propene	C_3H_6		−48 917		−45 780
Butene	C_4H_8		−48 453		−45 316
Pentene	C_5H_{10}		−48 134		−44 996
Hexene	C_6H_{12}		−47 937		−44 800
Heptene	C_7H_{14}		−47 800		−44 662
Octene	C_8H_{16}		−47 693		−44 556
Nonene	C_9H_{18}		−47 612		−44 475
Decene	$C_{10}H_{20}$		−47 547		−44 410
Alkylbenzene Family					
Benzene	C_6H_6	−41 831	−42 266	−40 141	−40 576
Methylbenzene	C_7H_8	−42 437	−42 847	−40 527	−40 937
Ethylbenzene	C_8H_{10}	−42 997	−43 395	−40 924	−41 322
Propylbenzene	C_9H_{12}	−43 416	−43 800	−41 219	−41 603
Butylbenzene	$C_{10}H_{14}$	−43 748	−44 123	−41 453	−41 828

EXAMPLE 13.11

Calculate the enthalpy of combustion of propane at 25°C on both a kilomole and kilogram basis under the following conditions.

1. Liquid propane with liquid water in the products.
2. Liquid propane with gaseous water in the products.

3. Gaseous propane with liquid water in the products.
4. Gaseous propane with gaseous water in the products.

This example is designed to show how the enthalpy of combustion can be determined from enthalpies of formation. The enthalpy of evaporation of propane is 370 kJ/kg.

Analysis and Solution

The basic combustion equation is

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

From Table A.15, $(\bar{h}_f^\circ)_{C_3H_8(g)} = -103\,900$ kJ/kmol. Therefore,

$$(\bar{h}_f^\circ)_{C_3H_8(l)} = -103\,900 - 44.097(370) = -120\,216 \text{ kJ/kmol}$$

1. Liquid propane–liquid water:

$$\begin{aligned}\bar{h}_{RP_0} &= 3(\bar{h}_f^\circ)_{CO_2} + 4(\bar{h}_f^\circ)_{H_2O(l)} - (\bar{h}_f^\circ)_{C_3H_8(l)} \\ &= 3(-393\,522) + 4(-285\,830) - (-120\,216) \\ &= -2\,203\,670 \text{ kJ/kmol} = -\frac{2\,203\,670}{44.097} = -49\,973 \text{ kJ/kg}\end{aligned}$$

   The higher heating value of gaseous propane is 50 343 kJ/kg.

2. Liquid propane–gaseous water:

$$\begin{aligned}\bar{h}_{RP_0} &= 3(\bar{h}_f^\circ)_{CO_2} + 4(\bar{h}_f^\circ)_{H_2O(g)} - (\bar{h}_f^\circ)_{C_3H_8(l)} \\ &= 3(-393\,522) + 4(-241\,826) - (-120\,216) \\ &= -2\,027\,654 \text{ kJ/kmol} = -\frac{2\,027\,654}{44.097} = -45\,982 \text{ kJ/kg}\end{aligned}$$

   The lower heating value of liquid propane is 45 982 kJ/kg.

3. Gaseous propane–liquid water:

$$\begin{aligned}\bar{h}_{RP_0} &= 3(\bar{h}_f^\circ)_{CO_2} + 4(\bar{h}_f^\circ)_{H_2O(l)} - (\bar{h}_f^\circ)_{C_3H_8(g)} \\ &= 3(-393\,522) + 4(-285\,830) - (-103\,900) \\ &= -2\,219\,986 \text{ kJ/kmol} = -\frac{2\,219\,986}{44.097} = -50\,343 \text{ kJ/kg}\end{aligned}$$

   The higher heating value of gaseous propane is 50 343 kJ/kg.

4. Gaseous propane–gaseous water:

$$\begin{aligned}\bar{h}_{RP_0} &= 3(\bar{h}_f^\circ)_{CO_2} + 4(\bar{h}_f^\circ)_{H_2O(g)} - (\bar{h}_f^\circ)_{C_3H_8(g)} \\ &= 3(-393\,522) + 4(-241\,826) - (-103\,900) \\ &= -2\,043\,970 \text{ kJ/kmol} = -\frac{2\,043\,970}{44.097} = -46\,352 \text{ kJ/kg}\end{aligned}$$

   The lower heating value of gaseous propane is 46 352 kJ/kg.

Each of the four values calculated in this example corresponds to the appropriate value given in Table 13.3.

EXAMPLE 13.12

Calculate the enthalpy of combustion of gaseous propane at 500 K. (At this temperature all the water formed during combustion will be vapor.) This example will demonstrate how the enthalpy of combustion of propane varies with temperature. The average constant-pressure specific heat of propane between 25°C and 500 K is 2.1 kJ/kg K.

Analysis: The combustion equation is

$$C_3H_8(g) + 5O_2 \rightarrow 3CO_2 + 4H_2O(g)$$

The enthalpy of combustion is, from Eq. 13.9,

$$(\bar{h}_{RP})_T = \sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h})_e - \sum_R n_i(\bar{h}_f^\circ + \Delta\bar{h})_i$$

Solution

$$\begin{aligned}
\bar{h}_{R_{500}} &= [\bar{h}_f^\circ + \bar{C}_{p\,av}(\Delta T)]_{C_3H_8(g)} + n_{O_2}(\Delta\bar{h})_{O_2} \\
&= -103\,900 + 2.1 \times 44.097(500 - 298.2) + 5(6095) \\
&= -54\,738 \text{ kJ} \\
\bar{h}_{P_{500}} &= n_{CO_2}(\bar{h}_f^\circ + \Delta\bar{h})_{CO_2} + n_{H_2O}(\bar{h}_f^\circ + \Delta\bar{h})_{H_2O} \\
&= 3(-393\,522 + 8297) + 4(-241\,826 + 6896) \\
&= -2\,095\,395 \text{ kJ} \\
\bar{h}_{RP_{500}} &= -2\,095\,395 - (-54\,738) = -2\,040\,657 \text{ kJ/kmol} \\
h_{RP_{500}} &= \frac{-2\,040\,657}{44.097} = -46\,277 \text{ kJ/kg}
\end{aligned}$$

This compares with a value of −46 352 at 25°C.

This problem could also have been solved using the given value of the enthalpy of combustion at 25°C by noting that

$$\begin{aligned}
\bar{h}_{RP_{500}} &= (H_P)_{500} - (H_R)_{500} \\
&= n_{CO_2}(\bar{h}_f^\circ + \Delta\bar{h})_{CO_2} + n_{H_2O}(\bar{h}_f^\circ + \Delta\bar{h})_{H_2O} \\
&\quad - [\bar{h}_f^\circ + \bar{C}_{p\,av}(\Delta T)]_{C_3H_8(g)} - n_{O_2}(\Delta\bar{h})_{O_2} \\
&= \bar{h}_{RP_0} + n_{CO_2}(\Delta\bar{h})_{CO_2} + n_{H_2O}(\Delta\bar{h})_{H_2O} \\
&\quad - \bar{C}_{p\,av}(\Delta T)_{C_3H_8(g)} - n_{O_2}(\Delta\bar{h})_{O_2} \\
\bar{h}_{RP_{500}} &= -46\,352 \times 44.097 + 3(8297) + 4(6896) \\
&\quad - 2.1 \times 44.097(500 - 298.2) - 5(6095) \\
&= -2\,040\,657 \text{ kJ/kmol} \\
h_{RP_{500}} &= \frac{-2\,040\,657}{44.097} = -46\,277 \text{ kJ/kg}
\end{aligned}$$

13.7 THE THIRD LAW OF THERMODYNAMICS AND ABSOLUTE ENTROPY

As we consider a second-law analysis of chemical reactions, we face the same problem we had with the first law: What base should be used for the entropy of the various substances? This problem leads directly to a consideration of the third law of thermodynamics.

The third law of thermodynamics was formulated during the early part of the twentieth century. The initial work was done primarily by W. H. Nernst (1864–1941) and Max Planck (1858–1947). The third law deals with the entropy of substances at the absolute zero of temperature, and in essence states that the entropy of a perfect crystal is zero at absolute zero. From a statistical point of view, this means that the crystal structure has the maximum degree of order. Further, because the temperature is absolute zero, the thermal energy is minimum. It also follows that a substance that does not have a perfect crystalline structure at absolute zero, but instead has a degree of randomness, such as a solid solution or a glassy solid, has a finite value of entropy at absolute zero. The experimental evidence on which the third law rests is primarily data on chemical reactions at low temperatures and measurements of heat capacity at temperatures approaching absolute zero. In contrast to the first and second laws, which lead, respectively, to the properties of internal energy and entropy, the third law deals only with the question of entropy at absolute zero. However, the implications of the third law are quite profound, particularly in respect to chemical equilibrium.

The particular relevance of the third law is that it provides an absolute base from which to measure the entropy of each substance. The entropy relative to this base is termed the absolute entropy. The increase in entropy between absolute zero and any given state can be found either from calorimetric data or by procedures based on statistical thermodynamics. The calorimetric method gives precise measurements of specific-heat data over the temperature range, as well as of the energy associated with phase transformations. These measurements are in agreement with the calculations based on statistical thermodynamics and observed molecular data.

Table A.15 gives the absolute entropy at 25°C and 0.1-MPa pressure for a number of substances. Table A.12 gives the absolute entropy for a number of gases at 0.1-MPa pressure and various temperatures. For gases the numbers in all these tables are the hypothetical ideal-gas values. The pressure P° of 0.1 MPa is termed the standard-state pressure, and the absolute entropy as given in these tables is designated $\bar{s}^\circ$. The temperature is designated in kelvins with a subscript such as $\bar{s}^\circ_{1000}$.

If the value of the absolute entropy is known at the standard-state pressure of 0.1 MPa and a given temperature, it is a straightforward procedure to calculate the entropy change from this state (whether hypothetical ideal gas or real substance) to another desired state following the procedure described in Section 12.14. If the substance is listed in Table A.12, then

$$\bar{s}_{T,P} = \bar{s}^\circ_T - \bar{R} \ln \frac{P}{P^\circ} + (\bar{s}_{T,P} - \bar{s}^*_{T,P}) \tag{13.12}$$

In this expression, the first term on the right side is the value from Table A.12, the second is the ideal-gas term to account for a change in pressure from P° to P, and the third is the term that corrects for real-substance behavior, as given in the generalized entropy chart or table in the Appendix. If the real-substance behavior is to be evaluated from an equation of state or thermodynamic table of properties, the term for the change in pressure should be made to a low pressure P^*, at which ideal-gas behavior is a reasonable assumption, but it is also listed in the tables. Then

$$\bar{s}_{T,P} = \bar{s}_T^\circ - \bar{R} \ln \frac{P^*}{P^\circ} + (\bar{s}_{T,P} - \bar{s}^*_{T,P^*}) \tag{13.13}$$

If the substance is not one of those listed in Table A.12, and the absolute entropy is known only at one temperature T_0, as given in Table A.15 for example, then it will be necessary to calculate $\bar{s}_T^\circ$ from

$$\bar{s}_T^\circ = \bar{s}_{T_0}^\circ + \int_{T_0}^{T} \frac{\bar{C}_{p0}}{T}\, dT \tag{13.14}$$

and then proceed with the calculation of Eq. 13.12 or 13.13.

It should be noted that if Eq. 13.12 is being used to calculate the absolute entropy of a substance in a region in which the ideal-gas model is a valid representation of the behavior of that substance, then the last term on the right-side of Eq. 13.12 simply drops out of the calculation.

For calculation of the absolute entropy of a mixture of ideal gases at T, P, the mixture entropy is given in terms of the component partial entropies as

$$\bar{s}^*_{\text{mix}} = \sum_i y_i \bar{S}_i^* \tag{13.15}$$

where

$$\bar{S}_i^* = \bar{s}_{i_T}^\circ - \bar{R} \ln \frac{P}{P^\circ} - \bar{R} \ln y_i = \bar{s}_{i_T}^\circ - \bar{R} \ln \frac{y_i P}{P^\circ} \tag{13.16}$$

For a real-gas mixture, a correction can be added to the ideal-gas entropy calculated from Eqs. 13.15 and 13.16 by using a pseudocritical method such as was discussed in Section 12.14. The corrected expression is

$$\bar{s}_{\text{mix}} = \bar{s}^*_{\text{mix}} + (\bar{s} - \bar{s}^*)_{T,P} \tag{13.17}$$

in which the second term on the right side is the correction term from the generalized entropy chart or table.

13.8 SECOND-LAW ANALYSIS OF REACTING SYSTEMS

The concepts of reversible work, irreversibility, and availability were introduced in Chapter 9. These concepts included both the first and second laws of thermodynamics. At the conclusion of Chapter 9, the Gibbs function was introduced, and we made the statement that this property is particularly relevant in dealing with chemical reactions. We proceed now to develop this matter further, and we

will be particularly concerned with determining the maximum work (availability) that can be done through a combustion process and with examining the irreversibilities associated with such processes.

The reversible work for a steady-state, steady-flow process in the absence of changes in kinetic and potential energy is, from Eq. 9.38,

$$W_{rev} = \sum m_i(h_i - T_0 s_i) - \sum m_e(h_e - T_0 s_e)$$

Applying this equation to an SSSF process that involves a chemical reaction, and introducing the symbols from this chapter, we have

$$W_{rev} = \sum_R n_i(\bar{h}_f^\circ + \Delta\bar{h} - T_0\bar{s})_i - \sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h} - T_0\bar{s})_e \tag{13.18}$$

Similarly, the irreversibility for such a process can be written as

$$I = W_{rev} - W = \sum_P n_e T_0 \bar{s}_e - \sum_R n_i T_0 \bar{s}_i - Q_{c.v.} \tag{13.19}$$

The availability, ψ, for an SSSF process, in the absence of kinetic and potential energy changes, was defined in Eq. 9.42 as

$$\psi = (h - T_0 s) - (h_0 - T_0 s_0)$$

It was also indicated in Chapter 9 that when an SSSF chemical reaction takes place in such a manner that both the reactants and products are in temperature equilibrium with the surroundings, the Gibbs function ($g = h - Ts$) becomes a significant variable, Eq. 9.54. For such a process, in the absence of changes in kinetic and potential energy, the reversible work is given by the relation

$$W_{rev} = \sum_R n_i \bar{g}_i - \sum_P n_e \bar{g}_e \tag{13.20}$$

Since the Gibbs function is so relevant for processes that involve chemical reactions, the Gibbs function of formation, $\bar{g}_f^\circ$, has been defined by a procedure similar to that used in defining the enthalpy of formation. That is, the Gibbs function of each of the elements at 25°C and 0.1-MPa pressure is assumed to be zero, and the Gibbs function of each substance is found relative to this base. Table A.15 lists the Gibbs function of formation of a number of substances at 25°C and 0.1-MPa pressure. It is also evident that the Gibbs function can be found directly from data for $\bar{h}_f^\circ$ and $\bar{s}^\circ$ at the given temperature, as indicated in the following example.

EXAMPLE 13.13

Determine the Gibbs function of formation of carbon dioxide.

Analysis: Consider the reaction

$$C + O_2 \rightarrow CO_2$$

Assume that the carbon and oxygen are each initially at 25°C and 0.1-MPa pressure, and that the carbon dioxide is finally at 25°C and 0.1-MPa pressure.

The change in Gibbs function for this reaction is found first.

$$G_P - G_R = (H_P - H_R) - T_0(S_P - S_R)$$

$$\sum_P n_e(\bar{g}_f^\circ)_e - \sum_R n_i(\bar{g}_f^\circ)_i = \sum_P n_e(\bar{h}_f^\circ)_e - \sum_R n_i(\bar{h}_f^\circ)_i - T_0\left[\sum_P n_e(\bar{s}_{298}^\circ)_e - \sum_R n_i(\bar{s}_{298}^\circ)_i\right]$$

Solution

$$\begin{aligned} G_P - G_R &= (\bar{h}_f^\circ)_{CO_2} - 298.15[(\bar{s}_{298}^\circ)_{CO_2} - (\bar{s}_{298}^\circ)_C - (\bar{s}_{298}^\circ)_{O_2}] \\ &= -393\,522 - 298.15(213.795 - 5.740 - 205.1) \\ &= -394\,389 \text{ kJ/kmol} \end{aligned}$$

Since the Gibbs function of the reactants, G_R, is zero (in accordance with the assumption that the Gibbs function of the elements is zero at 25°C and 0.1-MPa pressure), it follows that

$$G_P = (\bar{g}_f^\circ)_{CO_2} = -394\,389 \text{ kJ/kmol}$$

This is the value given in Table A.15.

Let us now consider the question of the maximum work that can be done during a chemical reaction. For example, consider 1 kmol of hydrocarbon fuel and the necessary air for complete combustion, each at 0.1-MPa pressure and 25°C, the pressure and temperature of the surroundings. What is the maximum work that can be done as this fuel reacts with the air? From the considerations covered in Chapter 9, we conclude that the maximum work would be done if this chemical reaction took place reversibly and the products were finally in pressure and temperature equilibrium with the surroundings. We conclude that this reversible work could be calculated from the relation in Eq. 13.20,

$$W_{rev} = \sum_R n_i \bar{g}_i - \sum_P n_e \bar{g}_e$$

However, since the final state is in equilibrium with the surroundings, we could consider this amount of work to be the availability of the fuel and air.

EXAMPLE 13.14

Ethene (g) at 25°C and 0.1-MPa pressure is burned with 400 percent theoretical air at 25°C and 0.1-MPa pressure. Assume that this reaction takes place reversibly at 25°C and that the products leave at 25°C and 0.1-MPa pressure. To simplify this problem further, assume that the oxygen and nitrogen are separated before the reaction takes place (each at 0.1 MPa, 25°C), that the constituents in the products are separated, and that each is at 25°C and 0.1 MPa. Thus, the reaction takes place as shown in Fig. 13.4. For purposes of comparison between this and the two subsequent examples, we consider all the water in the products to be a gas (a hypothetical situation in this example and Example 13.16).

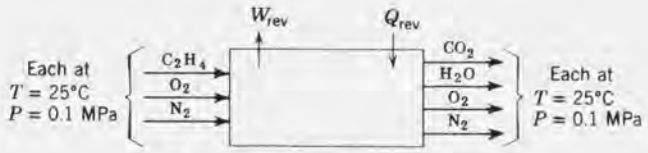


FIGURE 13.4 Sketch for Example 13.14.

Determine the reversible work for this process (that is, the work that would be done if this chemical action took place reversibly and isothermally).

Control volume: Combustion chamber.

Inlet states: P, T known for each gas.

Exit states: P, T known for each gas.

Model: All ideal gases, Tables A.12 and A.15.

Sketch: Figure 13.4.

Analysis: The equation for this chemical reaction is

$$C_2H_4(g) + 3(4)O_2 + 3(4)(3.76)N_2 \rightarrow 2CO_2 + 2H_2O(g) + 9O_2 + 45.1N_2$$

The reversible work for this process is equal to the decrease in Gibbs function during this reaction, Eq. 13.20. The values for the Gibbs function can be taken directly from Table A.15, since each is at 25°C and 0.1-MPa pressure. From Eq. 13.20, we have

$$W_{rev} = \sum_R n_i \bar{g}_i - \sum_P n_e \bar{g}_e$$

Solution

Since each of the reactants and each of the products are at 0.1-MPa pressure and 25°C, this equation reduces to

$$\begin{aligned} W_{rev} &= (\bar{g}_f^\circ)_{C_2H_4} - 2(\bar{g}_f^\circ)_{CO_2} - 2(\bar{g}_f^\circ)_{H_2O(g)} \\ &= 68\,421 - 2(-394\,389) - 2(-228\,582) \\ &= 1\,314\,363 \text{ kJ/kmol } C_2H_4 \\ &= \frac{1\,314\,363}{28.054} = 46\,851 \text{ kJ/kg} \end{aligned}$$

Therefore, we might say that when 1 kg of ethene is at 25°C, 0.1-MPa pressure, the temperature and pressure of the surroundings, it has an availability of 46 851 kJ.

Thus, it would seem logical to rate the efficiency of a device designed to do work by utilizing a combustion process, such as an internal-combustion engine or a steam power plant, as the ratio of the actual work to the reversible work, or in Example 13.14, the decrease in Gibbs function for the chemical reaction, instead of comparing the actual work to the heating value, as is commonly done. This is, in fact, the basic principle of the second-law efficiency, which was introduced in connection with availability analysis in Chapter 9. As noted from Example 13.14,

the difference between the decrease in Gibbs function and the heating value is small, which is typical for hydrocarbon fuels. The difference in the two types of efficiencies will, therefore, not usually be large. We must always be careful, however, when discussing efficiencies, to note the definition of the efficiency under consideration.

It is of particular interest to study the irreversibility that takes place during a combustion process. The following examples illustrate this matter. We consider the same hydrocarbon fuel that was used in Example 13.14—ethene (g) at 25°C and 0.1 MPa. We determined its availability and found it to be 46 851 kJ/kg. Now let us burn this fuel with 400 percent theoretical air in a steady-state, steady-flow adiabatic process. We can determine the irreversibility of this process in two ways. The first way is to calculate the increase in entropy for the process. Since the process is adiabatic, the increase in entropy is due entirely to the irreversibilities for the process, and we can find the irreversibility from Eq. 13.19. We can also calculate the availabilities of the products of combustion at the adiabatic flame temperature, and note that they are less than the availability of the fuel and air before the combustion process. The difference is the irreversibility that occurs during the combustion process.

EXAMPLE 13.15

Consider the same combustion process as in Example 13.14, but let it take place adiabatically. Assume that each constituent in the products is at 0.1-MPa pressure and at the adiabatic flame temperature. This combustion process is shown schematically in Fig. 13.5. The temperature of the surroundings is 25°C.

For this combustion process, determine (1) the increase in entropy during combustion and (2) the availability of the products of combustion.

Control volume: Combustion chamber.

Inlet states: P, T known for each gas.

Exit states: P known for each gas.

Sketch: Figure 13.5.

Model: All ideal gases, Table A.12; Table A.15 for ethene.

Analysis: The combustion equation is

$$C_2H_4 + 12O_2 + 12(3.76)N_2 \rightarrow 2CO_2 + 2H_2O(g) + 9O_2 + 45.1N_2$$

The adiabatic flame temperature is determined first.

First law:

$$H_R = H_P$$

$$\sum_R n_i(\bar{h}_f^\circ)_i = \sum_P n_e(\bar{h}_f^\circ + \Delta\bar{h})_e$$



FIGURE 13.5 Sketch for Example 13.15.

Solution

$$52\,467 = 2(-393\,522 + \Delta\bar{h}_{CO_2}) + 2(-241\,826 + \Delta\bar{h}_{H_2O(g)}) + 9\Delta\bar{h}_{O_2} + 45.1\Delta\bar{h}_{N_2}$$

By a trial-and-error solution we find the adiabatic flame temperature to be 1016 K.

We now proceed to find the change in entropy during this adiabatic combustion process.

$$\begin{aligned} S_R &= \sum_R (n_i\bar{s}_i^\circ)_{298} = (\bar{s}^\circ_{C_2H_4} + 12\bar{s}^\circ_{O_2} + 45.1\bar{s}^\circ_{N_2})_{298} \\ &= 219.330 + 12(205.147) + 45.1(191.610) \\ &= 11\,322.705 \text{ kJ/kmol (fuel) K} \\ S_P &= \sum_P (n_e\bar{s}_e^\circ)_{1016} = (2\bar{s}^\circ_{CO_2} + 2\bar{s}^\circ_{H_2O(g)} + 9\bar{s}^\circ_{O_2} + 45.1\bar{s}^\circ_{N_2})_{1016} \\ &= 2(270.194) + 2(233.355) + 9(244.135) + 45.1(228.691) \\ &= 13\,518.277 \text{ kJ/kmol (fuel) K} \\ S_P - S_R &= 2195.572 \text{ kJ/kmol (fuel) K} \end{aligned}$$

Since this is an adiabatic process, the increase in entropy indicates the irreversibility of the adiabatic combustion process. This irreversibility can be found from Eq. 13.19.

$$\begin{aligned} I &= T_0\left(\sum_P n_e\bar{s}_e - \sum_R n_i\bar{s}_i\right) \\ &= 298.15 \times 2195.572 = 654\,610 \text{ kJ/kmol} \\ &= \frac{654\,610}{28.054} = 23\,334 \text{ kJ/kg fuel} \end{aligned}$$

Therefore, the availability after the combustion process is

$$\psi_P = 46\,851 - 23\,334 = 23\,517 \text{ kJ/kg}$$

The availability of the products can also be found from the relation

$$\psi_P = \sum_P [(\bar{h}_e - T_0\bar{s}_e) - (\bar{h}_0 - T_0\bar{s}_0)]$$

Since in this problem the products are separated, and each is at 0.1-MPa pressure and the adiabatic flame temperature of 1016 K, this equation can be evaluated, yielding

$$\begin{aligned} \psi_P &= \sum_P n_e[(\bar{h}_e^\circ - \bar{h}_0^\circ) - T_0(\bar{s}_e^\circ - \bar{s}_0^\circ)] \\ &= 2(34\,271) + 2(26\,618) + 9(23\,268) + 45.1(21\,985) \\ &\quad - 298.15[2(270.194 - 213.795) + 2(233.355 - 188.834) \\ &\quad + 9(244.135 - 205.147) + 45.1(228.691 - 191.610)] \\ &= 659\,746 \text{ kJ/kmol} = 23\,517 \text{ kJ/kg} \end{aligned}$$

In other words, if every process after the adiabatic combustion process is reversible, the maximum amount of work that could be done is 23 517 kJ/kg fuel. This compares to a value of 46 851 kJ/kg for the reversible isothermal reaction. This means

that if we had an engine with the indicated adiabatic combustion process, and if all other processes were completely reversible, the efficiency would be about 50 percent.

In the two prior examples we assumed, for purposes of simplifying the calculation, that the constituents in the reactants and products were separated, and each was at 0.1-MPa pressure. This of course is not a realistic problem. In the following example, Example 13.14 is repeated with the assumption that the reactants and products each consist of a mixture at 0.1-MPa pressure.

EXAMPLE 13.16

Consider the same combustion process as in Example 13.14, but assume that the reactants consist of a mixture at 0.1-MPa pressure and 25°C and that the products also consist of a mixture at 0.1 MPa and 25°C. Thus, the combustion process is as shown in Fig. 13.6.

Determine the work that would be done if this combustion process took place reversibly and in pressure and temperature equilibrium with the surroundings.

Control volume: Combustion chamber.

Inlet state: P, T known.

Exit state: P, T known.

Sketch: Figure 13.6.

Model: Reactants—ideal-gas mixture, Table A.12. Products—ideal-gas mixture, Table A.12.

Analysis: The combustion equation, as noted previously, is

$$C_2H_4(g) + 3(4)O_2 + 3(4)(3.76)N_2 \rightarrow 2CO_2 + 2H_2O(g) + 9O_2 + 45.1N_2$$

In this case we must find the entropy of each substance as it exists in the mixture; that is, at its partial pressure and the given temperature of 25°C. Because the absolute entropies given in Tables A.12 and A.15 are at 0.1-MPa pressure and 25°C, the entropy of each constituent in the mixture can be found, using Eq. 13.16, from the relation

$$\bar{S}^* = \bar{s}^\circ - \bar{R} \ln y \frac{P}{P^\circ}$$

where $\bar{S}^*$ = partial entropy of the constituent in the mixture
$\bar{s}^\circ$ = absolute entropy at the same temperature and 0.1-MPa pressure
P = pressure of the mixture



FIGURE 13.6 Sketch for Example 13.16.

P° = 0.1-MPa pressure
y = mole fraction of the constituent

Since P° and the pressure of the mixture are both 0.1 MPa, the partial entropy of each constituent can be found by the relation

$$\bar{S}^* = \bar{s}^\circ - \bar{R} \ln y = \bar{s}^\circ + \bar{R} \ln \frac{1}{y}$$

Solution

For the reactants:

	n	$1/y$	$\bar{R} \ln 1/y$	$\bar{s}^\circ$	$\bar{S}^*$
C_2H_4	1	58.1	33.774	219.330	253.104
O_2	12	4.842	13.114	205.147	218.261
N_2	45.1	1.288	2.104	191.610	193.714
	58.1				

For the products:

	n	$1/y$	$\bar{R} \ln 1/y$	$\bar{s}^\circ$	$\bar{S}^*$
CO_2	2	29.05	28.011	213.795	241.806
H_2O	2	29.05	28.011	188.834	216.845
O_2	9	6.456	15.506	205.147	220.653
N_2	45.1	1.288	2.104	191.610	193.714
	58.1				

With the assumption of ideal-gas behavior, the enthalpy of each constituent is equal to the enthalpy of formation at 25°C. The values of entropy are as just calculated. Therefore, from Eq. 13.18,

$$\begin{aligned}
W_{\text{rev}} &= \sum_R n_i(\bar{h}_f^\circ)_i - \sum_P n_e(\bar{h}_f^\circ)_e - T_0\left(\sum_R n_i\bar{s}_i - \sum_P n_e\bar{s}_e\right) \\
&= (\bar{h}_f^\circ)_{C_2H_4} - 2(\bar{h}_f^\circ)_{CO_2} - 2(\bar{h}_f^\circ)_{H_2O(g)} \\
&\quad - 298.15(\bar{S}^*_{C_2H_4} + 12\bar{S}^*_{O_2} + 45.1\bar{S}^*_{N_2} - 2\bar{S}^*_{CO_2} \\
&\quad - 2\bar{S}^*_{H_2O(g)} - 9\bar{S}^*_{O_2} - 45.1\bar{S}^*_{N_2}) \\
&= 52\,467 - 2(-393\,522) - 2(-241\,826) \\
&\quad - 298.15[253.104 + 12(218.264) + 45.1(193.714) \\
&\quad - 2(241.806) - 2(216.845) - 9(220.653) - 45.1(193.714)] \\
&= 1\,332\,378 \text{ kJ/kmol} \\
&= \frac{1\,332\,378}{28.054} = 47\,493 \text{ kJ/kg}
\end{aligned}$$

Note that this value is essentially the same as the value that was obtained in Example 13.14, when the reactants and products were each separated and at 0.1-MPa pressure.

These examples raise the question of the possibility of a reversible chemical reaction. Some reactions can be made to approach reversibility by having them take place in an electrolytic cell, as described in Chapter 1. When a potential exactly equal to the electromotive force of the cell is applied, no reaction takes place. When the applied potential is increased slightly, the reaction proceeds in one direction, and if the applied potential is decreased slightly, the reaction proceeds in the opposite direction. The work done is the electrical energy supplied or delivered.

Consider a reversible reaction occuring at constant temperature equal to that of its environment. The work output of the fuel cell is

$$W = -(\sum n_e \bar{g}_e - \sum n_i \bar{g}_i) = -\Delta G$$

where ΔG is the change in Gibbs function for the overall chemical reaction. We also realize that the work is given in terms of the charged electrons flowing through an electrical potential $\mathscr{E}$ as

$$W = \mathscr{E} n_e N_0 e$$

in which n_e is the number of kilomoles of electrons flowing through the external circuit, and

$$N_0 e = 6.022\,045 \times 10^{26} \text{ elec/kmol} \times 1.602\,189 \times 10^{-22} \text{ kJ/elec V}$$

$$= 96\,485 \text{ kJ/kmol V}$$

Thus, for a given reaction, the maximum (reversible reaction) electrical potential $\mathscr{E}^\circ$ of a fuel cell at a given temperature is

$$\mathscr{E}^\circ = \frac{-\Delta G}{96\,485 n_e} \tag{13.21}$$

EXAMPLE 13.17

Calculate the reversible electromotive force (EMF) at 25°C for the hydrogen–oxygen fuel cell described in Section 1.2.

Solution

The anode side reaction was stated to be

$$2H_2 \rightarrow 4H^+ + 4e^-$$

and the cathode side reaction is

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O$$

Therefore, the overall reaction is, in kilomoles,

$$2H_2 + O_2 \rightarrow 2H_2O$$

for which 4 kmol of electrons flow through the external circuit. Let us assume that each component is at its standard-state pressure of 0.1 MPa and that the water formed is liquid. Then

$$\begin{aligned}\Delta G_{25^\circ C} &= 2(\overline{g}_f^\circ)_{H_2O} - 2(\overline{g}_f^\circ)_{H_2} - (\overline{g}_f^\circ)_{O_2} \\ &= 2(-237\,146) - 2(0) - 1(0) \\ &= -474\,292 \text{ kJ}\end{aligned}$$

Therefore, from Eq. 13.21,

$$\mathscr{E}^\circ = \frac{-(-474\,292)}{96\,485 \times 4} = 1.229 \text{ V}$$

Much effort is being directed toward the development of fuel cells in which carbon, hydrogen, or hydrocarbons will react with oxygen and produce electricity directly. If a fuel cell can be developed that utilizes a hydrocarbon fuel and has a sufficiently high efficiency and capacity (for a given volume or weight), our techniques for generating electricity on a commercial scale will undergo drastic changes. At the present time, however, fuel cells cannot compete with conventional power plants for the large-scale production of electricity.

13.9 EVALUATION OF ACTUAL COMBUSTION PROCESSES

A number of different parameters can be defined for evaluating the performance of an actual combustion process, depending on the nature of the process and the system considered. In the combustion chamber of a gas turbine, for example, the objective is to raise the temperature of the products to a given temperature (usually the maximum temperature the metals in the turbine can withstand). If we had a combustion process that achieved complete combustion and that was adiabatic, the temperature of the products would be the adiabatic flame temperature. Let us designate the fuel–air ratio needed to reach a given temperature under these conditions as the ideal fuel–air ratio. In the actual combustion chamber the combustion will be incomplete to some extent, and there will be some heat transfer to the surroundings. Therefore, more fuel will be required to reach the given temperature, and this we designate as the actual fuel–air ratio. The combustion efficiency, η_{comb}, is defined here as

$$\eta_{comb} = \frac{FA_{ideal}}{FA_{actual}} \tag{13.22}$$

On the other hand, in the furnace of a steam generator (boiler), the purpose is to transfer the maximum possible amount of heat to the steam (water). In practice, the efficiency of a steam generator is defined as the ratio of the heat transferred to the steam to the higher heating value of the fuel. For a coal this is the heating value as measured in a bomb calorimeter, which is the constant-volume heating value, and it corresponds to the internal energy of combustion. We observe a minor inconsistency, since the boiler involves a flow process, and the change in enthalpy

is the significant factor. In most cases, however, the error thus introduced is less than the experimental error involved in measuring the heating value, and the efficiency of a steam generator is defined by the relation

$$\eta_{\text{steam generator}} = \frac{\text{heat transferred to steam/kg fuel}}{\text{higher heating value of the fuel}} \tag{13.23}$$

In an internal-combustion engine the purpose is to do work. The logical way to evaluate the performance of an internal-combustion engine would be to compare the actual work done to the maximum work that would be done by a reversible change of state from the reactants to the products. This, as we noted previously, is called the second-law efficiency.

However, in practice the efficiency of an internal-combustion engine is defined as the ratio of the actual work to the negative of the enthalpy of combustion of the fuel (that is, the constant-pressure heating value). This ratio is usually called the thermal efficiency, η_{th}:

$$\eta_{\text{th}} = \frac{w}{-h_{RP_0}} = \frac{w}{\text{heating value}} \tag{13.24}$$

The overall efficiency of a gas turbine or steam power plant is defined in the same way. It should be pointed out that in an internal-combustion engine or fuel-burning steam power plant, the fact that the combustion is itself irreversible is a significant factor in the relatively low thermal efficiency of these devices.

One other factor should be pointed out regarding efficiency. We have noted that the enthalpy of combustion of a hydrocarbon fuel varies considerably with the phase of the water in the products, which leads to the concept of higher and lower heating values. Therefore, when we consider the thermal efficiency of an engine, the heating value used to determine this efficiency must be borne in mind. Two engines made by different manufacturers may have identical performance, but if one manufacturer bases his or her efficiency on the higher heating value and the other on the lower heating value, the latter will be able to claim a higher thermal efficiency. This claim is not significant, of course, as the performance is the same, and a consideration of how the efficiency was defined would reveal this.

The whole matter of the efficiencies of devices that undergo combustion processes is treated in detail in textbooks dealing with particular applications, and our discussion is intended only as an introduction to the subject. Two examples are given, however, to illustrate these remarks.

EXAMPLE 13.18

The combustion chamber of a gas turbine uses a liquid hydrocarbon fuel that has an approximate composition of C_8H_{18}. During testing the following data are obtained.

$T_{\text{air}} = 400$ K	$T_{\text{products}} = 1100$ K
$\mathbf{V}_{\text{air}} = 100$ m/s	$\mathbf{V}_{\text{products}} = 150$ m/s
$T_{\text{fuel}} = 50°\text{C}$	$FA_{\text{actual}} = 0.0211$ kg fuel/kg air

Calculate the combustion efficiency for this process.

Control volume: Combustion chamber.

Inlet states: T known for air and fuel.

Exit state: T known.

Model: Air and products—ideal gas, Table A.12. Fuel—Table A.15.

Analysis: For the ideal chemical reaction the heat transfer is zero. Therefore, writing the first law for a control volume that includes the combustion chamber, we have

$$H_R + \mathrm{KE}_R = H_P + \mathrm{KE}_P$$

$$H_R + \mathrm{KE}_R = \sum_R n_i\left(\bar{h}_f^\circ + \Delta\bar{h} + \frac{M\mathbf{V}^2}{2}\right)_i$$

$$= [\bar{h}_f^\circ + \bar{C}_p(50 - 25)]_{C_8H_{18}(l)} + n_{O_2}\left(\Delta\bar{h} + \frac{M\mathbf{V}^2}{2}\right)_{O_2}$$

$$+ 3.76n_{O_2}\left(\Delta\bar{h} + \frac{M\mathbf{V}^2}{2}\right)_{N_2}$$

$$H_P + \mathrm{KE}_P = \sum_P n_e\left(\bar{h}_f^\circ + \Delta\bar{h} + \frac{M\mathbf{V}^2}{2}\right)_e$$

$$= 8\left(\bar{h}_f^\circ + \Delta\bar{h} + \frac{M\mathbf{V}^2}{2}\right)_{CO_2} + 9\left(\bar{h}_f^\circ + \Delta\bar{h} + \frac{M\mathbf{V}^2}{2}\right)_{H_2O}$$

$$+ (n_{O_2} - 12.5)\left(\Delta\bar{h} + \frac{M\mathbf{V}^2}{2}\right)_{O_2} + 3.76n_{O_2}\left(\Delta\bar{h} + \frac{M\mathbf{V}^2}{2}\right)_{N_2}$$

Solution

$$H_R + \mathrm{KE}_R = -250\,105 + 1.7113 \times 114.23(50 - 25)$$

$$+ n_{O_2}\left[3034 + \frac{32 \times (100)^2}{2 \times 1000}\right]$$

$$+ 3.76n_{O_2}\left[2971 + \frac{28.02 \times (100)^2}{2 \times 1000}\right]$$

$$= -245\,218 + 14\,892n_{O_2}$$

$$H_P + \mathrm{KE}_P = 8\left[-393\,522 + 38\,891 + \frac{44.01 \times (150)^2}{2 \times 1000}\right]$$

$$+ 9\left[-241\,826 + 30\,147 + \frac{18.02 \times (150)^2}{2 \times 1000}\right]$$

$$+ (n_{O_2} - 12.5)\left[26\,218 + \frac{32 \times (150)^2}{2 \times 1000}\right]$$

$$+ 3.76n_{O_2}\left[24\,758 + \frac{28.02 \times (150)^2}{2 \times 1000}\right]$$

$$= -5\,068\,599 + 120\,853n_{O_2}$$

Therefore,

$$-245\,218 + 14\,892n_{O_2} = -5\,068\,599 + 120\,853n_{O_2}$$

$$n_{O_2} = 45.52 \text{ kmol } O_2/\text{kmol fuel}$$

$$\text{kmol air/kmol fuel} = 4.76(45.52) = 216.675$$

$$FA_{\text{ideal}} = \frac{114.23}{216.675 \times 28.97} = 0.0182 \text{ kg fuel/kg air}$$

$$\eta_{\text{comb}} = \frac{0.0182}{0.0211} \times 100 = 86.2 \text{ percent}$$

EXAMPLE 13.19

In a certain steam power plant 325 000 kg of water per hour enter the boiler at a pressure of 12.5 MPa and a temperature of 200°C. Steam leaves the boiler at 9 MPa, 500°C. The power output of the turbine is 81 000 kW. Coal is used at the rate of 26 700 kg/h and has a higher heating value of 33 250 kJ/kg. Determine the efficiency of the steam generator and the overall thermal efficiency of the plant.

In power plants the efficiency of both the boiler and the overall efficiency of the plant are based on the higher heating value of the fuel.

Solution

The efficiency of the boiler is defined by Eq. 13.23 as

$$\eta_{\text{steam generator}} = \frac{\text{heat transferred to } H_2O\text{/kg fuel}}{\text{higher heating value}}$$

Therefore

$$\eta_{\text{steam generator}} = \frac{325\,000(3386.1 - 857.1)}{26\,700 \times 33\,250} \times 100 = 92.6 \text{ percent}$$

The thermal efficiency is defined by Eq. 13.24.

$$\eta_{\text{th}} = \frac{w}{\text{heating value}} = \frac{81\,000 \times 3600}{26\,700 \times 33\,250} \times 100 = 32.8 \text{ percent}$$

PROBLEMS

13.1 A certain Pennsylvania coal contains 74.2 percent C, 5.1 percent H, 6.7 percent O (dry basis, mass percent) plus ash and small percentages of N and S. This coal is fed into a gasifier along with oxygen and steam, as shown in Fig. 13.7. The exiting product gas composition is measured and is found to include, on a mol basis, 39.9 percent CO, 30.8 percent H_2, 11.4 percent CO_2, 16.4 percent H_2O plus small percentages of CH_4, N_2, and H_2S. How many kilograms of coal are required to produce 100 kmol of product gas? How much oxygen and steam are required?

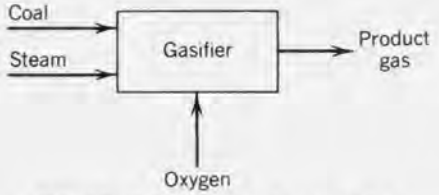


FIGURE 13.7 Sketch for Problem 13.1.

13.2 Repeat Problem 13.1 for a certain Utah coal that contains, according to the coal analysis, 68.2 percent C, 4.8 percent H, 15.7 percent O; the exiting product gas contains 30.9 percent CO, 26.7 percent H_2, 15.9 percent CO_2, 25.7 percent H_2O.

13.3 Liquid propane is burned with air. A volumetric analysis of the products of combustion yields the following percent composition on a dry basis:

Product	*Percent by Volume*
CO_2	8.6
CO	0.6
O_2	7.2
N_2	83.6

Determine the percent of theoretical air used in this combustion process.

13.4 A sample of pine bark has the following ultimate analysis on a dry basis, percent by mass:

Component	*Percent by Mass*
hydrogen	5.6
carbon	53.4
sulfur	0.1
nitrogen	0.1
oxygen	37.9
ash	2.9

This bark will be used as a fuel by burning it with 100 percent theoretical air in a furnace. Determine the air–fuel ratio on a mass basis.

13.5 Pentane is burned with 120 percent theoretical air in a constant-pressure process at 100 kPa. The products are cooled to ambient temperature, 20°C.

(a) How many kilograms of water are condensed per kilogram of fuel?

(b) Repeat part a, assuming that the air used in the combustion has a relative humidity of 90 percent.

13.5E Pentane is burned with 120 percent theoretical air in a constant-pressure process at 14.7 lbf/in.^{2}. The products are cooled to ambient temperature, 70 F.

(a) How many pounds-mass of water are condensed per pound-mass of fuel?

(b) Repeat part a, assuming that the air used in the combustion has a relative humidity of 90 percent.

13.6 The coal gasifier in an Integrated Gasification Combined Cycle power plant produces a gas mixture with the following volumetric percent composition:

Product	*Percent by Volume*
CH_4	0.3
H_2	29.6
CO	41.0
CO_2	10.0
N_2	0.8
H_2O	17.0
H_2S	1.1
NH_3	0.2

This gas is then cooled to 40°C, 3 MPa, and the H_2S and NH_3 are removed in water scrubbers. Assuming that the resulting mixture, which is to be sent to the combustors, is saturated with water, determine

(a) The mixture composition.
(b) The theoretical air–fuel ratio in the combustors.

13.7 The hot exhaust gas from an internal-combustion engine is analyzed and found to have the following percent composition on a volumetric basis at the engine exhaust manifold.

Product	*Percent by Volume*
CO_2	10
CO	2
H_2O	13
O_2	3
N_2	72

This gas is to be fed to an exhaust gas reactor and mixed with a certain amount of air to eliminate the carbon monoxide, as shown in Fig. 13.8. It is decided that a mole fraction of oxygen of 10 percent in the mixture at point 3 will ensure that no CO remains. What must the ratio of flows be entering the reactor?

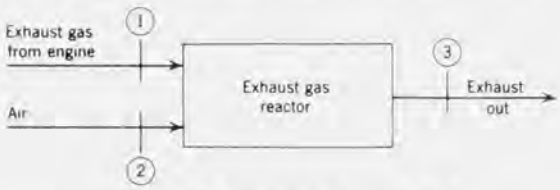


FIGURE 13.8 Sketch for Problem 13.7.

13.8 Many coals from the western United States have a high moisture content. Consider the following sample of Wyoming coal, for which the ultimate analysis on an as-received basis is, by mass,

Component	*Percent by Mass*
moisture	28.9
ash	5.8
sulfur	0.5
nitrogen	0.7
carbon	48.6
hydrogen	3.5
oxygen	12.0

This coal is to be burned in the steam generator of a large power plant with 120 percent theoretical air. Determine the air–fuel ratio on a mass basis.

13.9 The output gas mixture of a certain air-blown coal gasifier has the composition of producer gas as listed in Table 13.2. Consider the combustion of this gas with 120 percent theoretical air at 100-kPa pressure.

(a) Determine the dew point of the products.
(b) How many kilograms of water will be condensed per kilogram of fuel if the products are cooled 10°C below the dew-point temperature?

13.9E The output gas mixture of a certain air-blown coal gasifier has the composition of producer gas, as listed in Table 13.2. Consider the combustion of this gas with 120 percent theoretical air at 14.7-lbf/in.^{2} pressure.

(a) Determine the dew point of the products.

(b) How many pounds-mass of water will be condensed per pound-mass of fuel if the products are cooled 20 F below the dew-point temperature?

13.10 A gas mixture of 50 percent ethane and 50 percent propane by volume enters a combustion chamber at 350 K, 10 MPa. Determine the enthalpy per kilomole of this mixture relative to the thermochemical base of enthalpy.

13.11 A rigid vessel initially contains 2 kmol of carbon and 2 kmol of oxygen at 25°C, 200 kPa. Combustion occurs, and the resulting products consist of 1 kmol of carbon dioxide, 1 kmol of carbon monoxide, and excess oxygen at a temperature of 1000 K. Determine

(a) The final pressure in the vessel.

(b) The heat transfer from the vessel during the process.

13.12 In a test of rocket propellant performance, liquid hydrazine (N_2H_4) at 100 kPa, 25°C, and oxygen gas at 100 kPa, 25°C, are fed to a combustion chamber in the ratio of 0.5 kg O_2/kg N_2H_4. The heat transfer from the chamber to the surroundings is estimated to be 100 kJ/kg N_2H_4. Determine the temperature of the products exiting the chamber. Assume that only H_2O, H_2, and N_2 are present. The enthalpy of formation of liquid hydrazine is +50 417 kJ/kmol.

13.13 Repeat Problem 13.12, but assume that saturated-liquid oxygen at 90 K is used instead of 25°C oxygen gas in the combustion process. Use the generalized tables or charts to determine the properties of liquid oxygen.

13.14 One alternative to using petroleum or natural gas reserves as fuels is ethanol (C_2H_5OH), which is commonly produced from grain by fermentation. Consider a combustion process in which liquid ethanol is burned with 120 percent theoretical air in a SSSF process. The reactants enter the combustion chamber at 25°C, and the products exit at 60°C, 100 kPa. Calculate the heat transfer per kilomole of ethanol, using the enthalpy of formation of ethanol gas plus the generalized tables or charts.

13.15 Another alternative to using petroleum or natural gas as fuels is methanol (CH_3OH), which can be produced from coal. Both methanol and ethanol have been used in automotive engines. Repeat Problem 13.14 using liquid methanol as the fuel instead of ethanol.

13.16 Another alternative to be seriously considered as a fuel is hydrogen. It can be produced from water by various techniques that are under extensive study. Its biggest problems at the present time are in cost, storage, and safety. Repeat Problem 13.14 using hydrogen gas as the fuel instead of ethanol.

13.17 Hydrogen peroxide (H_2O_2) enters a gas generator at the rate of 0.1 kg/s and is decomposed to steam and oxygen. The resulting mixture is expanded through a turbine to atmospheric pressure, as shown in Fig. 13.9. Determine the power output of the turbine, and the heat-transfer rate in the gas generator. The enthalpy of formation of liquid H_2O_2 is −187 583 kJ/kmol.

13.18 In a new high-efficiency furnace, natural gas (assumed to be 90 percent methane and 10 percent ethane by volume) and 110 percent theoretical air each enter at

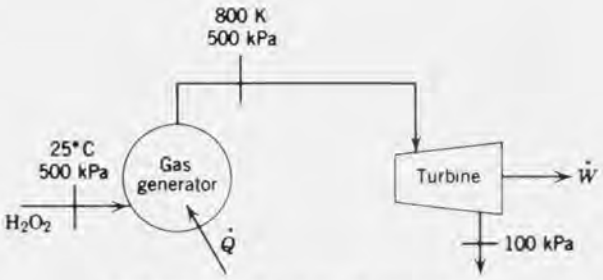


FIGURE 13.9 Sketch for Problem 13.17.

25°C, 100 kPa, and the products (assumed to be 100 percent gaseous) exit the furnace at 40°C, 100 kPa.

(a) What is the heat transfer for this process?

(b) Repeat part a for a furnace with an older design in which the combustion products exit at 250°C, 100 kPa.

13.18E In a new high-efficiency furnace, natural gas (assumed to be 90 percent methane and 10 percent ethane by volume) and 110 percent theoretical air each enter at 77 F, 14.7 lbf/in.^{2}, and the products (assumed to be 100 percent gaseous) exit the furnace at 100 F, 14.7 lbf/in.^{2}.

(a) What is the heat transfer for this process?

(b) Repeat part a for a furnace with an older design in which the combustion products exit at 450 F, 14.7 lbf/in.^{2}.

13.19 Repeat Problem 13.18, but take into account the actual phase behavior of the products exiting the furnace.

13.20 Butane gas at 25°C is mixed with 150 percent theoretical air at 600 K and is burned in an adiabatic SSSF combustor. What is the temperature of the products exiting the combustor?

13.21 Repeat Problem 13.20, but assume that the fuel is liquid butane instead of gaseous butane. Use the generalized tables or charts to determine the enthalpy difference.

13.22 How much error is introduced if the adiabatic flame temperature of Problem 13.20 is calculated, assuming that all substances have constant specific heat, with values at ambient temperature taken from Table A.9?

13.23 Consider the gas mixture fed to the combustors in an Integrated Gasification Combined Cycle power plant, as described in Problem 13.6. If the adiabatic flame temperature is to be limited to 1500 K, what percent theoretical air should be used in the combustors?

13.24 Acetylene gas at 100 kPa, 25°C, is fed to the head of a cutting torch. Calculate the adiabatic flame temperature if the acetylene is burned with

(a) 100 percent theoretical air at 25°C.

(b) 100 percent theoretical oxygen at 25°C.

13.24E Acetylene gas at 14.7 lbf/in.^{2}, 77 F, is fed to the head of a cutting torch. Calculate the adiabatic flame temperature if the acetylene is burned with

(a) 100 percent theoretical air at 77 F.

(b) 100 percent theoretical oxygen at 77 F.

13.25 Gaseous propane at 25°C is reacted with moist air (air containing water vapor) at 400 K in a steady-state, steady-flow process. The combustion process is adiabatic, and the exiting temperature is observed to be 1200 K. A sample of the products is tested and found to have a dew-point temperature of 70°C. Determine the percentage of theoretical air used and the relative humidity of this air. Assume that combustion is complete and that the pressure is 100 kPa throughout the process.

13.26 A study is to be made using liquid ammonia as the fuel in a gas-turbine engine. Consider the compressor (air) and combustion chamber of this engine.

(a) Air enters the compressor at 100 kPa, 25°C, and is compressed to 1600 kPa. The isentropic efficiency of the compressor is 87 percent. Determine the exit temperature and the work input per kilomole.

(b) Two kilomoles of liquid ammonia at 25°C and x times theoretical air from the compressor enter the combustion chamber. What is x if the adiabatic flame temperature is to be fixed at 1600 K?

13.27 A mixture of 80 percent ethane and 20 percent methane on a mole basis is throttled from 10 MPa, 65°C, to 100 kPa and is fed to a combustion chamber where it undergoes complete combustion with air, which enters at 100 kPa, 600 K. The amount of air is such that the products of combustion exit at 100 kPa, 1200 K. Assuming that the combustion process is adiabatic and that all components behave as ideal gases except the fuel mixture, which behaves according to the generalized tables or charts, with pseudocritical constants, determine

(a) The percentage of theoretical air used in the process.
(b) The dew-point temperature of the products.

13.28 Wet biomass waste from a food-processing plant is fed to a catalytic reactor, where in a SSSF process it is converted into a low-energy fuel gas suitable for firing the processing plant boilers. The fuel gas has a composition of 50 percent methane, 45 percent carbon dioxide, and 5 percent hydrogen on a volumetric basis. Determine the higher heating value of this fuel gas mixture per unit volume.

13.29 Determine the higher heating value of the sample of Wyoming coal as specified in Problem 13.8.

13.30 Consider natural gas A and natural gas D, both of which are listed in Table 13.2. Calculate the enthalpy of combustion of each gas at 25°C, assuming that the products include

(a) Vapor water.
(b) Liquid water.

13.31 Blast furnace gas in a steel mill is available at 250°C to be burned for the generation of steam. The composition of this gas is, on a volumetric basis,

Component	*Percent by Volume*
H_2	2.4
CH_4	0.1
CO	23.3
CO_2	14.4
N_2	56.4
H_2O	3.4

Determine the higher heating value (kJ/m^3) of this gas at ambient temperature and pressure.

13.31E Blast furnace gas in a steel mill is available at 500 F to be burned for the generation of steam. The composition of this gas is, on a volumetric basis,

Component	*Percent by Volume*
H_2	2.4
CH_4	0.1
CO	23.3
CO_2	14.4
N_2	56.4
H_2O	3.4

Determine the higher heating value (Btu/ft^3) of this gas at ambient temperature and pressure.

13.32 The enthalpy of formation of magnesium oxide, MgO(s), is −601 827 kJ/kmol at 25°C. The melting point of magnesium oxide is approximately 3000 K, and the increase in enthalpy between 298 and 3000 K is 128 449 kJ/kmol. The enthalpy of sublimation at 3000 K is estimated at 418 000 kJ/kmol, and the specific heat of magnesium oxide vapor above 3000 K is estimated at 37.24 kJ/kmol K.

(a) Determine the enthalpy of combustion per kilogram of magnesium.

(b) Estimate the adiabatic flame temperature when magnesium is burned with theoretical oxygen.

13.33 Pyrolysis, or partial oxidation, of a low-grade petroleum distillate yields a syngas of carbon monoxide and hydrogen in the molar ratio 1:2. This gas is fed directly to a steady-flow combustor at 800 K along with 120 percent theoretical air preheated to 600 K. Products exit the combustor at the adiabatic flame temperature. Calculate the irreversibility of this process.

13.34 Calculate the irreversibility for the process described in Problem 13.11.

13.35 A mixture of propane and 150 percent theoretical air enters a combustion chamber at 25°C, 200 kPa, and the products of combustion exit the chamber at 1400 K, 200 kPa. Assuming complete combustion, determine the heat transfer from the combustion chamber and the net entropy change for the process, both per kilomole of propane.

13.35E A mixture of propane and 150 percent theoretical air enters a combustion chamber at 77 F, 30 lbf/in.^{2}, and the products of combustion exit the chamber at 2060 F, 30 lbf/in.^{2}. Assuming complete combustion, determine the heat transfer from the combustion chamber and the net entropy change for the process, both per pound mole of propane.

13.36 Consider the combustion of methanol (CH_3OH) with 25 percent excess air. The combustion products are passed through a heat exchanger and exit at 200 kPa, 40°C. Calculate the absolute entropy of the products exiting the heat exchanger per kilomole of methanol burned, using whatever reference states are appropriate.

13.37 An inventor claims to have built a device that will take 0.001 kg/s of water from the faucet at 10°C, 100 kPa, and produce separate streams of hydrogen and oxygen gas, each at 400 K, 175 kPa. He says that his device will operate in a 25°C room on 10-kW electrical power input. How do you evaluate this claim?

13.38 Two kilomoles of ammonia are burned in a SSSF process with x kmol of oxygen. The products, consisting of H_2O, N_2, and the excess O_2, exit at 200°C, 7 MPa.

(a) Calculate x if half the water in the products is condensed.
(b) Calculate the absolute entropy of the products at the exit conditions.

13.38E Two pound moles of ammonia are burned in a SSSF process with x lb mol of oxygen. The products, consisting of H_2O, N_2, and the excess O_2, exit at 400 F, 1000 lbf/in.^{2}.

(a) Calculate x if half the water in the products is condensed.
(b) Calculate the absolute entropy of the products at the exit conditions.

13.39 Consider one cylinder of a spark-ignition, internal-combustion engine. Before the compression stroke, the cylinder is filled with a mixture of air and methane. Assume that 110 percent theoretical air has been used, that the pressure is 100 kPa, and that the temperature is 25°C before compression. The compression ratio of the engine is 9 to 1.

(a) Determine the pressure and temperature after compression. Assume that the process is reversible and adiabatic.
(b) Assume that complete combustion is achieved while the piston remains at top dead center (that is, after the reversible adiabatic compression), and that the combustion process is adiabatic. Determine the temperature and pressure after combustion, and the increase in entropy during the combustion process.
(c) What is the irreversibility for this process?

13.40 Consider the combustion process described in Problem 13.27.

(a) Calculate the absolute entropy of the fuel mixture before it is throttled into the combustion chamber.
(b) Calculate the irreversibility for the overall process.

13.41 Two kilomoles of ammonia at 25°C, 4 MPa, plus 200 percent theoretical oxygen at 25°C, 4 MPa, enter a SSSF combustion chamber. The products, a mixture of water, nitrogen, and oxygen, exit at 300°C, 4 MPa. Assuming that the behavior of the real-gas mixture is represented by pseudocritical constants and the generalized tables or charts, calculate

(a) The heat transfer from the combustion chamber.
(b) The net entropy change for the process.

13.42 A vertical cylinder fitted with a piston is divided into two parts, as shown in Fig. 13.10. Part A contains 1 kmol of saturated-liquid butane at 320 K, and part B contains 100 percent theoretical oxygen at 275 K. External force on top of the

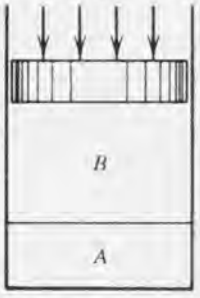


FIGURE 13.10 Sketch for Problem 13.42.

piston maintains a pressure of 10 MPa on the oxygen. The partition separating *A* and *B* is broken, and the two substances react to form carbon dioxide and water. During the reaction process, there is a heat transfer of 2.5×10^6 kJ out of the cylinder to the surroundings.

(a) What is the final temperature? Make an initial rough estimate of the temperature, and use this value to decide on detailed models, assumptions, and approximations to be used in the final solution.

(b) Calculate the absolute entropy of the cylinder contents at the final state.

13.43 In Example 13.17, a basic hydrogen–oxygen fuel cell reaction was analyzed at 25°C, 0.1 MPa. Repeat this calculation, assuming that the fuel cell operates on air at 25°C, 0.1 MPa, instead of on pure oxygen at this state.

13.44 Consider a methane–oxygen fuel cell in which the reaction at the anode is

$$CH_4 + 2H_2O \rightarrow CO_2 + 8e^- + 8H^+$$

The electrons produced by the reaction flow through the external load, and the positive ions migrate through the electrolyte to the cathode, at which the reaction is

$$8e^- + 8H^+ + 2O_2 \rightarrow 4H_2O$$

(a) Calculate the reversible work and the reversible EMF for the methane–oxygen fuel cell operating at 25°C, 100 kPa.

(b) Repeat part a, but assume that the fuel cell operates at 600 K instead of at room temperature.

13.45 A small air-cooled gasoline engine is tested, and the output is found to be 1.0 kW. The temperature of the products is measured and found to be 660 K. The products are analyzed on a dry volumetric basis, with the following results:

Product	*Percent by Volume*
CO_2	11.4
CO	2.9
O_2	1.6
N_2	84.1

The fuel may be considered to be liquid octane. The fuel and air enter the engine at 25°C, and the flow rate of the fuel to the engine is 0.000 15 kg/s. Determine

(a) The rate of heat transfer from the engine.

(b) The efficiency of the engine.

13.45E A small air-cooled gasoline engine is tested, and the output is found to be 2.0 hp. The temperature of the products is measured and found to be 730 F. The products are analyzed on a dry volumetric basis, with the following results:

Product	*Percent by Volume*
CO_2	11.4
CO	2.9
O_2	1.6
N_2	84.1

The fuel may be considered to be liquid octane. The fuel and air enter the engine at 77 F, and the flow rate of the fuel to the engine is 1.8 lbm/h. Determine

(a) The rate of heat transfer from the engine.

(b) The efficiency of the engine.

13.46 Consider the SSSF combustion of propane at 25°C with air at 400 K. The products exit the combustion chamber at 1200 K. It may be assumed that the combustion efficiency is 90 percent, and that 95 percent of the carbon in the propane burns to form carbon dioxide; the remaining 5 percent burns to form carbon monoxide. Determine

(a) The ideal fuel–air ratio.
(b) The heat transfer from the combustion chamber.

COMPUTER PROBLEMS

13.1C Write a program to solve the general case of Problem 13.3 for any hydrocarbon fuel C_aH_b, where a and b are input parameters. We wish to calculate the percentage of theoretical air for any given percentages of combustion products.

13.2C Write a program to solve the general case of Problem 13.6 for different proportions of the components listed and for different temperatures and pressures of the product gas, including water saturation.

13.3C Write a program to solve the general case of Problem 13.8 for different percentages of the components given in the ultimate analysis of the coal.

13.4C Write a program to solve the general case of Problem 13.11, in which the initial amounts of C and O_2, the final relative fractions of CO and CO_2, and the final temperature are all input parameters.

13.5C Write a program to solve the general case of the set of Problems 13.14, 13.15, and 13.16, in which the percentage of theoretical air and the product temperature and pressure are all input variables.

13.6C Write a program to solve the following problem. We wish to study the effect of the percentage of theoretical air on the adiabatic flame temperature for a (variable) hydrocarbon fuel. Assume that the fuel and air enter the combustion chamber at 25°C, and assume complete combustion. Use equations from Table A.10 to represent the specific heat of the various products of combustion.

13.7C Write a program to solve the general case of Problem 13.26, in which the compressor pressure ratio, the isentropic efficiency, and the adiabatic flame temperature are all input parameters.

13.8C Write a program to solve the general case of Problem 13.35, in which the percentage of theoretical air and the inlet and exit temperatures and pressures are all input variables.

13.9C Write a program to study the performance of the methane–oxygen fuel cell of Problem 13.44 as a function of temperature, for any value above ambient temperature.

14

INTRODUCTION TO PHASE AND CHEMICAL EQUILIBRIUM

Up to this point we have assumed that we dealt mostly with systems that are in equilibrium or with those whose deviation from equilibrium is infinitesimal, as in a quasi-equilibrium or reversible process. For irreversible processes we made no attempt to describe the state of the system during the process but dealt only with the initial and final states of the system, at which time we considered the system to be in equilibrium.

In this chapter we examine the criteria for equilibrium and from them derive certain relations that will enable us, under certain conditions, to determine the properties of a system when it is in equilibrium. The specific systems we will consider are those involving equilibrium between phases and those involving chemical equilibrium in a single phase (homogeneous equilibrium) as well as certain related topics.

14.1 REQUIREMENTS FOR EQUILIBRIUM

As a general requirement for a system's being in equilibrium, we postulate that there must be no possibility that the system can do any work when it is isolated from its surroundings. In applying this criterion to a system, we find it helpful to divide the system into two or more subsystems, and to consider the possibility of work being done by any conceivable interaction between these two subsystems. For example, in Fig. 14.1 a system has been divided into two systems and an engine, of any conceivable variety, placed between these subsystems. A system may be defined to include the immediate surroundings. Therefore, we can let the immediate surroundings be a subsystem and consider the general case of the equilibrium between a system and its surroundings.

The first requirement for equilibrium is that the two subsystems have the same temperature, for otherwise we could operate a heat engine between the two systems and do work. Thus, one requirement is that a system be at a uniform temperature to be in equilibrium. There must also be no unbalanced mechanical forces between the two systems, or a turbine or piston engine could operate between the two systems and do work.



FIGURE 14.1 Two subsystems that communicate through an engine.

However, we would like to establish general criteria for equilibrium that will apply to simple compressible systems, including those that undergo chemical reactions. We will find that the Gibbs function is a particularly significant property in defining the criteria for equilibrium.

Let us first consider a qualitative example to illustrate this point. Imagine a natural gas well that is 1 km deep, and assume that the temperature of the gas is constant throughout the gas well. Suppose we have analyzed the composition of the gas at the bottom of the well. Furthermore, let us assume that equilibrium conditions prevail in the well. If they do, we would expect an engine such as that shown in Fig. 14.2, which operates on the basis of the pressure and composition change with elevation (with no combustion), to be incapable of doing any work.

If we consider a steady-state, steady-flow process for a control volume around this engine, we could apply Eq. 9.59:

$$\dot{W}_{rev} = \dot{m}_i\left(g_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) - \dot{m}_e\left(g_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right)$$

However,

$$\dot{W}_{rev} = 0, \qquad \dot{m}_i = \dot{m}_e, \qquad \text{and} \qquad \frac{\mathbf{V}_i^2}{2} = \frac{\mathbf{V}_e^2}{2}$$

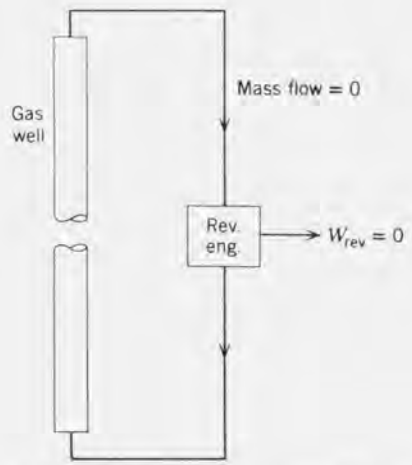


FIGURE 14.2 Illustration showing the relation between reversible work and the criteria for equilibrium.

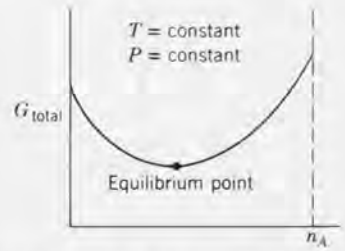


FIGURE 14.3 Illustration of the requirement for chemical equilibrium.

Then we can write

$$g_i + gZ_i = g_e + gZ_e$$

and the requirement for equilibrium in the well between two levels that are a distance dZ apart would be

$$dg_T + g\,dZ_T = 0$$

In contrast to a deep gas well, most of the systems that we consider are of such size that ΔZ is negligibly small, and therefore we consider the pressure in the system to be uniform.

This leads to the general statement of equilibrium that applies to simple compressible systems that may undergo a change in chemical composition, namely that at equilibrium,

$$dG_{T,P} = 0 \tag{14.1}$$

For a chemical reaction, it is helpful to think of the equilibrium state as the state in which the Gibbs function is a minimum. For example, consider a system consisting initially of n_A moles of substance A and n_B moles of substance B, which react in accordance with the relation

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$$

Let the reaction take place at constant pressure and temperature. If we plot G for this system as a function of n_A, the number of moles of A present, we would have the curve shown in Fig. 14.3. At the minimum point on the curve, $dG_{T,P} = 0$, and this will be the equilibrium composition for this system at the given temperature and pressure. The subject of chemical equilibrium will be developed further in Section 14.6.

14.2 EQUILIBRIUM BETWEEN TWO PHASES OF A PURE SUBSTANCE

As another example of this requirement for equilibrium, let us consider the equilibrium between two phases of a pure substance. Consider a system consisting of two phases of a pure substance at equilibrium. We know that under these conditions the two phases are at the same pressure and temperature. Consider the change of

state associated with a transfer of dn moles from phase 1 to phase 2 while the temperature and pressure remain constant. That is,

$$dn^1 = -dn^2$$

The Gibbs function of this system is given by

$$G = f(T, P, n^1, n^2)$$

where n^1 and n^2 designate the number of moles in each phase. Therefore,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n^1,n^2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n^1,n^2} dP + \left(\frac{\partial G}{\partial n^1}\right)_{T,P,n^2} dn^1 + \left(\frac{\partial G}{\partial n^2}\right)_{T,P,n^1} dn^2$$

By definition,

$$\left(\frac{\partial G}{\partial n^1}\right)_{T,P,n^2} = \bar{g}^1, \qquad \left(\frac{\partial G}{\partial n^2}\right)_{T,P,n^1} = \bar{g}^2$$

Therefore, at constant temperature and pressure,

$$dG = \bar{g}^1\, dn^1 + \bar{g}^2\, dn^2 = dn^1(\bar{g}^1 - \bar{g}^2)$$

Now at equilibrium (Eq. 14.1)

$$dG_{T,P} = 0$$

Therefore, at equilibrium, we have

$$\bar{g}^1 = \bar{g}^2 \tag{14.2}$$

That is, under equilibrium conditions, the Gibbs function of each phase of a pure substance is equal. Let us check this by determining the Gibbs function of saturated liquid (water) and saturated vapor (steam) at 300 kPa. From the steam tables,

For the liquid:

$$g_f = h_f - Ts_f = 561.47 - 406.7 \times 1.6718 = -118.4 \text{ kJ/kg}$$

For the vapor:

$$g_g = h_g - Ts_g = 2725.3 - 406.7 \times 6.9919 = -118.4 \text{ kJ/kg}$$

Equation 14.2 can also be derived by applying the relation

$$T\, ds = dh - v\, dP$$

to the change of phase that takes place at constant pressure and temperature. For this process this relation can be integrated as

$$\int_f^g T\, ds = \int_f^g dh$$
$$T(s_g - s_f) = (h_g - h_f)$$
$$h_f - Ts_f = h_g - Ts_g$$
$$g_f = g_g$$

The Clapeyron equation, which was derived in Section 12.4, can be derived by an alternate method. We begin by recalling that the Gibbs functions of two phases

in equilibrium are equal. In Chapter 12 we considered the relation (Eq. 12.9) for a simple compressible substance:

$$dg = v\,dP - s\,dT$$

Let us take a system that consists of a saturated liquid and a saturated vapor in equilibrium, and let this system undergo a change of pressure dP. The corresponding change in temperature, as determined from the vapor–pressure curve, is dT. Both phases will undergo the change in Gibbs function, dg, but since the phases always have the same value of the Gibbs function when they are in equilibrium, it follows that

$$dg_f = dg_g$$

But, from Eq. 12.9,

$$dg = v\,dP - s\,dT$$

it follows that

$$dg_f = v_f\,dP - s_f\,dT$$
$$dg_g = v_g\,dP - s_g\,dT$$

Since

$$dg_f = dg_g$$

it follows that

$$\begin{aligned} v_f\,dP - s_f\,dT &= v_g\,dP - s_g\,dT \\ dP(v_g - v_f) &= dT(s_g - s_f) \\ \frac{dP}{dT} &= \frac{s_{fg}}{v_{fg}} = \frac{h_{fg}}{Tv_{fg}} \end{aligned} \tag{14.3}$$

In summary, when different phases of a pure substance are in equilibrium, each phase has the same value of the Gibbs function per unit mass. This fact is relevant to different solid phases of a pure substance and is important in metallurgical applications of thermodynamics. Example 14.1 illustrates this principle.

EXAMPLE 14.1

How much pressure is required to make diamonds from graphite at a temperature of 25°C? The following data are given for a temperature of 25°C and a pressure of 0.1 MPa.

Property	*Graphite*	*Diamond*
$\bar{g}$	0	2867.8 kJ/kmol
v	0.000 444 m^3/kg	0.000 284 m^3/kg
β_T	0.304×10^{-6} 1/MPa	0.016×10^{-6} 1/MPa

Analysis and Solution

The basic principle in the solution is that graphite and diamond can exist in equilibrium when they have the same value of the Gibbs function. At 0.1-MPa

pressure the Gibbs function of the diamond is greater than that of the graphite. However, the rate of increase in Gibbs function with pressure is greater for the graphite than for the diamond and, therefore, at some pressure they can exist in equilibrium. Our problem is to find this pressure.

We have already considered the relation

$$dg = v\,dP - s\,dT$$

Because the process takes place at constant temperature, this reduces to

$$dg_T = v\,dP_T \tag{a}$$

Now at any pressure P and the given temperature, the specific volume can be found from the following relation, which utilizes the isothermal compressibility factor.

$$\begin{aligned} v &= v^\circ + \int_{P=0.1}^{P} \left(\frac{\partial v}{\partial P}\right)_T dP = v^\circ + \int_{P=0.1}^{P} \frac{v}{v}\left(\frac{\partial v}{\partial P}\right)_T dP \\ &= v^\circ - \int_{P=0.1}^{P} v\beta_T\,dP \end{aligned} \tag{b}$$

The superscript $^\circ$ used in this example indicates that the properties are at a pressure of 0.1 MPa and a temperature of 25°C.

The specific volume changes only slightly with pressure, so that $v \approx v^\circ$. In addition, we assume that β_T is constant and that we are considering a very high pressure. With these assumptions this equation can be integrated to give

$$v = v^\circ - v^\circ\beta_T P = v^\circ(1 - \beta_T P) \tag{c}$$

We can now substitute this into Eq. a to give the relation

$$\begin{aligned} dg_T &= [v^\circ(1 - \beta_T P)]\,dP_T \\ g - g^\circ &= v^\circ(P - P^\circ) - v^\circ\beta_T \frac{(P^2 - P^{\circ 2})}{2} \end{aligned} \tag{d}$$

If we assume that $P^\circ \ll P$, this reduces to

$$g - g^\circ = v^\circ\left(P - \frac{\beta_T P^2}{2}\right) \tag{e}$$

For the graphite, $g^\circ = 0$ and we can write

$$g_G = v_G^\circ\left[P - (\beta_T)_G \frac{P^2}{2}\right]$$

For the diamond, g° has a definite value and we have

$$g_D = g_D^\circ + v_D^\circ\left[P - (\beta_T)_D \frac{P^2}{2}\right]$$

But, at equilibrium the Gibbs function of the graphite and diamond are equal.

$$g_G = g_D$$

Therefore,

$$v_G^\circ\left[P - (\beta_T)_G \frac{P^2}{2}\right] = g_D^\circ + v_D^\circ\left[P - (\beta_T)_D \frac{P^2}{2}\right]$$

$$(v_G^\circ - v_D^\circ)P - [v_G^\circ(\beta_T)_G - v_D^\circ(\beta_T)_D]\frac{P^2}{2} = g_D^\circ$$

$$(0.000\,444 - 0.000\,284)P$$

$$- (0.000\,444 \times 0.304 \times 10^{-6} - 0.000\,284 \times 0.016 \times 10^{-6})\frac{P^2}{2} = \frac{2867.8}{12.011 \times 1000}$$

Solving this for P, we find

$$P = 1493 \text{ MPa}$$

That is, at 1493 MPa, 25°C, graphite and diamond can exist in equilibrium, and the possibility exists for conversion from graphite to diamonds.

The preceding example could also have evaluated the two forms of carbon in terms of the fugacities instead of the Gibbs functions. Similarly, the equilibrium requirement for liquid and vapor water discussed earlier could be expressed in terms of the fugacities of the two phases. That is,

$$f^L = f^V = f^{\text{sat}}$$

where f^{sat} is the fugacity of the substance determined at the given temperature and its saturation pressure P^{sat}.

The fugacity of a pure compressed-liquid or solid phase at pressures moderately greater than the saturation pressure can be calculated with considerable accuracy. For a pure substance at constant temperature,

$$dg_T = RT(d \ln f)_T = v\, dP_T$$

Integrating at constant temperature between the saturation state and the pressure P, we have

$$\int_{f^{\text{sat}}}^{f} RT(d \ln f)_T = \int_{P^{\text{sat}}}^{P} v\, dP_T$$

$$RT \ln \frac{f}{f^{\text{sat}}} = \int_{P^{\text{sat}}}^{P} v\, dP_T$$

If we assume that v is a constant, which often holds with considerable accuracy for liquids and solids, we have

$$RT \ln \frac{f}{f^{\text{sat}}} \approx v(P - P^{\text{sat}}) \tag{14.4}$$

Equation 14.4 determines the fugacity coefficients of compressed liquid presented in the generalized chart given in Fig. A.10.

Since v is small for the liquid and solid phases, the quantity $v(P - P^{sat})$ is small for moderate changes of pressure. Therefore, for liquids and solids at moderate pressures, we conclude that

$$f^L \approx f^{sat} \quad \text{and} \quad f^S \approx f^{sat} \tag{14.5}$$

14.3 EQUILIBRIUM OF A MULTICOMPONENT, MULTIPHASE SYSTEM

As an introduction to an analysis of equilibrium in multicomponent, multiphase systems, let us consider a system consisting of two components and two phases. To show the general characteristics of such a system, let us take a mixture of oxygen and nitrogen at a pressure of 0.1 MPa and in the range of temperature in which both the liquid and vapor phases are present.

Figure 14.4 shows the composition of the liquid and vapor phases that are in equilibrium as a function of temperature at a pressure of 0.1 MPa. The upper line, marked "vapor line," gives the composition of the vapor phase, and the lower line gives the composition of the liquid phase. If we have pure nitrogen, the boiling point is 77.3 K. If we have pure oxygen, the boiling point is 90.2 K. If we have a mixture of nitrogen and oxygen with both phases present at a temperature of 84 K, the vapor has a composition of 64 percent nitrogen and 36 percent oxygen. The liquid has a composition of 30 percent nitrogen and 70 percent oxygen.

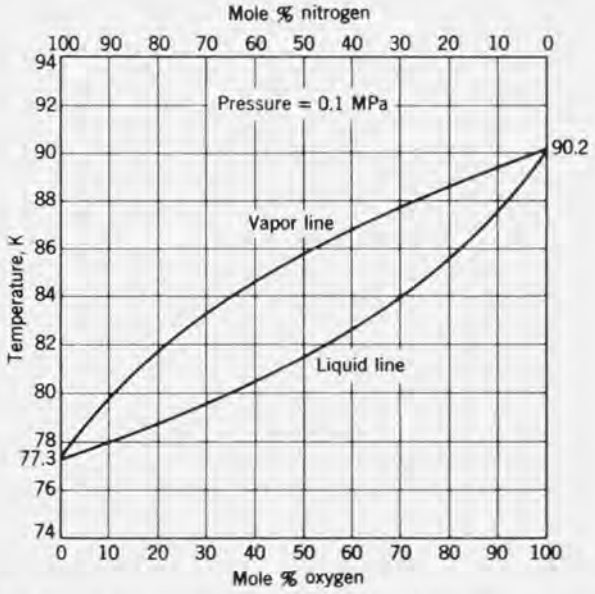


FIGURE 14.4 *Equilibrium diagram for liquid-vapor phases of the nitrogen-oxygen system at a pressure of 0.1 MPa.*

Consider a mixture that consists of 21 percent oxygen and 79 percent nitrogen (approximately the composition of air) at a pressure of 0.1 MPa and an initial temperature of 74 K. At this state the mixture is in the liquid phase. Let this liquid be slowly heated while the pressure remains constant. By referring to Fig. 14.4, we note that when the temperature reaches 78.8 K, the first bubble forms. This vapor will have a composition of approximately 6 percent oxygen and 94 percent nitrogen. As more heat is added, the temperature increases and the mole fraction of oxygen in the liquid increases. When the last drop of liquid remains, the vapor will have a composition of 21 percent oxygen and 79 percent nitrogen, the temperature will be 81.9 K, and the liquid composition will be 54 percent oxygen and 46 percent nitrogen.

A brief discussion of the more general phase diagram may help us understand the phase behavior of a system such as described here. We recall that the phase behavior for a pure substance is dictated by the saturation line on P–T coordinates, such as in Fig. 3.2. For a two-component system A and B, overall composition is now an additional independent property, and phase behavior is represented in terms of surfaces on a pressure–composition–temperature diagram, as shown in Fig. 14.5*a*. This diagram includes three constant-temperature planes to indicate that there is a lower vapor surface and an upper liquid surface, and together they form an equilibrium envelope between the two pure-substance saturation lines. Only within this envelope is it possible for two phases to be present in equilibrium. Beneath the envelope the two-component system is all superheated vapor, and above the envelope the system is all compressed liquid.

We realize now that a constant-pressure plane (at 0.1 MPa) of the three-dimensional phase diagram, as viewed from above, projects as the temperature–composition diagram, Fig. 14.4, discussed in some detail previously. The other two projections of such a diagram are shown in Figs. 14.5*b* and *c*.

While studying the characteristics of such a two-component system, we must ask the question, "What is the requirement for phase equilibrium in this system?" We can proceed in a manner analogous to that followed in Section 14.2 for a pure substance. Superscripts 1 and 2 denote the two phases, and subscripts A and B refer to the two components. It follows from applying Eq. 12.24 to each phase that

$$\begin{aligned} dG^1 &= -S^1\,dT + V^1\,dP + \mu_A^1\,dn_A^1 + \mu_B^1\,dn_B^1 \\ dG^2 &= -S^2\,dT + V^2\,dP + \mu_A^2\,dn_A^2 + \mu_B^2\,dn_B^2 \end{aligned} \tag{14.6}$$

Let us consider this two-phase, two-component mixture that is in equilibrium as a system, and let each phase be considered a subsystem. One possible change of state might be the transfer of a very small amount of component A to be transferred from phase 1 to phase 2 while the moles of B in each phase, the temperature, and the pressure remain constant. This is shown schematically in Fig. 14.6.

For this change of state

$$dn_A^2 = -dn_A^1 \tag{14.7}$$

Since this system is in equilibrium, $dG = 0$. Therefore,

$$dG = dG^1 + dG^2 = 0 \tag{14.8}$$

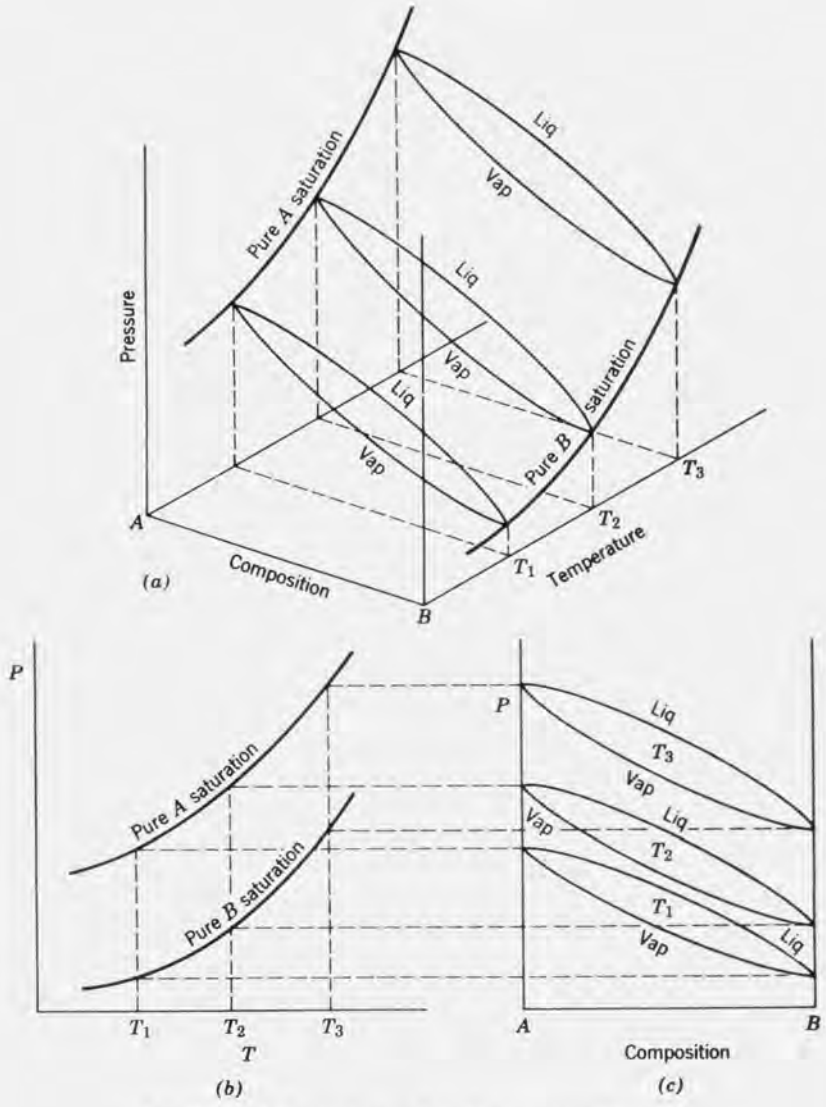


FIGURE 14.5 Phase diagram for a two-component system.

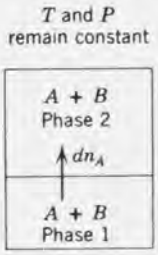


FIGURE 14.6 An equilibrium mixture involving two components and two phases.

Since T, P, n_B^1, and n_B^2 are all constant, it follows from Eqs. 14.6 and 14.8 that

$$\begin{aligned} dG &= \mu_A^1\, dn_A^1 + \mu_A^2\, dn_A^2 \\ &= \mu_A^1\, dn_A^1 - \mu_A^2\, dn_A^1 = dn_A^1(\mu_A^1 - \mu_A^2) \\ &= 0 \end{aligned}$$

Therefore, at equilibrium

$$\mu_A^1 = \mu_A^2 \tag{14.9}$$

Thus, the requirement of equilibrium is that the chemical potential of each component be the same in all phases. If the chemical potential is not the same in all phases, there is a tendency for mass to pass from one phase to the other. When the chemical potential of a component is the same in both phases, there is no tendency for a net transfer of mass from one phase to the other.

This requirement for equilibrium is readily extended to multicomponent, multiphase systems, for the chemical potential of each component must be the same in all phases.

$$\begin{aligned} &\mu_A^1 = \mu_A^2 = \mu_A^3 = \cdots \text{ for all phases} \\ &\mu_B^1 = \mu_B^2 = \mu_B^3 = \cdots \text{ for all phases} \\ &\quad\cdots \\ &\quad\cdots \\ &\quad\cdots \\ &\quad\cdots \\ &\text{for all components} \end{aligned} \tag{14.10}$$

The next question we might ask is whether we can predict the equilibrium composition of a two-phase mixture from the known properties of the pure substances that make up the mixture. Although we cannot do this in general, fairly accurate procedures have been developed for two-phase mixtures at moderate pressures. These procedures involve the use of Raoult's rule, which will be developed in the next few paragraphs by stating the simplifying assumptions on which it is based.

We found in Section 12.3, Eq. 12.25, that the chemical potential of component A is identical to the partial Gibbs function $\overline{G}_A$ of that component in the mixture. Thus, the requirement for equilibrium, Eq. 14.9, can also be expressed as

$$\overline{G}_A^1 = \overline{G}_A^2 \tag{14.11}$$

in which form the result is analogous to that for the phase equilibrium of a pure substance, Eq. 14.2. It also follows from the definition of fugacity, Eq. 12.72, that the fugacity of a component in a mixture can similarly be defined in terms of its partial Gibbs function as

$$(d\overline{G}_A)_T = \overline{R}T\, d(\ln \overline{f}_A)_T \tag{14.12}$$

with the requirement that

$$\lim_{P \to 0} (\overline{f}_A / y_A P) = 1 \tag{14.13}$$

As a result, the requirement for phase equilibrium, Eq. 14.9, can be expressed in terms of fugacity as

$$\bar{f}_A^1 = \bar{f}_A^2 \tag{14.14}$$

That is, at equilibrium the fugacity of a given component is the same in each phase. This statement is perhaps the most useful formulation of the requirement for equilibrium between phases at a given temperature and pressure for we have previous experience in evaluating fugacities. However, we have not had the occasion to examine the fugacity of a component in a mixture. Therefore, to utilize this result, we need to develop a specific model for determining the fugacities of components in a mixture.

In this text, we will consider only one simple model for phase equilibrium, which will be discussed in terms of a two-component, liquid–vapor system. The requirement for equilibrium at temperature T and pressure P is

$$\begin{aligned} \bar{f}_A^L &= \bar{f}_A^V \\ \bar{f}_B^L &= \bar{f}_B^V \end{aligned} \tag{14.15}$$

Let us first examine the behavior of the liquid phase, in which we denote molal composition by the symbol, x_A, to distinguish it from the vapor phase composition, y_A. Our liquid model requires three separate assumptions.

1. The fugacity of a component A in the liquid can be expressed as the product of its mole fraction and the fugacity of the pure liquid A at the same pressure and temperature as the system, or

$$\bar{f}_A^L = x_A f_A^L \tag{14.16}$$

This is termed the Lewis–Randall rule, and is derived from general thermodynamic considerations of mixtures by assuming that there is no volume change on mixing two substances at constant T and P. This assumption has been closely verified experimentally for many simple systems at low pressures.

2. The fugacity of pure liquid A at T and P of the system is equal to the fugacity of saturated A (liquid or vapor) at the same T and its corresponding saturation pressure P_A^{sat}, or

$$f_A^L = f_A^{\text{sat}} \tag{14.17}$$

This is equivalent to assuming that the $\int v\, dP$ correction of Eq. 14.4 is negligibly small.

3. Pure saturated vapor A at T and P_A^{sat} behaves as an ideal gas, or

$$f_A^{\text{sat}} = P_A^{\text{sat}} \tag{14.18}$$

Combining these assumptions, Eqs. 14.16 through 14.18, we obtain

$$\bar{f}_A^L = x_A P_A^{\text{sat}} \tag{14.19}$$

which is commonly termed Raoult's rule.

We next examine the behavior of the equilibrium vapor phase, which we assume to behave as a mixture of ideal gases. From Eq. 14.13, it follows that

$$\bar{f}_A^V = y_A P \tag{14.20}$$

Now, substituting Eqs. 14.19 and 14.20 for each component into Eqs. 14.15, we obtain a set of equations for the Raoult's rule–ideal gas model,

$$x_A P_A^{\text{sat}} = y_A P \tag{14.21}$$

$$x_B P_B^{\text{sat}} = y_B P \tag{14.22}$$

which together with

$$x_A + x_B = 1 \tag{14.23}$$

$$y_A + y_B = 1 \tag{14.24}$$

forms a set of four equations in four unknowns at a given T and P (P_A^{sat} and P_B^{sat} depend only on T). This set of equations can then be solved to determine the equilibrium compositions in each phase.

The assumptions made in developing this model for phase equilibrium are clearly dependent on pressure and are not suitable for high-pressure or complex systems. However, the model has been found to give reasonable predictions for the behavior of many simple systems at low pressures.

EXAMPLE 14.2

Air (assumed to be 21 percent oxygen, 79 percent nitrogen) is cooled to 80 K, 0.1-MPa pressure. Calculate the composition of the liquid and vapor phases at this condition, assuming the Raoult's rule–ideal gas model. Compare the results with Fig. 14.4. At 80 K,

$$P_{N_2}^{\text{sat}} = 0.1370 \text{ MPa}, \qquad P_{O_2}^{\text{sat}} = 0.030\,06 \text{ MPa}$$

Analysis and Solution

For convenience, let $N_2 = A$ and $O_2 = B$ in the calculations. Using Eqs. 14.21 and 14.22, we have

$$x_A P_A^{\text{sat}} = y_A P$$

$$x_B P_B^{\text{sat}} = y_B P$$

Therefore, at 80 K, 0.1-MPa pressure,

$$x_A(0.137) = y_A(0.1)$$

$$x_B(0.030\,06) = y_B(0.1)$$

But

$$x_A + x_B = 1$$

$$y_A + y_B = 1$$

Substituting for y_A, y_B in the last equation gives

$$\frac{0.137}{0.1}x_A + \frac{0.030\,60}{0.1}x_B = 1.37x_A + 0.3006(1 - x_A) = 1$$

$$x_A = 0.654, \qquad y_A = 0.896$$

From Fig. 14.4, which is based on experimental data, we find that at 80 K, 0.1 MPa,

$$x_A = 0.66, \qquad y_A = 0.89$$

Thus, we conclude that for this system at this temperature and pressure, Raoult's rule gives quite accurate results.

14.4 THE GIBBS PHASE RULE (WITHOUT CHEMICAL REACTION)

The Gibbs phase rule, which was derived by Professor Josiah Willard Gibbs of Yale University in 1875, ranks among the truly significant contributions to physical science. In this section we consider the Gibbs phase rule for a system that does not involve a chemical reaction. For such a system the Gibbs phase rule is

$$\mathscr{P} + \mathscr{V} = \mathscr{C} + 2 \tag{14.25}$$

where $\mathscr{P}$ is the number of phases present. $\mathscr{V}$ is the variance, and $\mathscr{C}$ is the number of components present. The term variance designates the number of intensive properties that must be specified to fix the state of the system completely. For example, in Example 14.2 we considered a two-phase mixture of oxygen and nitrogen. For this system the number of phases $\mathscr{P}$ equals 2, the number of components $\mathscr{C}$ is 2, and therefore the variance $\mathscr{V}$ is 2. This is evident from Fig. 14.4, for this diagram is for a fixed pressure (0.1 MPa), and the fixing of one additional intensive property, such as temperature, mole fraction of a given component in the liquid phase, or mole fraction of a given component in the vapor phase, will completely determine all other intensive properties and thus fix the state of the system (although not the relative amounts of the two phases).

Let us consider further the application of the Gibbs phase rule to a pure substance. In this case $\mathscr{C} = 1$. When we have one phase present, such as superheated vapor, $\mathscr{P} = 1$, and we conclude that $\mathscr{V} = \mathscr{C} + 2 - 1 = 2$. That is, two intensive properties must be specified to fix the state. We are already familiar with the superheated-vapor tables for a number of substances and recognize that these tables are presented with pressure and temperature as the two independent properties. Such a system is referred to as a bivariant system.

Suppose we have two phases of a pure substance in equilibrium, such as saturated liquid and saturated vapor. In this case $\mathscr{C} = 1$, $\mathscr{P} = 2$, and $\mathscr{V} = 1 + 2 - 2 = 1$. That is, one intensive property fixes the value of all other intensive properties and thus determines the state of each phase. Again, from our familiarity with tables of thermodynamic properties, we recall that either pressure or temperature is used as the independent intensive property for tabulating liquid–vapor equilibrium data for a pure substance. Such a system is known as monovariant.

Consider also the triple point of a pure substance. In this case $\mathscr{C} = 1$ and $\mathscr{P} = 3$. Therefore, $\mathscr{V} = 1 + 2 - 3 = 0$. That is, at the triple point all intensive properties are fixed, and if any intensive property is varied, we are no longer at the triple point. This is known as an invariant system.

It might be well at this point to emphasize again that a pure substance can have several phases in the solid state. For example, Fig. 3.6 shows the various phases of water. Note that there are several states at which three phases exist in equilibrium, and each of these states is a triple point.

The application of the phase rule to a two-component, two-phase system has already been made. As a final application let us consider a two-component, three-phase system. For such a system, $\mathscr{V} = 2 + 2 - 3 = 1$. That is, it is a monovariant system, and specifying one property, such as pressure or temperature, fixes the state of the system.

The validity of the Gibbs phase rule can be outlined by considering a system that consists of $\mathscr{C}$ components and $\mathscr{P}$ phases in equilibrium at a given temperature and pressure. Assuming that each component exists in each phase, the state of the system could be completely specified if the concentration of each component in each phase and the temperature and pressure were specified. This would be a total of $\mathscr{C}\mathscr{P} + 2$ intensive properties.

We know, however, that these are not all independent intensive properties. If we determine the number of equations we have between these intensive properties, we can subtract this from the $\mathscr{C}\mathscr{P} + 2$ intensive properties and find the number of independent intensive properties or, as it has been defined, the variance. The fact that at equilibrium the chemical potential of each component is the same in all phases gives rise to a total of $\mathscr{C}(\mathscr{P} - 1)$ equations between the intensive properties of the mixture.

Furthermore, the fact that the sum of the mole fractions equals unity in each of the $\mathscr{P}$ phases gives $\mathscr{P}$ additional equations. Therefore, the variance is

$$\mathscr{V} = \mathscr{C}\mathscr{P} + 2 - \mathscr{P} - \mathscr{C}(\mathscr{P} - 1) = \mathscr{C} + 2 - \mathscr{P}$$

14.5 METASTABLE EQUILIBRIUM

Although the limited scope of this book precludes an extensive treatment of metastable equilibrium, a brief introduction to the subject is presented here. Let us first consider an example of metastable equilibrium.

A slightly superheated vapor, such as steam, is expanding in a convergent–divergent nozzle, as shown in Fig. 14.7. Assuming the process is reversible and adiabatic, the steam will follow path 1–a on the T–s diagram, and at point a we would expect condensation to occur. However, if point a is reached in the divergent section of the nozzle, no condensation occurs until point b is reached, and at this point the condensation occurs very abruptly in what is referred to as a condensation shock. Between points a and b the steam exists as a vapor, but the temperature is below the saturation temperature for the given pressure. This is known as a metastable state. The possibility of a metastable state exists with any phase transformation. The dotted lines on the equilibrium diagram shown in Fig. 14.8 represent possible metastable states for solid–liquid–vapor equilibrium.

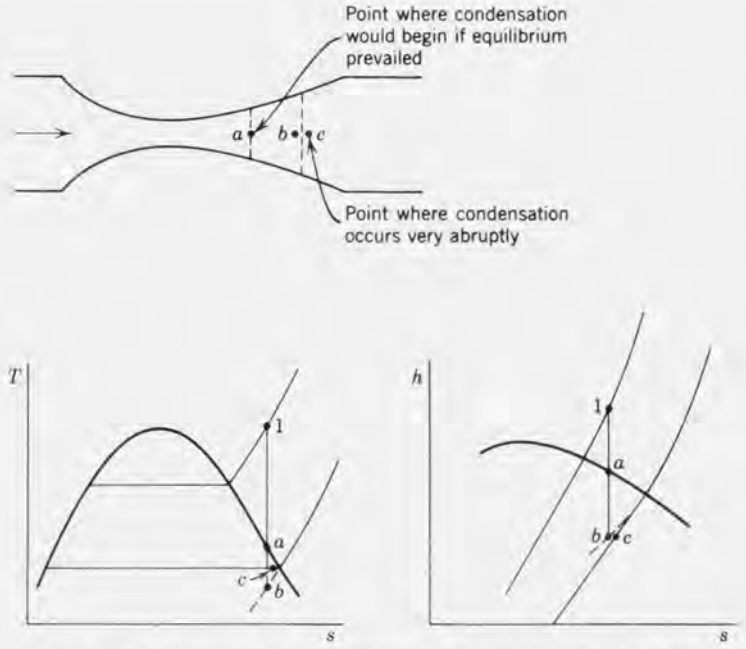


FIGURE 14.7 Illustration of the phenomenon of supersaturation in a nozzle.

The nature of a metastable state is often pictured schematically by the kind of diagram shown in Fig. 14.9. The ball is in a stable position (the "metastable state") for small displacements, but with a large displacement it moves to a new equilibrium position. The steam expanding in the nozzle is in a metastable state between *a* and *b*. This means that droplets smaller than a certain critical size will reevaporate, and only when droplets of larger than this critical size have formed (this corresponds to moving the ball out of the depression) will the new equilibrium state appear.

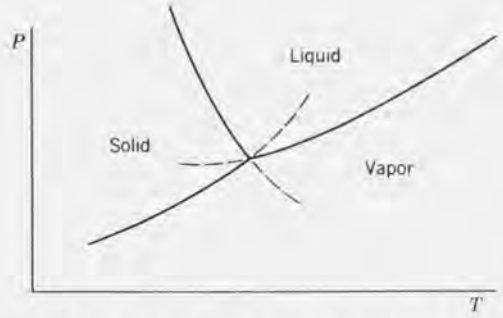


FIGURE 14.8 Metastable states for solid–liquid–vapor equilibrium

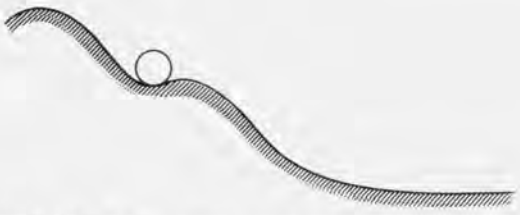


FIGURE 14.9 Schematic diagram illustrating a metastable state.

14.6 CHEMICAL EQUILIBRIUM

We now turn our attention to chemical equilibrium and consider a chemical reaction having only one phase. This is referred to as a homogeneous chemical reaction. It may be helpful to visualize this as a gaseous phase, but the basic considerations apply to any phase.

Consider a vessel, Fig. 14.10, that contains four compounds, A, B, C, and D, which are in chemical equilibrium at a given pressure and temperature. For example, these compounds might consist of CO_2, H_2, CO, and H_2O in equilibrium. Let the number of moles of each component be designated n_A, n_B, n_C, and n_D. Further, let the chemical reaction that takes place between these four constituents be

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \tag{14.26}$$

where the ν's are the stoichiometric coefficients. It should be emphasized that there is a very definite relation between the ν's (the stoichiometric coefficients), but the n's (the number of moles present) for any constituent can be varied simply by varying the amount of that component in the reaction vessel.

Let us now consider how the requirement for equilibrium, namely that $dG_{T,P} = 0$ at equilibrium, applies to a homogeneous chemical reaction. When we considered phase equilibrium (Section 14.3), we assumed that the two phases were in equilibrium at a given temperature and pressure, and then let a small quantity of one component be transferred from one phase to the other. In a similar manner, let us assume that the four components are in chemical equilibrium and that from this equilibrium state, while the temperature and pressure remain constant, the reaction proceeds an infinitesimal amount toward the right as Eq. 14.26 is written. This action decreases the moles of A and B and increases the moles of C and D.

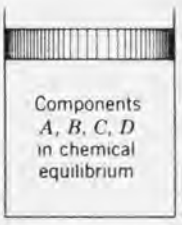


FIGURE 14.10 Schematic diagram for consideration of chemical equilibrium.

Let us designate the degree of reaction by ϵ, and define the degree of reaction by the relations

$$\begin{aligned} dn_A &= -\nu_A\, d\epsilon \\ dn_B &= -\nu_B\, d\epsilon \\ dn_C &= +\nu_C\, d\epsilon \\ dn_D &= +\nu_D\, d\epsilon \end{aligned} \tag{14.27}$$

That is, the change in the number of moles of any component during a chemical reaction is given by the product of the stoichiometric coefficients (the ν's) and the degree of reaction.

Let us evaluate the change in the Gibbs function associated with this chemical reaction that proceeds to the right in the amount $d\epsilon$. In doing so, we use, as would be expected, the Gibbs function of each component in the mixture—the partial molal Gibbs function (or its equivalent, the chemical potential).

$$dG_{T,P} = \overline{G}_C\, dn_C + \overline{G}_D\, dn_D + \overline{G}_A\, dn_A + \overline{G}_B\, dn_B$$

Substituting Eq. 14.27, we have

$$dG_{T,P} = (\nu_C\overline{G}_C + \nu_D\overline{G}_D - \nu_A\overline{G}_A - \nu_B\overline{G}_B)\, d\epsilon \tag{14.28}$$

At this point, we need to be able to express $\overline{G}_i$ for each component in terms of properties that can be readily evaluated. In this text we consider chemical equilibrium for mixtures of ideal gases only. For this circumstance, and using as a reference state the standard-state pressure P° and the same temperature as that of the mixture, we have

$$\begin{aligned} \overline{G}_i &= \overline{H}_i - T\overline{S}_i \\ &= \overline{h}_i^\circ - T\overline{s}_i^\circ + \overline{R}T\ln\frac{y_iP}{P^\circ} \\ &= \overline{g}_i^\circ + \overline{R}T\ln\frac{y_iP}{P^\circ} \end{aligned} \tag{14.29}$$

That is, the partial Gibbs function of each component in the mixture (at T and P) is expressed in terms of the standard-state Gibbs function for the pure substance (at T and P°) plus a function of P, y_i, and T. Substituting this relation into Eq. 14.28, we have

$$\begin{aligned} dG_{T,P} = \Bigg[&\nu_C\left(\overline{g}_C^\circ + \overline{R}T\ln\frac{y_CP}{P^\circ}\right) + \nu_D\left(\overline{g}_D^\circ + \overline{R}T\ln\frac{y_DP}{P^\circ}\right) \\ &- \nu_A\left(\overline{g}_A^\circ + \overline{R}T\ln\frac{y_AP}{P^\circ}\right) - \nu_B\left(\overline{g}_B^\circ + \overline{R}T\ln\frac{y_BP}{P^\circ}\right)\Bigg]\, d\epsilon \end{aligned} \tag{14.30}$$

Let us define ΔG° as:

$$\Delta G^\circ = \nu_C\overline{g}_C^\circ + \nu_D\overline{g}_D^\circ - \nu_A\overline{g}_A^\circ - \nu_B\overline{g}_B^\circ \tag{14.31}$$

That is, ΔG° is the change in the Gibbs function that would occur if the chemical reaction given by Eq. 14.26 (which involves the stoichiometric amounts of each component) proceeded completely from left to right, with the reactants A and B

initially separated and each at temperature T and the standard-state pressure, and the products C and D finally separated and each at temperature T and the standard-state pressure. Note also that ΔG° for a given reaction is a function of only the temperature. This observation will be very important to bear in mind as we proceed with our developments of homogeneous chemical equilibrium.

Let us now digress from our development to consider an example in which ΔG° is calculated.

EXAMPLE 14.3

Determine the value of ΔG° for the reaction $2H_2O \rightleftharpoons 2H_2 + O_2$ at 298 K and at 2000 K with the water in the gaseous phase.

Solution

We take 0.1 MPa as our standard-state pressure, and recall that $\bar{g}$ for all the elements is assumed to be zero at 0.1-MPa pressure and 298 K. Therefore, at 298 K,

$$(\bar{g}_f^\circ)_{H_2} = 0, \qquad (\bar{g}_f^\circ)_{O_2} = 0$$

From Table A.15, at 298 K,

$$(\bar{g}_f^\circ)_{H_2O} = -228\,582 \text{ kJ/kmol}$$

$$\Delta G^\circ = 2(\bar{g}_f^\circ)_{H_2} + (\bar{g}_f^\circ)_{O_2} - 2(\bar{g}_f^\circ)_{H_2O}$$

$$= 0 + 0 - 2(-228\,582) = 457\,164 \text{ kJ}$$

At 2000 K, from Table A.12,

$$\bar{g}_{H_2}^\circ = \bar{g}_{2000}^\circ - \bar{g}_{298}^\circ = (\bar{h}_{2000}^\circ - \bar{h}_{298}^\circ) - (2000\bar{s}_{2000}^\circ - 298.15\bar{s}_{298}^\circ)$$

$$= 52\,942 - (2000 \times 188.419 - 298.15 \times 130.678)$$

$$= -284\,934 \text{ kJ/kmol}$$

Similarly, for the oxygen at 2000 K,

$$\bar{g}_{O_2}^\circ = (\bar{h}_{2000}^\circ - \bar{h}_{298}^\circ) - (2000\bar{s}_{2000}^\circ - 298.15\bar{s}_{298}^\circ)$$

$$= 59\,176 - (2000 \times 268.748 - 298.15 \times 205.148)$$

$$= -417\,155 \text{ kJ/kmol}$$

For the water,

$$\bar{g}_{H_2O}^\circ = \bar{g}_f^\circ + \bar{g}_{2000}^\circ - \bar{g}_{298}^\circ$$

$$= -228\,582 + 72\,788 - (2000 \times 264.769 - 298.15 \times 188.835)$$

$$= -629\,031 \text{ kJ/kmol}$$

Therefore, at 2000 K,

$$\Delta G^\circ = 2(-284\,934) + (-417\,155) - 2(-629\,031) = 271\,039 \text{ kJ}$$

The value for ΔG° at 2000 K can alternately be evaluated by using the fact that at constant T,

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$

At 2000 K,

$$\begin{aligned}\Delta H^\circ &= 2(\bar{h}^\circ_{2000} - \bar{h}^\circ_{298})_{H_2} + (\bar{h}^\circ_{2000} - \bar{h}^\circ_{298})_{O_2} - 2(\bar{h}^\circ_f + \bar{h}^\circ_{2000} - \bar{h}^\circ_{298})_{H_2O} \\ &= 2(52\,942) + (59\,176) - 2(-241\,826 + 72\,788) \\ &= 503\,136 \text{ kJ} \\ \Delta S^\circ &= 2(\bar{s}^\circ_{2000})_{H_2} + (\bar{s}^\circ_{2000})_{O_2} - 2(\bar{s}^\circ_{2000})_{H_2O} \\ &= 2(188.419) + (268.748) - 2(264.769) \\ &= 116.048 \text{ kJ/K}\end{aligned}$$

Therefore,

$$\Delta G^\circ = 503\,136 - 2000 \times 116.048 = 271\,040 \text{ kJ}$$

Note that although the two methods are identical in result, the second method requires fewer calculations and is therefore simpler to use.

Returning now to our development, substituting Eq. 14.31 into Eq. 14.30, and rearranging, we can write

$$dG_{T,P} = \left\{ \Delta G^\circ + \bar{R}T \ln \left[\frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_A} y_B^{\nu_B}} \left(\frac{P}{P^\circ} \right)^{\nu_C + \nu_D - \nu_A - \nu_B} \right] \right\} d\epsilon \tag{14.32}$$

At equilibrium $dG_{T,P} = 0$. Therefore, since $d\epsilon$ is arbitrary,

$$\ln \left[\frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_A} y_B^{\nu_B}} \left(\frac{P}{P^\circ} \right)^{\nu_C + \nu_D - \nu_A - \nu_B} \right] = -\frac{\Delta G^\circ}{\bar{R}T} \tag{14.33}$$

For convenience, we define the equilibrium constant K as

$$\ln K = -\frac{\Delta G^\circ}{\bar{R}T} \tag{14.34}$$

which we note must be a function of temperature only for a given reaction, since ΔG° is given by Eq. 14.31 in terms of the properties of the pure substances at a given temperature and the standard-state pressure.

EXAMPLE 14.4

Determine the equilibrium constant K, expressed as $\ln K$, for the reaction $2H_2O \rightleftharpoons 2H_2 + O_2$ at 298 K and at 2000 K.

Solution

In Example 14.3 we have already found ΔG° for this reaction at these two temperatures. Therefore, at 298 K,

$$(\ln K)_{298} = -\frac{\Delta G^\circ_{298}}{\bar{R}T} = \frac{-457\,155}{8.3144 \times 298.15} = -184.42$$

At 2000 K, we have

$$(\ln K)_{2000} = \frac{-\Delta G^\circ_{2000}}{\bar{R}T} = \frac{-271\,040}{8.3144 \times 2000} = -16.299$$

Table A.16 gives the values of the equilibrium constant for a number of reactions. Note again that for each reaction the value of the equilibrium constant is determined from the properties of each of the pure constituents at the standard-state pressure and is a function of temperature only.

Substituting the definition of equilibrium constant according to Eq. 14.34 into the equilibrium expression Eq. 14.33 yields

$$K = \frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_A} y_B^{\nu_B}} \left(\frac{P}{P^\circ}\right)^{\nu_C + \nu_D - \nu_A - \nu_B} \tag{14.35}$$

which is the form of the chemical equilibrium equation for ideal-gas reactions that we will use to evaluate equilibrium composition.

Let us now consider a number of examples that illustrate the procedure for determining the equilibrium composition for a homogeneous reaction and the influence of certain variables on the equilibrium composition.

EXAMPLE 14.5

One kilomole of carbon at 25°C and 0.1-MPa pressure reacts with 1 kmol of oxygen at 25°C and 0.1-MPa pressure to form an equilibrium mixture of CO_2, CO, and O_2 at 3000 K, 0.1-MPa pressure, in a steady-flow process. Determine the equilibrium composition and the heat transfer for this process.

Control volume: Combustion chamber.

Inlet states: P, T known for carbon and for oxygen.

Exit state: P, T known.

Process: SSSF.

Sketch: Figure 14.11.

Model: Table A.15 for carbon; ideal gases, Tables A.12 and A.15.

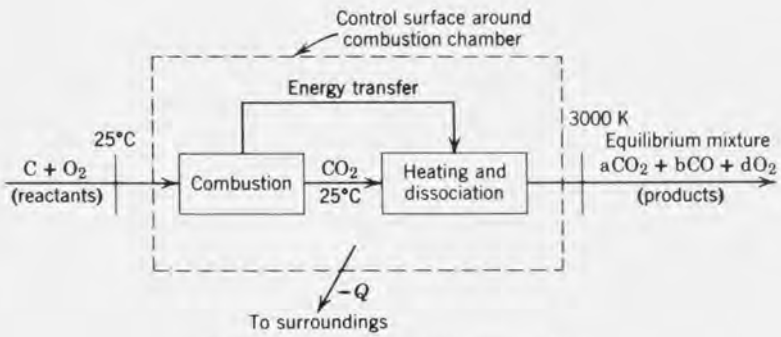


FIGURE 14.11 Sketch for Example 14.5.

Analysis and Solution

It is convenient to view the overall process as though it occurs in two separate steps, a combustion process followed by a heating and dissociation of the combustion product carbon dioxide, as indicated in Fig. 14.11. This two-step process is represented as

Combustion: $C + O_2 \rightarrow CO_2$

Dissociation reaction: $2CO_2 \rightleftharpoons 2CO + O_2$

That is, the energy released by the combustion of C and O_2 heats the CO_2 formed to high temperature, which causes dissociation of part of the CO_2 to CO and O_2. Thus, the overall reaction can be written

$$C + O_2 \rightarrow aCO_2 + bCO + dO_2$$

where the unknown coefficients a, b, and d must be found by solving the equilibrium equation associated with the dissociation reaction. Once this is accomplished, we can write the first law for a control volume around the combustion chamber to calculate the heat transfer.

From the combustion equation we find that the initial composition for the dissociation reaction is 1 kmol CO_2. Therefore, letting $2z$ be the number of kilomoles of CO_2 dissociated, we find

	$2CO_2$	$\rightleftharpoons$	$2CO$	$+ O_2$
Initial:	1		0	0
Change:	$-2z$		$+2z$	$+z$
At equilibrium:	$(1-2z)$		$2z$	z

Therefore, the overall reaction is

$$C + O_2 \rightarrow (1-2z)CO_2 + 2zCO + zO_2$$

and the total number of kilomoles at equilibrium is

$$n = (1-2z) + 2z + z = 1 + z$$

The equilibrium mole fractions are

$$y_{CO_2} = \frac{1-2z}{1+z}, \qquad y_{CO} = \frac{2z}{1+z}, \qquad y_{O_2} = \frac{z}{1+z}$$

From Table A.16 we find that the value of the equilibrium constant at 3000 K for the dissociation reaction considered here is

$$\ln K = -2.217, \qquad K = 0.1089$$

Substituting these quantities along with $P = 0.1$ MPa into Eq. 14.35, we have the equilibrium equation,

$$K = 0.1089 = \frac{y_{CO}^2 y_{O_2}}{y_{CO_2}^2}\left(\frac{P}{P^\circ}\right)^{2+1-2} = \frac{\left(\frac{2z}{1+z}\right)^2\left(\frac{z}{1+z}\right)(1)}{\left(\frac{1-2z}{1+z}\right)^2}$$

or, in more convenient form,

$$\frac{K}{P/P^\circ} = \frac{0.1089}{1} = \left(\frac{2z}{1-2z}\right)^2 \left(\frac{z}{1+z}\right)$$

To obtain the physically meaningful root of this mathematical relation, we note that the number of moles of each component must be greater than zero. Thus, the root of interest to us must lie in the range

$$0 \leqslant z \leqslant 0.5$$

Solving the equilibrium equation by trial and error, we find

$$z = 0.2189$$

Therefore, the overall process is

$$C + O_2 \rightarrow 0.5622CO_2 + 0.4378CO + 0.2189O_2$$

where the equilibrium mole fractions are

$$y_{CO_2} = \frac{0.5622}{1.2189} = 0.4612$$

$$y_{CO} = \frac{0.4378}{1.2189} = 0.3592$$

$$y_{O_2} = \frac{0.2189}{1.2189} = 0.1796$$

The heat transfer from the combustion chamber to the surroundings can be calculated using the enthalpies of formation and Table A.12. For this process

$$H_R = (\bar{h}_f^\circ)_C + (\bar{h}_f^\circ)_{O_2} = 0 + 0 = 0$$

The equilibrium products leave the chamber at 3000 K. Therefore,

$$\begin{aligned} H_P &= n_{CO_2}(\bar{h}_f^\circ + \bar{h}_{3000}^\circ - \bar{h}_{298}^\circ)_{CO_2} \\ &\quad + n_{CO}(\bar{h}_f^\circ + \bar{h}_{3000}^\circ - \bar{h}_{298}^\circ)_{CO} \\ &\quad + n_{O_2}(\bar{h}_f^\circ + \bar{h}_{3000}^\circ - \bar{h}_{298}^\circ)_{O_2} \\ &= 0.5622(-393\,522 + 152\,853) \\ &\quad + 0.4378(-110\,527 + 93\,504) \\ &\quad + 0.2189(98\,013) \\ &= -121\,302 \text{ kJ} \end{aligned}$$

Substituting into the first law gives

$$\begin{aligned} Q_{c.v.} &= H_P - H_R \\ &= -121\,302 \text{ kJ/kmol C burned} \end{aligned}$$

EXAMPLE 14.6

One kilomole of carbon at 25°C reacts with 2 kmol of oxygen at 25°C to form an equilibrium mixture of CO_2, CO, and O_2 at 3000 K, 0.1-MPa pressure. Determine the equilibrium composition.

Control volume: Combustion chamber.
Inlet states: T known for carbon and for oxygen.
Exit state: P, T known.
Process: SSSF.
Model: Ideal-gas mixture at equilibrium.

Analysis and Solution

The overall process can be imagined to occur in two steps as in the previous example. The combustion process is

$$C + 2O_2 \rightarrow CO_2 + O_2$$

and the subsequent dissociation reaction is

	$2CO_2$	$\rightleftharpoons$	$2CO$	$+ O_2$
Initial:	1		0	1
Change:	$-2z$		$+2z$	$+z$
At equilibrium:	$(1-2z)$		$2z$	$(1+z)$

We find that the overall process is

$$C + 2O_2 \rightarrow (1-2z)CO_2 + 2zCO + (1+z)O_2$$

and the total number of kilomoles at equilibrium is

$$n = (1-2z) + 2z + (1+z) = 2 + z$$

The mole fractions are

$$y_{CO_2} = \frac{1-2z}{2+z}, \qquad y_{CO} = \frac{2z}{2+z}, \qquad y_{O_2} = \frac{1+z}{2+z}$$

The equilibrium constant for the reaction $2CO_2 \rightleftharpoons 2CO + O_2$ at 3000 K was found in Example 14.5 to be 0.1089. Therefore, with these expressions, quantities, and $P = 0.1$ MPa substituted, the equilibrium equation is

$$K = 0.1089 = \frac{y_{CO}^2 y_{O_2}}{y_{CO_2}^2}\left(\frac{P}{P^\circ}\right)^{2+1-2}$$
$$= \frac{\left(\dfrac{2z}{2+z}\right)^2\left(\dfrac{1+z}{2+z}\right)}{\left(\dfrac{1-2z}{2+z}\right)^2} \quad (1)$$

or

$$\frac{K}{P/P^\circ} = \frac{0.1089}{1} = \left(\frac{2z}{1-2z}\right)^2\left(\frac{1+z}{2+z}\right)$$

We note that in order for the number of kilomoles of each component to be greater than zero,

$$0 \leqslant z \leqslant 0.5$$

Solving the equilibrium equation for z, we find

$$z = 0.1553$$

so that the overall process is

$$C + 2O_2 \rightarrow 0.6894CO_2 + 0.3106CO + 1.1553O_2$$

The mole fractions of the components in the equilibrium mixture are

$$y_{CO_2} = \frac{0.6894}{2.1553} = 0.320$$

$$y_{CO} = \frac{0.3106}{2.1553} = 0.144$$

$$y_{O_2} = \frac{1.1553}{2.1553} = 0.536$$

The heat transferred from the chamber in this process could be found by the same procedure followed in Example 14.5, considering the overall process.

14.7 SIMULTANEOUS REACTIONS

In developing the equilibrium equation and equilibrium constant expressions of Section 14.6, we assumed that there was only a single chemical reaction equation relating the substances present in the system. In the more general situation, however, there is more than one chemical reaction. We will now analyze a system having two simultaneous reactions by a procedure analogous to that followed in Section 14.6. These results are then readily extended to systems having several simultaneous reactions.

Consider a mixture of substances A, B, C, D, L, M, and N as indicated in Fig. 14.12. These substances exist at a condition of chemical equilibrium at temperature T and pressure P, and are related by the two independent reactions

$$(1) \quad \nu_{A1}A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \tag{14.36}$$

$$(2) \quad \nu_{A2}A + \nu_L L \rightleftharpoons \nu_M M + \nu_N N \tag{14.37}$$

We have already considered the situation in which one of the components (substance A) is involved in each of the reactions to demonstrate the effect of this

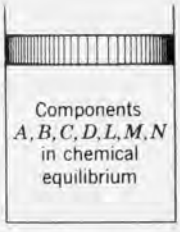


FIGURE 14.12 Sketch demonstrating simultaneous reactions.

condition on the resulting equations. As in the previous section, the changes in the amounts of the components are related by the various stoichiometric coefficients (which are not the same as the number of moles of each substance present in the vessel). We also realize that the coefficients, ν_{A1} and ν_{A2}, are not necessarily the same. That is, substance A does not in general take part in each of the reactions to the same extent.

Development of the requirement for equilibrium is completely analogous to that of Section 14.6. We consider that each reaction proceeds an infinitesimal amount toward the right side. The numbers of moles of A, B, and L decrease, and the numbers of moles of C, D, M, and N increase. If we let the degrees of reaction be ϵ_1 and ϵ_2 for reactions 1 and 2, respectively, the changes in the number of moles are, for infinitesimal shifts from the equilibrium composition,

$$\begin{aligned} dn_A &= -\nu_{A1}\, d\epsilon_1 - \nu_{A2}\, d\epsilon_2 \\ dn_B &= -\nu_B\, d\epsilon_1 \\ dn_L &= -\nu_L\, d\epsilon_2 \\ dn_C &= +\nu_C\, d\epsilon_1 \\ dn_D &= +\nu_D\, d\epsilon_1 \\ dn_M &= +\nu_M\, d\epsilon_2 \\ dn_N &= +\nu_N\, d\epsilon_2 \end{aligned} \tag{14.38}$$

The change in Gibbs function for the mixture in the vessel at constant temperature and pressure is

$$dG_{T,P} = \overline{G}_A\, dn_A + \overline{G}_B\, dn_B + \overline{G}_C\, dn_C + \overline{G}_D\, dn_D + \overline{G}_L\, dn_L + \overline{G}_M\, dn_M + \overline{G}_N\, dn_N$$

Substituting the expressions of Eq. 14.38 and collecting terms, we have

$$dG_{T,P} = (\nu_C\overline{G}_C + \nu_D\overline{G}_D - \nu_{A1}\overline{G}_A - \nu_B\overline{G}_B)\, d\epsilon_1 + (\nu_M\overline{G}_M + \nu_N\overline{G}_N - \nu_{A2}\overline{G}_A - \nu_L\overline{G}_L)\, d\epsilon_2 \tag{14.39}$$

Assuming an ideal-gas mixture, we find it convenient to express again each of the partial molal Gibbs functions as

$$\overline{G}_i = \overline{g}_i^\circ + \overline{R}T \ln y_i \frac{P}{P^\circ}$$

Equation 14.39 written in this form becomes

$$\begin{aligned} dG_{T,P} = &\left\{\Delta G_1^\circ + \overline{R}T \ln\left[\frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_{A1}} y_B^{\nu_B}}\left(\frac{P}{P^\circ}\right)^{\nu_C+\nu_D-\nu_{A1}-\nu_B}\right]\right\} d\epsilon_1 \\ &+ \left\{\Delta G_2^\circ + \overline{R}T \ln\left[\frac{y_M^{\nu_M} y_N^{\nu_N}}{y_A^{\nu_{A2}} y_L^{\nu_L}}\left(\frac{P}{P^\circ}\right)^{\nu_M+\nu_N-\nu_{A2}-\nu_L}\right]\right\} d\epsilon_2 \end{aligned} \tag{14.40}$$

In this equation the standard-state change in Gibbs function for each reaction is defined as

$$\Delta G_1^\circ = \nu_C\overline{g}_C^\circ + \nu_D\overline{g}_D^\circ - \nu_{A1}\overline{g}_A^\circ - \nu_B\overline{g}_B^\circ \tag{14.41}$$

$$\Delta G_2^\circ = \nu_M\overline{g}_M^\circ + \nu_N\overline{g}_N^\circ - \nu_{A2}\overline{g}_A^\circ - \nu_L\overline{g}_L^\circ \tag{14.42}$$

Equation 14.40 expresses the change in Gibbs function of the system at constant T, P, for infinitesimal degrees of reaction of both reactions 1 and 2, Eqs. 14.36 and 14.37. The requirement for equilibrium is that $dG_{T,P} = 0$. Therefore, since reactions 1 and 2 are independent, $d\epsilon_1$ and $d\epsilon_2$ can be independently varied. It follows that at equilibrium each of the bracketed terms of Eq. 14.40 must be zero. Defining equilibrium constants for the two reactions by

$$\ln K_1 = -\frac{\Delta G_1^\circ}{\bar{R}T} \tag{14.43}$$

and

$$\ln K_2 = -\frac{\Delta G_2^\circ}{\bar{R}T} \tag{14.44}$$

we find that, at equilibrium

$$K_1 = \frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_{A1}} y_B^{\nu_B}} \left(\frac{P}{P^\circ}\right)^{\nu_C + \nu_D - \nu_{A1} - \nu_B} \tag{14.45}$$

and

$$K_2 = \frac{y_M^{\nu_M} y_N^{\nu_N}}{y_A^{\nu_{A2}} y_L^{\nu_L}} \left(\frac{P}{P^\circ}\right)^{\nu_M + \nu_N - \nu_{A2} - \nu_L} \tag{14.46}$$

These expressions for the equilibrium composition of the mixture must be solved simultaneously. The following example demonstrates and clarifies this procedure.

EXAMPLE 14.7

One kilomole of water vapor is heated to 3000 K, 0.1-MPa pressure. Determine the equilibrium composition, assuming that H_2O, H_2, O_2, and OH are present.

Control volume: Heat exchanger.

Exit state: P, T known.

Model: Ideal-gas mixture at equilibrium.

Analysis and Solution

There are two independent reactions relating the four components of the mixture at equilibrium. These reactions can be written as

$$(1)\quad 2H_2O \rightleftharpoons 2H_2 + O_2$$
$$(2)\quad 2H_2O \rightleftharpoons H_2 + 2OH$$

Let $2a$ be the number of kilomoles of water dissociating according to reaction 1 during the heating, and let $2b$ be the number of kilomoles of water dissociating according to reaction 2. Since the initial composition is 1 kmol water, the changes according to the two reactions are

Change:	(1)	$2H_2O$	$\rightleftharpoons$	$2H_2$	$+ O_2$
		$-2a$		$+2a$	$+a$
Change:	(2)	$2H_2O$	$\rightleftharpoons$	H_2	$+ 2OH$
		$-2b$		$+b$	$+2b$

Therefore, the number of kilomoles of each component at equilibrium is its initial number plus the change, so that at equilibrium

$$\begin{aligned} n_{H_2O} &= 1 - 2a - 2b \\ n_{H_2} &= 2a + b \\ n_{O_2} &= a \\ n_{OH} &= 2b \\ \hline n &= 1 + a + b \end{aligned}$$

The overall chemical reaction that occurs during the heating process can be written

$$H_2O \rightarrow (1 - 2a - 2b)H_2O + (2a + b)H_2 + aO_2 + 2bOH$$

The right-hand side of this expression is the equilibrium composition of the system. Since the number of kilomoles of each substance must necessarily be greater than zero, we find that the possible values of a and b are restricted to

$$\begin{aligned} a &\geqslant 0 \\ b &\geqslant 0 \\ (a + b) &\leqslant 0.5 \end{aligned}$$

The two equilibrium equations are, assuming that the mixture behaves as an ideal gas,

$$\begin{aligned} K_1 &= \frac{y_{H_2}^2 y_{O_2}}{y_{H_2O}^2} \left(\frac{P}{P^\circ}\right)^{2+1-2} \\ K_2 &= \frac{y_{H_2} y_{OH}^2}{y_{H_2O}^2} \left(\frac{P}{P^\circ}\right)^{1+2-2} \end{aligned}$$

Since the mole fraction of each component is the ratio of the number of kilomoles of the component to the total number of kilomoles of the mixture, these equations can be written in the form

$$\begin{aligned} K_1 &= \frac{\left(\dfrac{2a+b}{1+a+b}\right)^2 \left(\dfrac{a}{1+a+b}\right)}{\left(\dfrac{1-2a-2b}{1+a+b}\right)^2} \left(\frac{P}{P^\circ}\right) \\ &= \left(\frac{2a+b}{1-2a-2b}\right)^2 \left(\frac{a}{1+a+b}\right) \left(\frac{P}{P^\circ}\right) \end{aligned}$$

and

$$\begin{aligned} K_2 &= \frac{\left(\dfrac{2a+b}{1+a+b}\right)\left(\dfrac{2b}{1+a+b}\right)^2}{\left(\dfrac{1-2a-2b}{1+a+b}\right)^2} \left(\frac{P}{P^\circ}\right) \\ &= \left(\frac{2a+b}{1+a+b}\right)\left(\frac{2b}{1-2a-2b}\right)^2 \left(\frac{P}{P^\circ}\right) \end{aligned}$$

giving two equations in the two unknowns a and b, since $P = 0.1$ MPa and the values of K_1, K_2 are known. From Table A.16 at 3000 K, we find

$$K_1 = 0.002\,062, \qquad K_2 = 0.002\,893$$

Therefore, the equations can be solved simultaneously for a and b. The values satisfying the equations are

$$a = 0.0534, \qquad b = 0.0551$$

Substituting these values into the expressions for the number of kilomoles of each component and of the mixture, we find the equilibrium mole fractions to be

$$y_{H_2O} = 0.7063$$
$$y_{H_2} = 0.1461$$
$$y_{O_2} = 0.0482$$
$$y_{OH} = 0.0994$$

The methods used in this section can readily be extended to equilibrium systems having more than two independent reactions. In each case, the number of simultaneous equilibrium equations is equal to the number of independent reactions. The solution of a large set of nonlinear simultaneous equations naturally becomes quite difficult, however, and is not easily accomplished by hand calculations. These problems are normally solved using iterative procedures on a digital computer.

14.8 IONIZATION

In the final section of this chapter, we consider the equilibrium of systems that are made up of ionized gases, or plasmas, a field that has been studied and applied increasingly in recent years. In previous sections we discussed chemical equilibrium, with a particular emphasis on molecular dissociation, as for example the reaction

$$N_2 \rightleftharpoons 2N$$

which occurs to an appreciable extent for most molecules only at high temperature, of the order of magnitude 3000 to 10 000 K. At still higher temperatures, such as those found in electric arcs, the gas becomes ionized. That is, some of the atoms lose an electron, according to the reaction

$$N \rightleftharpoons N^+ + e^-$$

where N^+ denotes a singly ionized nitrogen atom, one that has lost one electron and consequently has a positive charge, and e^- represents the free electron. As the temperature rises still higher, many of the ionized atoms lose another electron, according to the reaction

$$N^+ \rightleftharpoons N^{++} + e^-$$

and thus become doubly ionized. As the temperature continues to rise, the process continues until a temperature is reached at which all the electrons have been stripped from the nucleus.

Ionization generally is appreciable only at high temperature. However, dissociation and ionization both tend to occur to greater extents at low pressure, and consequently dissociation and ionization may be appreciable in such environments as the upper atmosphere, even at moderate temperature. Other effects such as radiation will also cause ionization, but these effects are not considered here.

The problems of analyzing the composition in a plasma become much more difficult than for an ordinary chemical reaction, for in an electric field the free electrons in the mixture do not exchange energy with the positive ions and neutral atoms at the same rate that they do with the field. Consequently, in a plasma in an electric field, the electron gas is not at exactly the same temperature as the heavy particles. However, for moderate fields, assuming a condition of thermal equilibrium in the plasma is a reasonable approximation, at least for preliminary calculations. Under this condition we can treat the ionization equilibrium in exactly the same manner as an ordinary chemical equilibrium analysis.

At these extremely high temperatures, we may assume that the plasma behaves as an ideal-gas mixture of neutral atoms, positive ions, and electron gas. Thus, for the ionization of some atomic species A,

$$A \rightleftharpoons A^+ + e^- \tag{14.47}$$

we may write the ionization equilibrium equation in the form

$$K = \frac{y_{A^+} y_{e^-}}{y_A} \left(\frac{P}{P^\circ}\right)^{1+1-1} \tag{14.48}$$

The ionization equilibrium constant K is defined in the ordinary manner

$$\ln K = -\frac{\Delta G^\circ}{\bar{R}T} \tag{14.49}$$

and is a function of temperature only. The standard-state Gibbs function change for reaction 14.47 is found from

$$\Delta G^\circ = \bar{g}^\circ_{A^+} + \bar{g}^\circ_{e^-} - \bar{g}^\circ_A \tag{14.50}$$

The standard-state Gibbs function for each component at the given plasma temperature can be calculated using the procedures of statistical thermodynamics, so that ionization equilibrium constants can be tabulated as functions of temperature.

Solution of the ionization equilibrium equation, Eq. 14.48, is then accomplished in the same manner as for an ordinary chemical reaction equilibrium.

EXAMPLE 14.8

Calculate the equilibrium composition if argon gas is heated in an arc to 10 000 K, 1 kPa, assuming the plasma to consist of Ar, Ar^+, e^-. The ionization equilibrium constant for the reaction

$$Ar \rightleftharpoons Ar^+ + e^-$$

at this temperature is 0.000 42

Control volume: Heating arc.

Exit state: P, T known.
Model: Ideal-gas mixture at equilibrium.

Analysis and Solution

Consider an initial composition of 1 kmol neutral argon, and let z be the number of kilomoles ionized during the heating process. Therefore,

	Ar	$\rightleftharpoons$	Ar^+	$+ e^-$
Initial:	1		0	0
Change:	$-z$		$+z$	$+z$
Equilibrium:	$(1-z)$		z	z

and

$$n = (1 - z) + z + z = 1 + z$$

Since the number of kilomoles of each component must be positive, the variable z is restricted to the range

$$0 \leqslant z \leqslant 1$$

The equilibrium mole fractions are

$$y_{Ar} = \frac{n_{Ar}}{n} = \frac{1 - z}{1 + z}$$

$$y_{Ar^+} = \frac{n_{Ar^+}}{n} = \frac{z}{1 + z}$$

$$y_{e^-} = \frac{n_{e^-}}{n} = \frac{z}{1 + z}$$

The equilibrium equation is

$$K = \frac{y_{Ar^+} y_{e^-}}{y_{Ar}} \left(\frac{P}{P^\circ}\right)^{1+1-1} = \frac{\left(\frac{z}{1+z}\right)\left(\frac{z}{1+z}\right)}{\frac{1-z}{1+z}} \left(\frac{P}{P^\circ}\right)$$

so that, at 10 000 K, 1 kPa,

$$0.000\,42 = \left(\frac{z^2}{1 - z^2}\right)(0.01)$$

Solving, we have

$$z = 0.2008$$

and the composition is found to be

$$y_{Ar} = 0.6656$$

$$y_{Ar^+} = 0.1672$$

$$y_{e^-} = 0.1672$$

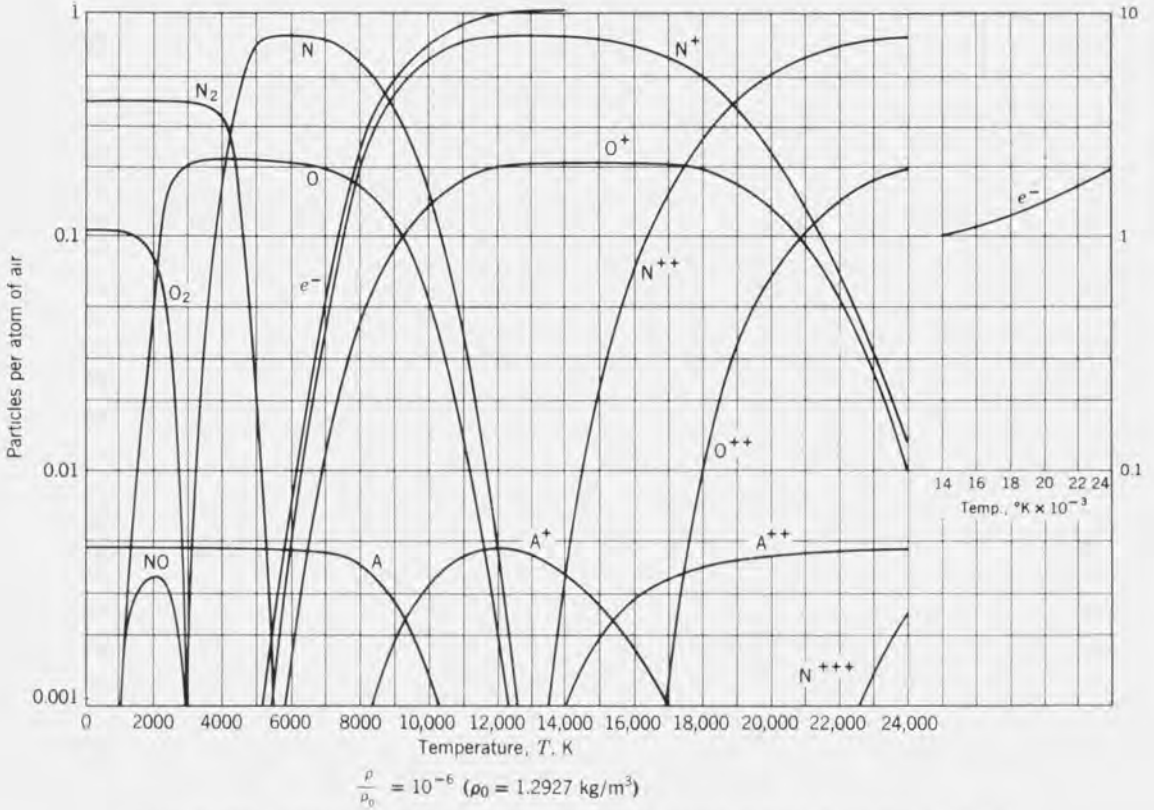


FIGURE 14.13 Equilibrium composition of air. [From W. E. Moeckel and K. C. Weston, NACA TN 4265 (1958).]

Simultaneous reactions, such as simultaneous molecular dissociation and ionization reactions or multiple ionization reactions, can be analyzed in the same manner as the ordinary simultaneous chemical reactions of Section 14.7. We again assume thermal equilibrium in the plasma, which as mentioned before is, in many cases, a reasonable approximation. Figure 14.13 shows the equilibrium composition of air at high temperature and low density, and indicates the overlapping regions of the various dissociation and ionization processes.

PROBLEMS

14.1 Carbon dioxide at 15 MPa is injected into the top of a 5-km deep well in connection with an enhanced oil recovery process. The fluid column standing in the well is at a uniform temperature of 40°C. What is the pressure at the bottom of the well?

14.1E Carbon dioxide at 2200 lbf/in.^{2} is injected into the top of a 3-mile deep well in connection with an enhanced oil recovery process. The fluid column standing in the well is at a uniform temperature of 100 F. What is the pressure at the bottom of the well?

14.2 Consider a 2-km-deep gas well containing a gas mixture of methane and ethane at a uniform temperature of 30°C. The pressure at the top of the well is 14 MPa, and the composition on a mole basis is 90 percent methane, 10 percent ethane. Determine the pressure and composition at the bottom of the well, assuming an ideal gas mixture.

14.3 On the basis of the most recent observations, Titan, the large moon of the planet Saturn, is believed to have an atmosphere made up largely of nitrogen and methane, with surface conditions of about 94 K, 0.13 MPa. Assuming equilibrium between a gaseous atmosphere and a liquid ocean of these two substances at this temperature and pressure, what is the composition of each?

14.4 Ethylene gas is burned with air, and the products exit at 120°C, 3.5 MPa. Assuming complete combustion, what is the minimum percent theoretical air if there is to be no condensation of the products?

14.5 Consider the liquid–vapor equilibrium system of nitrogen–methane at a temperature of 100 K. Plot to scale the liquid- and vapor-phase boundary lines on a pressure-versus-composition diagram. Repeat this process for a temperature of 120 K.

14.6 A mixture of 3 kmol hydrogen and 1 kmol carbon monoxide is contained in a rigid vessel at 25°C and an unknown pressure, P_1. A chemical reaction occurs, and the products consist solely of methane and water, at 200°C and 4 MPa.

(a) Determine the initial pressure P_1.
(b) Calculate $S_2 - S_1$ for the contents of the vessel.

14.6E A mixture of 3 lb mol hydrogen and 1 lb mol carbon monoxide is contained in a rigid vessel at 77 F and an unknown pressure, P_1. A chemical reaction occurs, and the products consist solely of methane and water, at 400 F and 40 atm.

(a) Determine the initial pressure P_1.
(b) Calculate $S_2 - S_1$ for the contents of the vessel.

14.7 Consider a SSSF process for the production of a synthetic fuel, methanol, from waste material that has initially been partially oxidized to produce a gas mixture of one-third hydrogen and two-thirds carbon monoxide, by mole. This mixture enters the reactor at 600 K, 4 MPa, at the rate of 3 kmol/s, and steam at 300°C, 4 MPa, enters the reactor separately at the rate of 1 kmol/s. Exiting the reactor is a mixture of methanol and carbon dioxide at 450 K, 4 MPa. What is the rate of entropy change for this process?

14.8 Hydrogen gas enters a steady-state, steady-flow combustion chamber at 25°C, 5 MPa. A separate line supplies 80 percent theoretical air, which is throttled from 25°C, 15 MPa, into the chamber. The products, consisting of H_2O, H_2, and N_2, exit from the chamber at 175°C, 5 MPa. What is the irreversibility of this process?

14.8E Hydrogen gas enters a steady-state, steady-flow combustion chamber at 77 F, 50 atm. A separate line supplies 80 percent theoretical air, which is throttled from 77 F, 150 atm, into the chamber. The products, consisting of H_2O, H_2, and N_2, exit from the chamber at 350 F, 50 atm. What is the irreversibility of this process?

14.9 At a certain point in a synthetic fuel production process, the product, which consists of equal amounts of ethanol and carbon dioxide, is stored in a 1-m^3 tank at 400 K, 2 MPa, before being processed further. Determine

(a) The absolute entropy per kmol of product at this state.
(b) The total amount of product in the tank.

14.10 Calculate the equilibrium constant for the reaction $O_2 \rightleftharpoons 2O$ at temperatures of 298 K and 6000 K.

14.11 Plot to scale the values of ln K versus $1/T$ for the reaction $2CO_2 \rightleftharpoons 2CO + O_2$. Write an equation for ln K as a function of temperature.

14.12 A new technique for catalytically reducing nitrogen oxides in combustion products involves spraying air-diluted ammonia vapor into the products and then passing the mixture through a catalytic converter. Calculate the equilibrium constant at 350°C for each of the two following reactions:

$$4NO + 4NH_3 + O_2 \rightleftharpoons 4N_2 + 6H_2O$$
$$2NO_2 + 4NH_3 + O_2 \rightleftharpoons 3N_2 + 6H_2O$$

14.13 Air (assumed to be 79 percent nitrogen and 21 percent oxygen) is heated in a SSSF process at a constant pressure of 100 kPa, and some NO is formed. At what temperature will the mole fraction of NO be 0.001?

14.13E Air (assumed to be 79 percent nitrogen and 21 percent oxygen) is heated in a SSSF process at a constant pressure of 14.7 lbf/in.^{2}, and some NO is formed. At what temperature will the mole fraction of NO be 0.001?

14.14 Hydrogen gas is heated from room temperature to 4000 K, 500 kPa, at which state the diatomic species has partially dissociated to the monatomic form. Determine the equilibrium composition at this state.

14.15 Which of the nitrogen oxides, NO or NO_2, is the more stable at ambient conditions? What about at 2000 K?

14.16 A mixture of 1 kmol carbon dioxide, 2 kmol carbon monoxide, and 2 kmol oxygen, at 25°C and 150-kPa pressure, is heated in a constant-pressure SSSF process to

3000 K. Assuming that only these same substances are present in the exiting chemical equilibrium mixture, determine the composition of that mixture.

14.17 Repeat Problem 14.16 for an initial mixture that also includes 2 kmol of nitrogen, which does not dissociate during the process.

14.18 Gasification of the char (primarily carbon) with steam following coal pyrolysis yields a gas mixture of 1 kmol CO and 1 kmol H_2. We wish to upgrade the hydrogen content of this syngas fuel mixture, so it is fed to an appropriate catalytic reactor along with 1 kmol of H_2O. Exiting the reactor is a chemical equilibrium gas mixture of CO, H_2, H_2O, and CO_2 at 600 K, 500 kPa. Determine the equilibrium composition.

14.19 A gas mixture of 1 kmol carbon monoxide, 1 kmol nitrogen, and 1 kmol oxygen at 25°C, 150 kPa, is heated in a constant-pressure SSSF process. The exit mixture can be assumed to be in chemical equilibrium, with CO_2, CO, O_2 and N_2 present. The mole fraction of CO_2 at this point is 0.176. Calculate the heat transfer for the process.

14.19E A gas mixture of 1 lb mol carbon monoxide, 1 lb mol nitrogen, and 1 lb mol oxygen at 77 F, 20 lbf/in.^{2}, is heated in a constant-pressure SSSF process. The exit mixture can be assumed to be in chemical equilibrium, with CO_2, CO, O_2 and N_2 present. The mole fraction of CO_2 at this point is 0.176. Calculate the heat transfer for the process.

14.20 One approach to using a hydrocarbon fuel in a fuel cell is to "reform" the hydrocarbon to obtain hydrogen, which is then fed to the fuel cell. As a part of the analysis of such a procedure, consider the reforming reaction

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO$$

(a) Determine the equilibrium constant for this reaction at a temperature of 800 K.

(b) One kilomole each of methane and water are fed to a catalytic reformer. A mixture of CH_4, H_2O, H_2, and CO exits in chemical equilibrium at 800 K, 100 kPa. Determine the equilibrium composition of this mixture.

14.21 In a test of a gas-turbine combustor, saturated-liquid methane at 115 K is to be burned with excess air to hold the adiabatic flame temperature to 1600 K. It is assumed that the products consist of a mixture of CO_2, H_2O, N_2, O_2, and NO in chemical equilibrium. Determine the percent excess air used in the combustion, and the percentage of NO in the products.

14.22 Catalytic gas generators are frequently used to decompose a liquid, providing a desired gas mixture (spacecraft control systems, fuel cell gas supply, and so forth). Consider feeding pure liquid hydrazine, N_2H_4, to a gas generator, from which exits a gas mixture of N_2, H_2, and NH_3 in chemical equilibrium at 100°C, 350 kPa. Calculate the percent composition of the equilibrium mixture.

14.23 Acetylene gas at 25°C is burned with 140 percent theoretical air, which enters the burner at 25°C, 100 kPa, 80 percent relative humidity. The combustion products form a mixture of CO_2, H_2O, NO, O_2, and N_2 in chemical equilibrium at 2200 K, 100 kPa. This mixture is then cooled to 1000 K very rapidly, so that the composition does not change. Determine

(a) The mole fraction of NO in the products.
(b) The heat transfer for the overall process.

14.23E Acetylene gas at 77 F is burned with 140 percent theoretical air, which enters the burner at 77 F, 14.7 lbf/in.^{2}, 80 percent relative humidity. The combustion products form a mixture of CO_2, H_2O, NO, O_2 and N_2 in chemical equilibrium at 3500 F, 14.7 lbf/in.^{2}. This mixture is then cooled to 1340 F very rapidly, so that the composition does not change. Determine

(a) The mole fraction of NO in the products.
(b) The heat transfer for the overall process.

14.24 A step in the production of a synthetic liquid fuel from organic waste matter is the following conversion process: 1 kmol of ethylene gas (converted from the waste) at 25°C, 5 MPa, and 2 kmol of steam at 300°C, 5 MPa, enter a catalytic reactor. An ideal-gas mixture of ethanol, ethylene, and water in chemical equilibrium leaves the reactor at 700 K, 5 MPa.

(a) Determine the composition of the mixture.
(b) Calculate the heat transfer for the reactor.
(c) Would it be more desirable to operate this system with different inlet proportions?

14.25 Methane at 25°C, 100 kPa, is burned with 200 percent theoretical oxygen at 400 K, 100 kPa, in an adiabatic SSSF process, and the products of combustion exit at 100 kPa. Assume that the only significant dissociation reaction in the products is that of carbon dioxide going to carbon monoxide and oxygen. Determine the equilibrium composition of the products and also their temperature at the combustor exit.

14.26 Calculate the irreversibility for the adiabatic combustion process described in Problem 14.25.

14.27 An important step in the manufacture of chemical fertilizer is the production of ammonia, according to the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(a) Calculate the equilibrium constant for this reaction at 150°C.
(b) For an initial composition of 25 percent nitrogen, 75 percent hydrogen, on a mole basis, calculate the equilibrium composition at 150°C, 5 MPa.

14.28 Consider the following simplification of the production of a synthetic fuel (methanol) from coal. A gas mixture of 50 percent carbon monoxide and 50 percent hydrogen leaves a coal gasifier at 500 K, 1 MPa, and enters a catalytic converter. A gas mixture of methanol, carbon monoxide, and hydrogen in chemical equilibrium leaves the converter at the same temperature and pressure.

(a) Calculate the equilibrium constant for an appropriate reaction equation, and determine the equilibrium composition of the mixture leaving the converter.
(b) Would it be more desirable to operate the converter at ambient pressure?
(c) Would it be more desirable to operate the converter at ambient temperature?
(d) Would it be desirable to change the composition of the inlet mixture before feeding it into the catalytic converter?

14.29 Consider the following coal gasifier proposed for supplying a syngas fuel to a gas turbine power plant. Fifty kilograms per second of dry coal (represented thermochemically as 48 kg C plus 2 kg H) enter the gasifier, along with 4.76 kmol/s

of air and 2 kmol/s of steam. The output stream from this unit is a gas mixture containing H_2, CO, N_2, CH_4, and CO_2 in chemical equilibrium at 900 K, 1 MPa.

(a) Set up the reaction and equilibrium equation(s) for this system, and calculate the appropriate equilibrium constant(s).

(b) Determine the composition of the gas mixture leaving the gasifier.

14.30 Ethane is burned with 150 percent theoretical air in a gas-turbine combustor. The products exiting consist of a mixture of CO_2, H_2O, O_2, N_2, and NO in chemical equilibrium at 1800 K, 1 MPa.

(a) Determine the mole fraction of NO in the products.

(b) Is it reasonable to ignore CO in the products?

14.30E Ethane is burned with 150 percent theoretical air in a gas-turbine combustor. The products exiting consist of a mixture of CO_2, H_2O, O_2, N_2, and NO in chemical equilibrium at 2800 F, 150 lbf/in.^{2}.

(a) Determine the mole fraction of NO in the products.

(b) Is it reasonable to ignore CO in the products?

14.31 Butane is burned with 200 percent theoretical air, and the products of combustion, an equilibrium mixture containing only CO_2, O_2, H_2O, N_2, NO, and NO_2, exit from the combustion chamber at 1400 K, 2 MPa. Determine the equilibrium composition at this state.

14.32 A mixture of 1 kmol water and 1 kmol oxygen at 400 K is heated to 3000 K, 200 kPa, in a SSSF process. Determine the equilibrium composition at the outlet of the heat exchanger, assuming that the mixture consists of H_2O, H_2, O_2, and OH.

14.33 One kilomole of air (assumed to be 78 percent nitrogen, 21 percent oxygen, and 1 percent argon) at room temperature is heated to 4000 K, 200 kPa. Find the equilibrium composition at this state, assuming that only N_2, O_2, NO, O, and Ar are present.

14.33E One pound mole of air (assumed to be 78 percent nitrogen, 21 percent oxygen, and 1 percent argon) at room temperature is heated to 7200 R, 30 lbf/in.^{2}. Find the equilibrium composition at this state, assuming that only N_2, O_2, NO, O, and Ar are present.

14.34 A new technique for reducing nitrogen oxides in combustion products was discussed in Problem 14.12, in which equilibrium constants were calculated for the two related reaction equations at the catalyst operating temperature, 350°C. As a preliminary test of this new unit, a gas mixture of 97 percent N_2, 2 percent NO, and 1 percent NO_2 is fed into the unit at the rate of 1 kmol/s. A second mixture, 80 percent NH_3 and 20 percent O_2, is fed into the unit at the rate of 0.05 kmol/s. Assuming that a mixture in chemical equilibrium according to the listed reactions exits the unit at 350°C, 100 kPa, how much NO and NO_2 does it contain?

14.35 Acetylene gas and x times theoretical air ($x > 1$) at room temperature and 500 kPa are burned at constant pressure in an adiabatic SSSF process. The flame temperature is 2600 K, and the combustion products are assumed to consist of N_2, O_2, CO_2, H_2O, CO, and NO. Determine the value of x.

14.36 The char residue (assumed to be pure carbon) from a coal pyrolysis process producing methane is to be gasified to produce a syngas fuel. At the gasifier inlet,

0.5 kmol of oxygen and x kmol of water enter for each kilomole of char. Exiting the gasifier is a homogeneous ideal-gas mixture in chemical equilibrium at T and P. This mixture contains CH_4, H_2, H_2O, CO, and CO_2.

(a) Determine the number of independent reaction equations for this system.

(b) Set up the equilibrium equations, and specify the procedure to solve for the composition.

(c) Comment on any restrictions on x, and on whether it is desirable to have x as small or as large as possible.

14.37 One kilomole of water vapor at 100 kPa, 400 K, is heated to 3000 K in a constant-pressure SSSF process. Determine the final composition, assuming that H_2O, H_2, H, O_2, and OH are present at equilibrium.

14.38 Methane is burned with theoretical oxygen in a SSSF process, and the products exit the combustion chamber at 3200 K, 700 kPa. Calculate the equilibrium composition at this state, assuming that only CO_2, CO, H_2O, H_2, O_2, and OH are present.

14.38E Methane is burned with theoretical oxygen in a SSSF process, and the products exit the combustion chamber at 5300 F, 100 lbf/in.^{2}. Calculate the equilibrium composition at this state, assuming that only CO_2, CO, H_2O, H_2, O_2, and OH are present.

14.39 Operation of an MHD converter requires an electrically conducting gas. It is proposed to use helium gas "seeded" with 1.0 mole percent cesium, as shown in Fig. 14.14. The cesium is partly ionized ($Cs \rightleftharpoons Cs^+ + e^-$) by heating the mixture to 2500 K, 1 MPa, in a nuclear reactor to provide free electrons. No helium is ionized in this process, so that the mixture entering the converter consists of He, Cs, Cs^+, and e^-. To analyze the converter process, we need to know the precise mole fraction of electrons in the mixture. Determine this fraction. At 2500 K, $\ln K = -13.4$ for the cesium ionization reaction described.

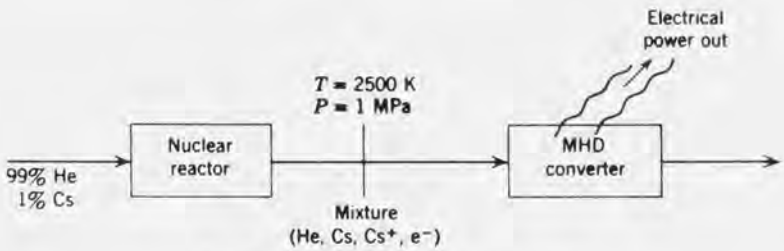


FIGURE 14.14 Sketch for Problem 14.39.

14.40 One kilomole of argon gas at room temperature is heated to 20 000 K, 100 kPa. Assume that the plasma in this condition consists of an equilibrium mixture of Ar, Ar^+, Ar^{++}, and e^- according to the simultaneous reactions

$$(1) \quad Ar \rightleftharpoons Ar^+ + e^-$$

$$(2) \quad Ar^+ \rightleftharpoons Ar^{++} + e^-$$

The ionization equilibrium constants for these reactions at 20 000 K have been

calculated from spectroscopic data as

$$\ln K_1 = 3.11, \qquad \ln K_2 = -4.92.$$

Determine the equilibrium composition of the plasma.

14.41 Plot to scale the equilibrium composition of nitrogen at 10-kPa pressure over the temperature range 5000 K to 15 000 K, assuming that N_2, N, N^+, and e^- are present. For the ionization reaction $N \rightleftharpoons N^+ + e^-$, the ionization equilibrium constant K has been calculated from spectroscopic data as

T, K	K
10 000	6.26×10^{-4}
12 000	1.51×10^{-2}
14 000	0.151
16 000	0.92

COMPUTER PROBLEMS

14.1C Write a program to solve the general case of Problem 14.18. The effects of varying the relative amount of steam input and the effects of equilibrium temperature and pressure on the equilibrium composition are to be studied.

14.2C Write a program to solve the following problem. One kmol of carbon at 25°C is burned with b kmol of oxygen in a constant-pressure adiabatic process. The products consist of an equilibrium mixture of CO_2, CO, and O_2. We wish to determine the flame temperature for various combinations of b and the pressure P, assuming variable specific heat for the components and equations from Table A.10.

14.3C Write a program to solve the general case of Problem 14.23, in which the percent theoretical air and the combustion products temperature are input variables.

14.4C Write a program to solve the general case of Problem 14.24, in which the relative amount of steam input and the reactor temperature and pressure are input variables.

14.5C Write a program to solve the general case of Problem 14.36. The effects of different operating temperatures and pressures of the gasifier are to be studied.

14.6C Write a program to solve the general case of Problem 14.38. The effects of the percent theoretical oxygen input and the exit temperature and pressure are to be studied.

14.7C Write a program to solve the following problem. One kilomole of water is heated to temperature T and pressure P, at which exists a mixture of H_2O, H_2, and O_2 in chemical equilibrium. We wish to find the equilibrium composition at this T and P by directly determining the minimum value of the system's Gibbs function in terms of the amount of water that has dissociated (see Fig. 14.3), and to compare this result with that found using the analytical procedure developed in Section 14.6.

14.8C Extend the program written for the solution of Problem 14.7C to include OH in the equilibrium mixture, in addition to the other components given in that problem.

15

Quantum Mechanics

The developments and discussions of thermodynamics to this point in the text have been principally from the macroscopic or bulk point of view. In the remaining chapters we reconsider these same fundamental concepts and laws within the framework of the microscopic or molecular view. This task requires an introduction to the fundamentals of quantum mechanics, statistical mechanics and statistical thermodynamics. We will not study each of these subjects in depth, but will instead give only an introduction to each. In this chapter, we introduce the subject of quantum mechanics, with particular attention to the discrete, or quantized, energy states available to particles.

15.1 THE BOHR THEORY OF THE ATOM

As an introduction to the subject of quantum mechanics, we will describe the Bohr theory of the atom, which was presented originally by Niels Bohr in 1913 and was frequently modified during the succeeding decade until its general replacement by the new quantum mechanics.

Bohr's theory is fundamentally a combination of classical mechanics and Planck's quantum theory of radiation. The atomic model consists of electrons orbiting around a central nucleus. The hydrogen atom, a single electron revolving about a nucleus made up of one proton, is the simplest case. The force exerted on the electron by the nucleus is the Coulomb potential, $C\mathscr{Z}e^2/r^2$, where C is the proportionality constant, $\mathscr{Z}$ is the atomic number of the substance (that is, the charge on the nucleus, which is equal to unity for hydrogen), e is the electron charge, and r is the radius of the orbit. Bohr postulated that only discrete orbits are permissible. The orbits are specified by the requirement that the angular momentum of the electron be equal to $\mathbf{n}(h/2\pi)$, where $\mathbf{n}$ is the principal quantum number, which may have only integral values 1, 2, 3, ... For an electron to jump from one orbit to a higher one, it must receive a quantum of radiation (energy according to Planck's theory) of exactly the appropriate frequency. This absorption of energy gives a discrete line in the spectrum observed for hydrogen. The various wavelengths at which hydrogen and other atoms absorb or emit energy will be discussed in Section 15.6. Using Bohr's hypothesis and the Coulomb potential, we find from Newton's second law of motion that the radii of these allowed orbits are directly proportional to $\mathbf{n}^2$.

This basic theory is far too simple to explain the observed spectral lines for even the hydrogen atom, much less those for more complex atoms. Modifications

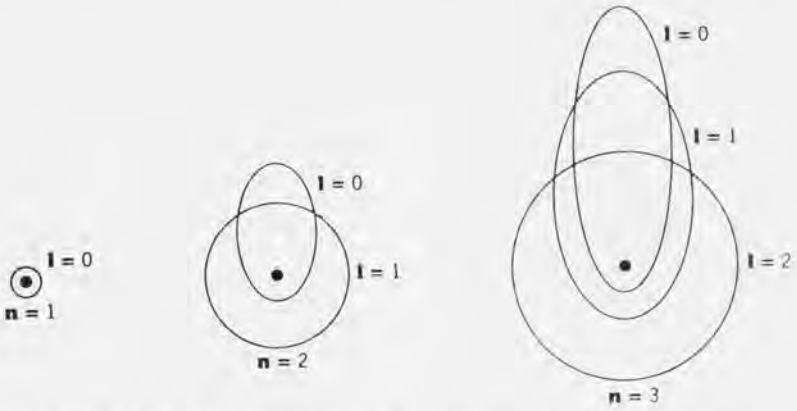


FIGURE 15.1 Electron orbits for the Bohr theory of the hydrogen atom.

to the theory allow for elliptical orbits as well as circular, as specified by the azimuthal quantum number $\mathbf{l}$, which may take on only the values $\mathbf{l} = 0, 1, 2, \ldots, \mathbf{n} - 1$. Figure 15.1 shows the Bohr orbits for the first few values of the quantum numbers $\mathbf{n}$ and $\mathbf{l}$. The energy is dependent primarily on the principal quantum number $\mathbf{n}$, and energy differences for different values of $\mathbf{l}$ are very small for the hydrogen atom. The magnetic quantum number $\mathbf{m}_l$, with allowed values $\mathbf{m}_l = 0, \pm 1, \pm 2, \ldots, \pm \mathbf{l}$, was introduced to account for the observed splitting of spectral lines in a magnetic field. The electron spin quantum number $\mathbf{m}_s = \pm \frac{1}{2}$ was introduced to explain the behavior of helium and other more complex substances.

In spite of its growing complexity, the Bohr theory was still unable to account for or explain many of the observed phenomena, and it was therefore discarded in favor of the new quantum mechanics. The model is still useful today, however, as a tool for many calculations and especially as a convenient pictorial representation of the atom.

15.2 WAVE CHARACTERISTICS OF ELECTRONS AND THE HEISENBERG UNCERTAINTY PRINCIPLE

The introduction of Planck's quantum theory of radiation began a great controversy about the fundamental nature of light and electromagnetic radiation in general. Radiation, having a corpuscular nature, could not easily explain dispersion, reflection, interference, diffraction, and other problems handled so readily by the wave theory. On the other hand, quantum theory could rather simply explain the problem of energy exchange—the photoelectric effect, in particular—and other difficulties that had plagued the wave theory for years. Furthermore, it seemed for a time that Bohr's atomic model, which incorporated the quantum theory, would provide a basis for explaining spectra and atomic behavior in general.

Let us consider a photon of electromagnetic radiation. From Planck's equation for energy exchange,

$$\epsilon = h\nu \tag{15.1}$$

where ν is the frequency, and from Einstein's equation,

$$\epsilon = mc^2 \tag{15.2}$$

we find that, although a photon or quantum of radiation has no mass, it does have associated with it a momentum (mc),

$$(mc) = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{15.3}$$

in which the wavelength λ is given by

$$\lambda = \frac{c}{\nu} \tag{15.4}$$

We view radiation, then, as having a dualistic nature—the wave properties of frequency and wavelength and the particle or corpuscular property of momentum.

In 1923, when the controversy over the nature of radiation had essentially reached an impasse, with each view capable of only partial success, de Broglie postulated that matter may possess a similar dualistic nature. His hypothesis that a wavelength given by the relation

$$\lambda = \frac{h}{m\mathbf{V}} \tag{15.5}$$

can be associated with an electron of mass m and velocity $\mathbf{V}$ was first confirmed by Davisson and Germer in 1925, and later by others. It was found that passing a narrow beam of electrons through a thin metal foil produces a set of concentric diffraction rings, similar to the optical rings of light diffraction. This phenomenon could be explained by wave interference. The electron ring spacings could also be predicted according to Eq. 15.5. From the magnitude of Planck's constant h, it is clear that the de Broglie matter wavelengths for large macroscopic bodies are so small that they are a totally negligible influence, but for electrons and other atomic-scale considerations, a clear distinction between particle and wave is not always possible.

The Heisenberg uncertainty principle can be demonstrated by the following thought experiment. Suppose that we wish to observe an electron through some powerful microscope. It is impossible, even in theory, to determine the exact position of the electron at any instant of time, inasmuch as some source of radiation must be used to illuminate the electron. Consequently, the minimum uncertainty Δx in the position of the electron is of the order of magnitude of the wavelength of the illuminating radiation. That is,

$$\Delta x \sim \lambda$$

We conclude that to minimize the uncertainty in position of the electron, it would be desirable to have a microscope using radiation of a very short wavelength.

However, in making this measurement or observation, at least one photon of radiation must strike the electron and be reflected to the observer. This photon possesses a momentum h/λ, at least part of which is transferred to the electron as they collide. Consequently, there is a resulting uncertainty about the momentum of the electron of the order of magnitude h/λ, or

$$\Delta(m\mathbf{V}_x) \sim \frac{h}{\lambda}$$

with the opposite dependency on λ. We find that radiation having a short wavelength gives the position of the electron with only a small uncertainty but its momentum with a large uncertainty. Conversely, radiation of long wavelength can determine the momentum of an electron quite accurately but is very uncertain about its position. The product of these effects,

$$\Delta x \times \Delta(m\mathbf{V}_x) \sim h \tag{15.6}$$

is an approximate statement of Heisenberg's uncertainty principle—one of the fundamental equations of quantum mechanics. This basic uncertainty principle is not observed or of consequence in ordinary macroscopic measurements, because of the extremely small magnitude of Planck's constant. However, because of the small masses and distances it is of prime importance on the atomic scale.

15.3 THE SCHRÖDINGER WAVE EQUATION

As a preliminary to a consideration of the Schrödinger wave equation for matter waves, we examine the partial differential equation representing a vibrating string, as developed in classical physics. This equation is found to be, from Newton's second law,

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{\mathbf{V}_p^2}\left(\frac{\partial^2 y}{\partial t^2}\right) \tag{15.7}$$

where $\mathbf{V}_p$ is the phase velocity and the variable y denotes the amplitude of vibration at time t for any distance x from the fixed end point.

In general, the amplitude y is a function of both x and t. Let us assume that this dependency is separable into the form

$$y(x, t) = f(x)g(t) \tag{15.8}$$

Taking the partial derivatives of Eq. 15.8 and substituting into Eq. 15.7, we obtain

$$\frac{1}{f}\left(\frac{d^2 f}{dx^2}\right) = \frac{1}{g\mathbf{V}_p^2}\left(\frac{d^2 g}{dt^2}\right) = -\alpha^2 \tag{15.9}$$

One side of this equation is a function only of x and the other a function only of t. Inasmuch as x and t are independent variables, Eq. 15.9 can be valid only if both sides are constant, which for convenience we have set equal to $-\alpha^2$.

The second equality of Eq. 15.9 can be written as

$$\frac{d^2 g}{dt^2} + \alpha^2 \mathbf{V}_p^2 g = 0 \tag{15.10}$$

The solution to this ordinary differential equation is

$$g = C_1 \cos(\alpha \mathbf{V}_p t) + C_2 \sin(\alpha \mathbf{V}_p t) \tag{15.11}$$

from which we conclude that g is a periodic function of time having the frequency

$$\nu = \frac{\alpha \mathbf{V}_p}{2\pi} \tag{15.12}$$

Therefore, the constant α can be expressed as

$$\alpha = \frac{2\pi\nu}{\mathbf{V}_p} = \frac{2\pi}{\lambda} \tag{15.13}$$

where λ is the wavelength.

From Eq. 15.13 and the equality involving f and α in Eq. 15.7, it follows that

$$\frac{d^2 f}{dx^2} + \frac{4\pi^2}{\lambda^2} f = 0 \tag{15.14}$$

The function f then represents the amplitude of the standing wave at any position x for a vibration of associated wavelength λ.

In 1926, Schrödinger applied the differential wave equation to de Broglie's matter waves. Using the symbol Ψ_x for the x-direction amplitude or wave function (the physical interpretation of which will be discussed shortly) and the de Broglie equation (Eq. 15.5), we have for the differential equation

$$\frac{d^2\Psi_x}{dx^2} + \frac{4\pi^2(m\mathbf{V}_x)^2}{h^2}\Psi_x = 0 \tag{15.15}$$

It is more convenient to use the total energy ϵ_x, where

$$\epsilon_x = (\mathrm{KE})_x + (\mathrm{PE})_x = \tfrac{1}{2}m\mathbf{V}_x^2 + \Phi_x \tag{15.16}$$

Here Φ_x is the potential energy.

The one-dimensional wave equation then becomes

$$\frac{d^2\Psi_x}{dx^2} + \frac{8\pi^2 m}{h^2}(\epsilon_x - \Phi_x)\Psi_x = 0 \tag{15.17}$$

To generalize the equation to three dimensions, we define a wave function Ψ as

$$\Psi = \Psi_x \Psi_y \Psi_z \tag{15.18}$$

and recognize that

$$\epsilon = \epsilon_x + \epsilon_y + \epsilon_z \tag{15.19}$$

and

$$\Phi = \Phi_x + \Phi_y + \Phi_z \tag{15.20}$$

so that, in three dimensions,

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}(\epsilon - \Phi)\Psi = 0 \tag{15.21}$$

where the Laplacian operator ∇^2 is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{15.22}$$

Equation 15.21 is known as the time-independent Schrödinger wave equation. In general, as for the vibrating string, the wave function Ψ is dependent on time as well as position and may even be a complex function having real and imaginary parts. Consequently, there is a corresponding general time-dependent Schrödinger wave equation, but for stationary states of the system (standing waves), the case of interest to us here, we need consider only the special form, Eq. 15.21.

A basic hypothesis of wave mechanics is that the wave function Ψ has the characteristic of a probability function. Since Ψ may in general be complex although a probability must be real, the product of Ψ and its complex conjugate Ψ^* is taken as representing probability. Furthermore, a probability function must be continuous and single-valued and must approach zero for large values of distance. It is found that a Ψ function having the required behavior is obtained from solutions of the Schrödinger wave equation (Eq. 15.21) only for discrete energy states of the system. When the function Ψ is real, the product $\Psi\Psi^*$ reduces to Ψ^2, so that for stationary states, where the particle being represented is presumed to have a definite energy ϵ_i, the quantity

$$\Psi_i^2 \, dx \, dy \, dz$$

becomes the probability of finding the particle of energy ϵ_i in the element of space x to $x + dx$, y to $y + dy$, z to $z + dz$.

15.4 TRANSLATION

In applying the Schrödinger wave equation to the molecules of a gas, we assume that the various energy modes are separable. We consider first the translational energy, which would constitute the entire energy of a monatomic ideal gas with all the atoms in the electronic ground level.

The gas is confined in a box of dimensions X, Y, and Z, but to simplify the problem, let us consider a one-dimensional case, in which the particles move only in the x-direction, between 0 and X. Applying the Schrödinger equation to a single particle, for the x-direction only, yields

$$\frac{d^2\Psi_x}{dx^2} + \frac{8\pi^2 m}{h^2}(\epsilon_x - \Phi_x)\Psi_x = 0 \tag{15.23}$$

However, since the particle must remain inside the box, the probability, and consequently the wave function Ψ_x, must be zero for all x outside this range. This physical requirement is satisfied by making the potential energy $\Phi_x = \infty$ for $x < 0$ and $x > X$. We also note that, for an ideal gas, $\Phi_x = 0$ inside the box. Therefore, for the range

$$0 < x < X \tag{15.24}$$

the Schrödinger wave equation is

$$\frac{d^2\Psi_x}{dx^2} + \frac{8\pi^2 m}{h^2}\epsilon_x\Psi_x = 0 \tag{15.25}$$

with the boundary conditions

$$\Psi_x(0) = 0 \tag{15.26}$$

$$\Psi_x(X) = 0 \tag{15.27}$$

The solution to Eq. 15.25 can be written in the form

$$\Psi_x = C_1 \sin\left(x\sqrt{\frac{8\pi^2 m\epsilon_x}{h^2}}\right) + C_2 \cos\left(x\sqrt{\frac{8\pi^2 m\epsilon_x}{h^2}}\right) \tag{15.28}$$

From the boundary condition at $x = 0$ (Eq. 15.26), it follows that

$$0 = C_1(0) + C_2(1)$$

and we conclude that

$$C_2 = 0 \tag{15.29}$$

From the boundary condition at $x = X$ (Eq. 15.27),

$$0 = C_1 \sin\left(X\sqrt{\frac{8\pi^2 m\epsilon_x}{h^2}}\right) \tag{15.30}$$

Now the possibility that $C_1 = 0$ would lead to the physically impossible solution that $\Psi_x = 0$ for all values of x. The only alternative is that

$$\sin\left(X\sqrt{\frac{8\pi^2 m\epsilon_x}{h^2}}\right) = 0$$

or

$$X\sqrt{\frac{8\pi^2 m\epsilon_x}{h^2}} = \mathbf{k}_x\pi \tag{15.31}$$

with

$$\mathbf{k}_x = 1, 2, 3, \ldots$$

The value $\mathbf{k}_x = 0$ leads to a trivial solution ($\Psi_x = 0$ for all x) and is therefore not permissible.

It is seen from Eq. 15.31 that only discrete energy states are allowed. These states are given in terms of the x-direction translational quantum number $\mathbf{k}_x$ as

$$\epsilon_{\mathbf{k}_x} = \frac{h^2}{8mX^2}\mathbf{k}_x^2, \qquad \mathbf{k}_x = 1, 2, 3, \ldots \tag{15.32}$$

For each energy state $\epsilon_{\mathbf{k}_x}$ as specified by the quantum number $\mathbf{k}_x$, there is a corresponding x-direction wave function $\Psi_{\mathbf{k}_x}$, which from Eqs. 15.28, 15.29, and 15.31 can be expressed in the form

$$\Psi_{\mathbf{k}_x}(x) = C_1 \sin\left(\mathbf{k}_x\pi\frac{x}{X}\right) \tag{15.33}$$

The constant C_1 in this equation can be evaluated by normalization, because the square of the wave function represents the probability. Therefore

$$\int_{x=0}^{X} \Psi_{\mathbf{k}_x}^2(x)\, dx = 1 \tag{15.34}$$

since for each $\mathbf{k}_x$, a particle having the corresponding energy $\epsilon_{\mathbf{k}_x}$ must be found somewhere in the box, according to Eq. 15.24. If we substitute Eq. 15.33 into Eq. 15.34,

$$C_1^2 \int_0^X \sin^2\left(\mathbf{k}_x \pi \frac{x}{X}\right) dx = 1 \tag{15.35}$$

and integrate, we find

$$C_1 = \sqrt{\frac{2}{X}} \tag{15.36}$$

Therefore, each quantum state as specified by $\mathbf{k}_x$ has associated with it the wave function

$$\Psi_{\mathbf{k}_x}(x) = \sqrt{\frac{2}{X}} \sin\left(\mathbf{k}_x \pi \frac{x}{X}\right) \tag{15.37}$$

The diagrams of Fig. 15.2 show the wave functions and the square of the wave functions for the first few quantum states available to the particle in the one-dimensional box.

To this point we have discussed only the one-dimensional case, whereby the particle is restricted to the range from $x = 0$ to $x = X$. If we now generalize the problem to three dimensions, so that $0 < x < X$, $0 < y < Y$, $0 < z < Z$, then, since the x-, y-, z-directions are assumed to be independent, it follows that

$$\epsilon = \epsilon_x + \epsilon_y + \epsilon_z \tag{15.38}$$

From the Schrödinger time-independent equation, Eq. 15.21, and the boundary conditions, it is found that only discrete energy states are permissible. These energies

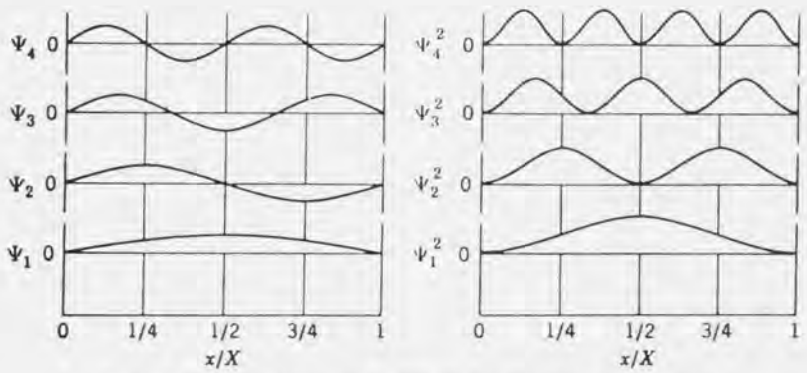


FIGURE 15.2 The functions ψ_{k_x} and $\psi_{k_x}^2$ for x-directional translation.

are given in terms of three quantum numbers for translation by the expression

$$\epsilon_{\mathbf{k}_x,\mathbf{k}_y,\mathbf{k}_z} = \frac{h^2}{8m}\left(\frac{\mathbf{k}_x^2}{X^2} + \frac{\mathbf{k}_y^2}{Y^2} + \frac{\mathbf{k}_z^2}{Z^2}\right) \tag{15.39}$$

in which each of the quantum numbers $\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z$ may have any integral value 1, 2, 3, ... A particular quantum state is then specified by the values of each of these numbers. It is important to realize that the states (5, 2, 3), (5, 3, 2), (2, 5, 3), and so forth, are all different quantum states, although all have exactly the same magnitude of energy. Thus, we may speak of an energy level as being degenerate. Degeneracy is the condition of a number of quantum states having the same amount of energy. Moreover, the number of quantum states at a particular energy level is termed the degeneracy of that level. Each of the energy states $\epsilon_{\mathbf{k}_x,\mathbf{k}_y,\mathbf{k}_z}$ has associated with it a wave function

$$\Psi_{\mathbf{k}_x,\mathbf{k}_y,\mathbf{k}_z}(x, y, z) = \sqrt{\frac{8}{XYZ}} \sin\left(\mathbf{k}_x\pi\frac{x}{X}\right) \sin\left(\mathbf{k}_y\pi\frac{y}{Y}\right) \sin\left(\mathbf{k}_z\pi\frac{z}{Z}\right) \tag{15.40}$$

where the constant has been evaluated by normalizing the wave function, as in the one-dimensional problem.

Very commonly, we are concerned with a system for which

$$X = Y = Z = V^{1/3} \tag{15.41}$$

so that Eq. 15.39 can be simplified to the form

$$\epsilon_{\mathbf{k}_x,\mathbf{k}_y,\mathbf{k}_z} = \frac{h^2}{8mV^{2/3}}(\mathbf{k}_x^2 + \mathbf{k}_y^2 + \mathbf{k}_z^2) \tag{15.42}$$

with $\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z = 1, 2, 3, \ldots$. In this form, we see that the energy associated with a given quantum state is dependent on the volume of the system. Conversely, for any given substance, specification of the boundary parameter, volume, fixes the energy of each quantum state, according to Eq. 15.42.

15.5 APPLICATION OF THE WAVE EQUATION TO MOLECULES

In the preceding section, we applied the Schrödinger wave equation to translation, which is the only energy mode for a monatomic ideal gas with all the atoms in the electronic ground level. For the more general case of a molecule comprising more than a single atom, the problem becomes relatively more complex because there may be several modes of energy storage. Let us consider a system of independent particles (an ideal gas) so that there is no system energy from intermolecular forces and we may therefore speak of the energy per molecule.

We assume that the energy of the molecule can be separated into two parts: the translational energy of the molecule as a whole, expressed in terms of the motion of the center of mass of the molecule; and the energy internal to the molecule itself, that is, energy with respect to a coordinate system having its origin at the center of mass of the molecule. For the energy of the molecule, we may write

$$\epsilon = \epsilon_t + \epsilon_{\text{int}} \tag{15.43}$$

and, for the wave function,

$$\Psi = \Psi_t \Psi_{\text{int}} \tag{15.44}$$

Because we are concerned with independent particles, any potential energy is associated with the internal modes of energy. The Schrödinger wave equation can then be separated into two parts, one dependent solely on the motion of the center of mass and the other only on the energy of the component atoms with respect to the center of mass. The first of these parts,

$$\left(\frac{\partial^2 \Psi_t}{\partial x_{\text{C.M.}}^2} + \frac{\partial^2 \Psi_t}{\partial y_{\text{C.M.}}^2} + \frac{\partial^2 \Psi_t}{\partial z_{\text{C.M.}}^2}\right) + \frac{8\pi^2 m}{h^2} \epsilon_t \Psi_t = 0 \tag{15.45}$$

has been evaluated in Section 15.4 for translational energies and wave functions for a monatomic ideal gas. The same results apply for the translation of a molecule consisting of more than one atom, provided that the x, y, z in Eq. 15.45 are the coordinates of the center of mass of the molecule (relative to an external coordinate frame) and that m is the mass of the molecule, that is, the sum of the masses of the component atoms.

The second equation, dependent only on the internal modes, becomes

$$\left(\frac{\partial^2 \Psi_{\text{int}}}{\partial x^2} + \frac{\partial^2 \Psi_{\text{int}}}{\partial y^2} + \frac{\partial^2 \Psi_{\text{int}}}{\partial z^2}\right) + \frac{8\pi^2 m}{h^2} (\epsilon_{\text{int}} - \Phi_{\text{int}}) \Psi_{\text{int}} = 0 \tag{15.46}$$

In this equation, the coordinate system x, y, z is taken with respect to the center of mass of the molecule. The energy may include contributions from rotational, vibrational, and electronic states, as discussed in Chapter 2. These energy modes are not strictly independent. For most substances, however, the interactions at ordinary temperatures are small and are treated as correction terms to a model consisting of independent rigid rotation, harmonic oscillation, and the necessary electronic states. Since these modes are assumed to be independent, the internal mode energy contribution is

$$\epsilon_{\text{int}} = \epsilon_r + \epsilon_v + \epsilon_e \tag{15.47}$$

and, for the internal wave function,

$$\Psi_{\text{int}} = \Psi_r \Psi_v \Psi_e \tag{15.48}$$

We find that Eqs. 15.47 and 15.48 permit a separation of the wave equation, Eq. 15.46, into separate parts for the different modes. These parts can then be solved for the corresponding discrete states to determine each contribution to the energy. In this text we will not carry through the rather difficult solutions for rotation and for vibration. In the following section we discuss the electronic states for atoms only in a qualitative sense.

15.6 ELECTRONIC STATES OF ATOMS

When we applied the Schrödinger wave equation to the internal energy modes of a molecule, we assumed the various modes to be independent of one another. In a monatomic gas, the only internal mode is the electronic, as there is no rotation

or vibration. Thus, the internal mode energy and wave function of Eqs. 15.47 and 15.48 are simply the electronic terms, and the internal wave equation, Eq. 15.46, is then written in these terms. We will not solve this equation in detail, because for most substances in the temperature range of interest the electronic energy levels are so widely spaced that essentially all the particles are found in the ground level at any instant of time. Nevertheless, we should be familiar enough with the subject to be able to recognize the exceptions to this statement. A second and still more important reason for at least a qualitative discussion of electronic states is that the ground level of an atom may be degenerate, which contributes to the entropy of the substance.

Let us again consider the most elementary case, the hydrogen atom, as we did at the beginning of the chapter in our discussion of Bohr's theory. We apply the Schrödinger wave equation, Eq. 15.46, to the atom's single electron, which is under the influence of the nucleus according to the Coulomb potential. It is convenient here to work in spherical polar coordinates, as shown in Fig. 15.3. The relations between the two coordinate systems are seen to be

$$\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned} \tag{15.49}$$

and using the Coulomb potential, we have

$$\Phi_{\text{int}} = -\int_{\infty}^{r} F\, dr = -\frac{C\mathscr{Z}e^2}{r} = -\frac{C_1}{r} \tag{15.50}$$

The wave equation, Eq. 15.46, becomes

$$\frac{h^2}{8\pi^2 m}\nabla^2\Psi_e + \left(\epsilon_e + \frac{C_1}{r}\right)\Psi_e = 0 \tag{15.51}$$

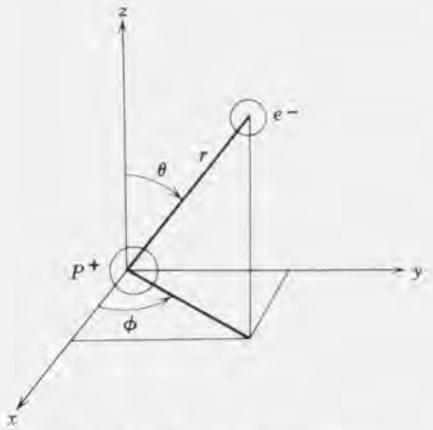


FIGURE 15.3 The hydrogen atom.

where the Laplacian operator ∇^2 (Eq. 15.22) is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{15.52}$$

To solve the differential equation, we assume that the wave function can be expressed as the product

$$\Psi(r, \theta, \phi) = \Psi_r(r)\Psi_\theta(\theta)\Psi_\phi(\phi) \tag{15.53}$$

where each of the three functions is dependent on only one of the coordinates. Substituting Eq. 15.53 into the wave equation separates the differential equation into three equations, each in terms of an ordinary derivative. Since the variables r, θ, and ϕ, are independent, we conclude that each term must be a constant. Solution of the θ and ϕ terms (which incidently is similar mathematically to molecular rotation) leads to a pair of quantum numbers $\mathbf{l}$, a nonnegative integer, and $\mathbf{m}_l$, where

$$\mathbf{m}_l = 0, \pm 1, \pm 2, \ldots, \pm\mathbf{l} \tag{15.54}$$

The remaining second-order differential equation in r then includes the potential energy from the Coulomb force and a term in $\mathbf{l}(\mathbf{l}+1)$. A solution of this difficult equation is valid only if the energy is quantized according to the relation

$$\epsilon = \left(\frac{2\pi^2 C^2 \mathscr{Y}^2 e^4 m}{h^2}\right)\frac{1}{\mathbf{n}^2} \tag{15.55}$$

where the quantum number $\mathbf{n}$, called the principal quantum number, can assume only positive integral values,

$$\mathbf{n} = 1, 2, 3, \ldots \tag{15.56}$$

For an acceptable solution the azimuthal number $\mathbf{l}$ must also be restricted to the values

$$\mathbf{l} = 0, 1, 2, \ldots, (\mathbf{n}-1) \tag{15.57}$$

and the values of $\mathbf{m}_l$, the magnetic quantum number, are as given by Eq. 15.54.

For our solution, we find that the energy levels for atomic hydrogen are dependent only on the principal quantum number $\mathbf{n}$, as given by Eq. 15.55 and shown in Fig. 15.4. Energies are given in units of reciprocal millimeters (ϵ/hc) with respect to the ground state. The limiting value for very large $\mathbf{n}$ is 10 965 mm^{-1} (this is called the ionization potential). Under this condition the electron leaves the influence of the nucleus. The vertical lines in the diagram show some of the transitions observed in the spectra of the hydrogen atom; the length of the line between any two levels is proportional to the wave number of the observed spectral line, and the width is proportional to its intensity. Since the energy levels depend only on $\mathbf{n}$, the levels must be degenerate according to the number of allowed values of the quantum numbers $\mathbf{l}$ and $\mathbf{m}_l$. Actually, from a more general solution that includes the effects of relativity and electron spin, very slight differences in energy are found for different values of $\mathbf{l}$ and $\mathbf{m}_l$; this is in agreement with very precise spectral observations. The energy levels for atomic hydrogen, including the azimuthal num-

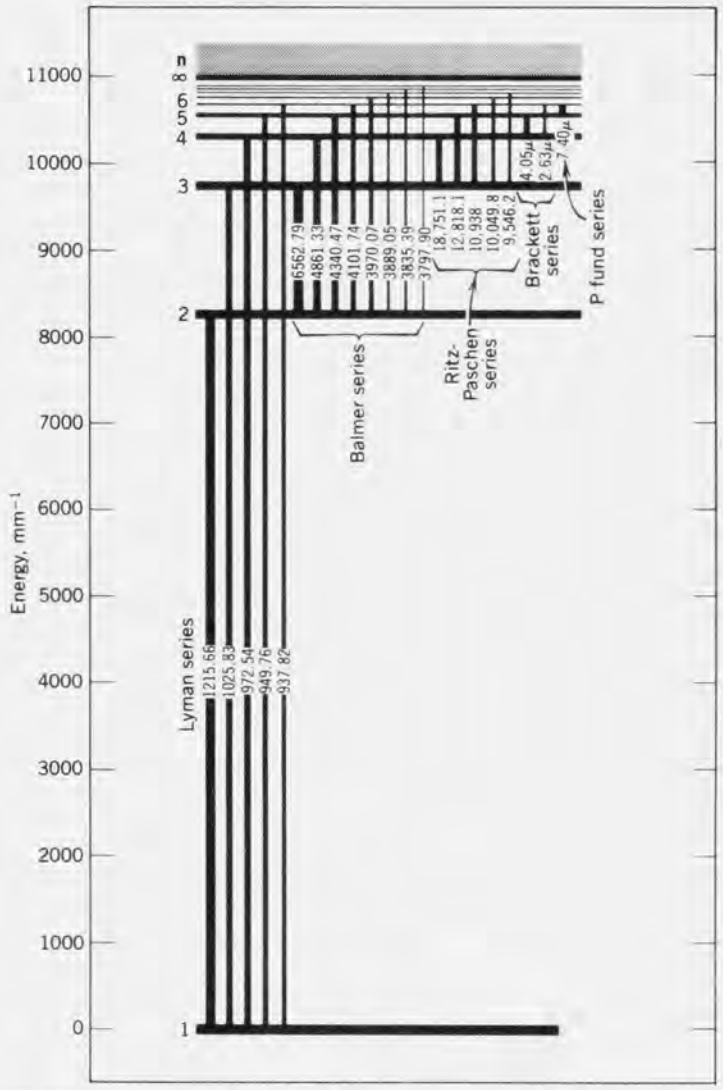


FIGURE 15.4 *Electronic energy levels of the hydrogen atom (From G. Herzberg, Atomic Spectra and Atomic Structure, Dover Publications, New York, 1944, p. 24).*

ber l, are shown in Fig. 15.5. The dashed lines indicate so-called forbidden transitions, which ordinarily are not observed in the spectra.

The results discussed here for the hydrogen atom are the same as those found from Bohr's theory. We find very striking differences between the theories, however, even for hydrogen. In the new quantum or wave mechanics, the results follow directly from the sole assumption of the validity of the wave equation. Another important point is that, although the energy is sharply defined according to Eq. 15.55, there has been no mention of the nature of orbits as assumed by Bohr. Indeed, if we evaluate the wave function of Eq. 15.53 in terms of r, θ, and ϕ and

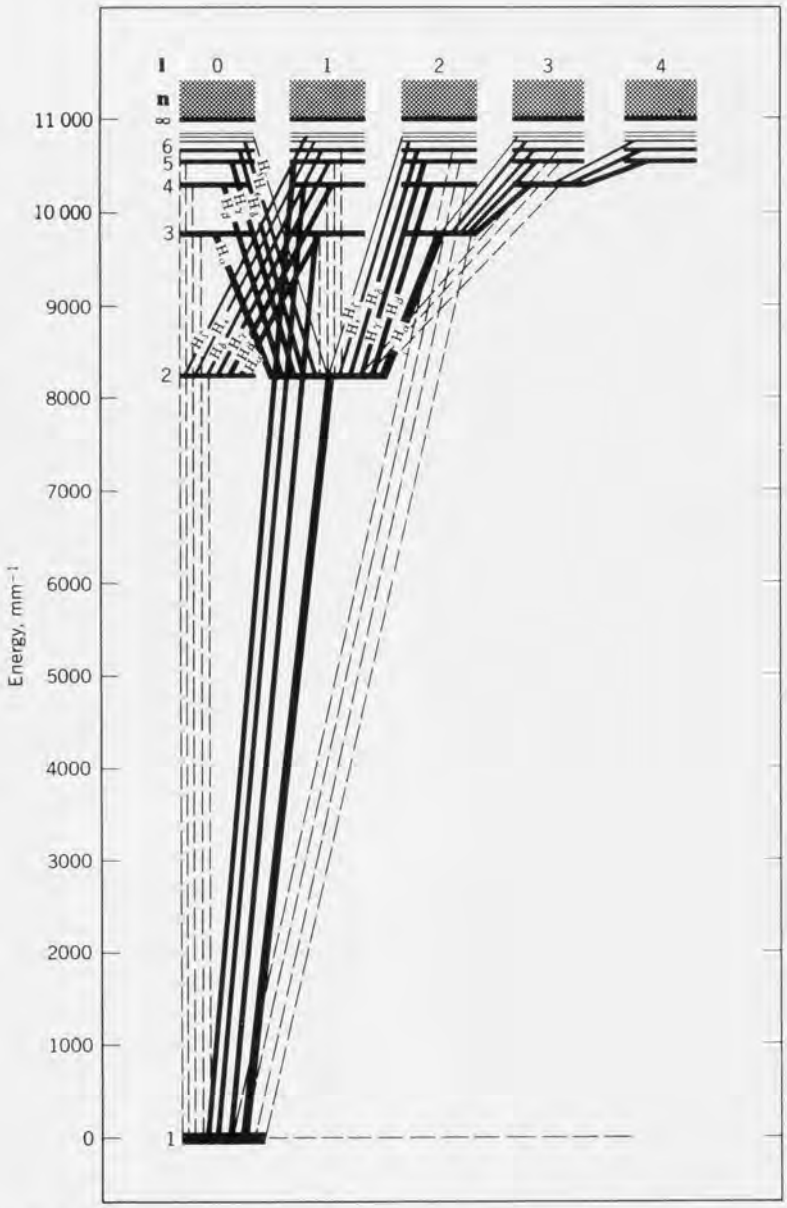


FIGURE 15.5 Electronic energy levels of the hydrogen atom (From G. Herzberg, *Atomic Spectra and Atomic Structure*, Dover Publications, New York, 1944, p. 26).

normalize in the three directions, the square of the result designates the probability of locating the electron in a certain position with respect to the nucleus. Let us consider here the radial direction r only. For given values of **n** (and energy) and **l**, the quantity Ψ^2 represents the probability of locating the electron within an element of volume. Since the volume element is represented by $4\pi r^2\, dr$, the probability that the electron will be found between r and $r + dr$ and with any values

of θ, ϕ is

$$4\pi\Psi^2 r^2\, dr$$

The nature of the function $\Psi^2 r^2$ is depicted in Fig. 15.6 for the first few values of **n** and **l**. It is of particular interest to compare the probability functions of Fig. 15.6 with the corresponding orbits of the Bohr theory shown in Fig. 15.1. The marks on the r-axes in Fig. 15.6 indicate the radii of the corresponding circular Bohr orbits, which are seen to coincide with the maxima of the probability function whenever $\mathbf{l} = \mathbf{n} - 1$. Whenever $\mathbf{l} \neq \mathbf{n} - 1$, there is more than one peak in the probability function, which corresponds to the elliptical orbits of the old theory. From this comparison, we can understand why Bohr's theory was able to predict certain behavior as well as it did, although it failed in other instances.

It should also be noted that in this model the values of the azimuthal and magnetic quantum numbers **l** and $\mathbf{m}_l$ give shape to the atom as they influence the wave function and, consequently, the probability in the θ and ϕ directions.

The fourth quantum number of the atom, the electron spin number $\mathbf{m}_s$, does not appear in our solution of the wave equation, but it does result logically in the more general solution. We can justify the existence of such a number here in the same way as it was done before the development of wave mechanics. It is observed that the spectral lines of certain atoms split into even-numbered multiples under the influence of a magnetic field, although the states of different $\mathbf{m}_l$'s split only into odd numbers 1, 3, 5, ... Therefore, there must be a fourth quantum number to account for this observed phenomenon. An electron that behaves as a tiny spinning

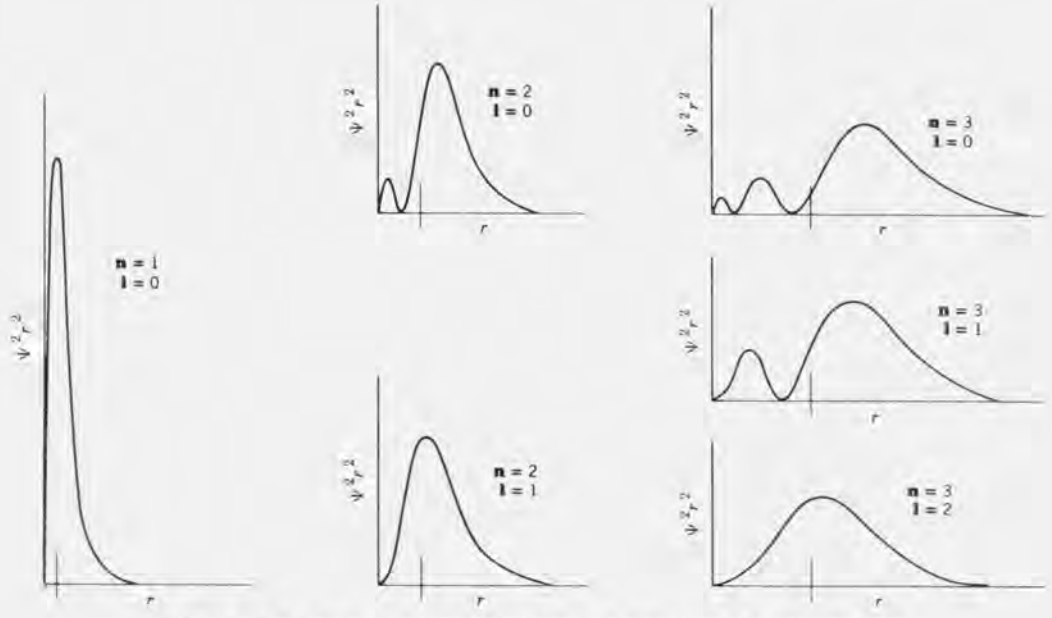


FIGURE 15.6 The radial probability function for the electron of a hydrogen atom.

TABLE 15.1

Electron State	$\mathbf{n}$	$\mathbf{l}$	$\mathbf{m}_l$	$\mathbf{m}_s$
$1s$	1	0	0	$\pm\frac{1}{2}$
$2s$	2	0	0	$\pm\frac{1}{2}$
$2p$		1	-1	$\pm\frac{1}{2}$
			0	$\pm\frac{1}{2}$
			$+1$	$\pm\frac{1}{2}$
$3s$	3	0	0	$\pm\frac{1}{2}$
$3p$		1	-1	$\pm\frac{1}{2}$
			0	$\pm\frac{1}{2}$
			$+1$	$\pm\frac{1}{2}$
$3d$		2	-2	$\pm\frac{1}{2}$
			-1	$\pm\frac{1}{2}$
			0	$\pm\frac{1}{2}$
			$+1$	$\pm\frac{1}{2}$
			$+2$	$\pm\frac{1}{2}$

magnet with $\mathbf{m}_s = \pm\frac{1}{2}$ (indicating the orientation of the spin angular momentum vector) resolves this problem. Table 15.1 lists the first few quantum states for the single electron of the hydrogen atom and shows the restrictions on the four quantum numbers. For the hydrogen atom in the absence of a magnetic field, the energy is primarily a function of the principal quantum number. Thus, there are two states of the same energy for the ground level ($\mathbf{n} = 1$), eight states of approximately the same energy for the first excited level ($\mathbf{n} = 2$), eighteen for the second excited level ($\mathbf{n} = 3$), and so forth. Since the energy actually depends slightly on $\mathbf{l}$ and $\mathbf{m}_l$, even for hydrogen, we must be careful not to say that these states have exactly the same energy.

The spectroscopic notation used to designate electron configuration is also listed in Table 15.1. In this notation the number refers to the value of $\mathbf{n}$ and the letter following denotes the azimuthal number $\mathbf{l}$. Values of $\mathbf{l}$ equal to 0, 1, 2, 3, . . . are designated by the letters s, p, d, f, ... For atoms having more than one electron, a superscript after the letter gives the number of electrons with those values of $\mathbf{n}$ and $\mathbf{l}$. For example, the symbol $2p^4$ means that four electrons have the numbers $\mathbf{n} = 2$, $\mathbf{l} = 1$.

So far we have discussed only the hydrogen atom because of its simplicity. The first logical extension of the theory would be to the He^+ ion, which has a nucleus of two protons, two neutrons, and a single electron. Evaluation of this problem is the same as for the H atom, except for a different Coulomb potential between the nucleus and electron. The complexity grows rapidly when we consider the helium atom, however, because there are two electrons instead of a single one. There will thus be a potential between each electron and the nucleus, and another between the two electrons. However, the potential between the electrons is relatively small,

and this is neglected to achieve a solution to the problem. The wave equation is then written for each electron, and after combination it is found that valid solutions exist only for sets of the quantum numbers discussed previously and as given in Table 15.1. There is an additional consideration now, namely the Pauli exclusion principle, which will be discussed in a later section. For the present, let us say that one statement of the exclusion principle is that no two electrons in a single atom may simultaneously have an identical set of quantum numbers. Therefore, again referring to Table 15.1, we conclude that, for the ground state of the helium atom, one electron has the numbers 1, 0, 0, $+\frac{1}{2}$, and the other has 1, 0, 0, $-\frac{1}{2}$. That is, if the numbers $\mathbf{n}$, $\mathbf{l}$, $\mathbf{m}_l$ are all the same for two electrons, their spins must be in opposite directions.

For more complex atoms with greater numbers of electrons, we find that, according to Pauli's exclusion principle, additional electrons must fall in successively higher states because the lower ones are already filled. As an example, the ground level of the oxygen atom has the electron configuration $1s^2 2s^2 2p^4$.

The periodic table of the elements is also readily understood in light of this theory. We consider two examples, the inert gases and the halogens. The inert gases—helium (2 electrons), neon (10), argon (18), krypton (36), xenon (54)—all have closed or filled outer shells or subshells and are therefore very stable and chemically inactive. (For Xe, there are no $4f$ electrons, which would have a higher energy than $5s$ and $5p$ electrons; hence the closed outer shell is $5p^6$.) On the other hand, the halogens—fluorine (9 electrons), chlorine (17), bromine (35), iodine (53)—all lack a single electron to complete a shell or subshell and are consequently very active chemically. (The situation with I is like that for Xe, the outer shell being $5p^5$.) Each of the halogens has a low-lying electronic state. The first few electronic states observed for several simple atoms are given in Table 15.2.

For the majority of substances the energy of the first excited electronic level is so high that at moderate temperature all but a negligible fraction of the atoms are in the ground level at any time. Even for such substances, it is necessary that the degeneracy of the ground level be known, and this can be found from the term symbol for the level.

The letters used for the atomic term symbols are similar to the lowercase letters used to indicate electron configuration. Of interest to us here, however, is the right-hand subscript on the term symbol, which gives the total angular momentum number $\mathbf{J}$ for the atom.

For each term there are $2\mathbf{J} + 1$ components of the total angular momentum along a chosen axis, each with essentially the same energy in the absence of a magnetic field. Therefore, there are $2\mathbf{J} + 1$ wave functions for each $\mathbf{J}$, and the degeneracy of each term is given by that quantity, $2\mathbf{J} + 1$. For example, the ground electronic level of monatomic oxygen is ${}^3P_2$, and the first two excited levels are ${}^3P_1$, ${}^3P_0$. Consequently, the corresponding degeneracies are 5, 3, 1, respectively. For hydrogen only the ground level is important at moderate temperature, since the first excited level is so high, but we draw the most important conclusion that the ground level degeneracy is equal to 2. We note also that the degeneracies of the next three terms are 2, 2, 4, for a total of eight states, all having very nearly the same observed energy, which of course is in agreement with our previous discussion and Table 15.1, where there are eight states of $\mathbf{n} = 2$.

TABLE 15.2 Atomic Energy Levels

Substance	Electron Configuration	Term Symbol	Energy, mm^{-1}
H (1 electron)	$1s$	$^2S_{1/2}$	0.00
	$2p$	$^2P_{1/2}$	8225.8907
	$2s$	$^2S_{1/2}$	8225.8942
	$2p$	$^2P_{3/2}$	8225.9272
	$3p$	$^2P_{1/2}$	9749.2198
He (2)	$1s^2$	$^1S_0$	0
	$1s2s$	$^3S_1$	15 985.0318
		$^1S_0$	16 627.170
N (7)	$1s^22s^22p^3$	$^4S_{3/2}$	0
		$^2D_{5/2}$	1 922.39
		$^2D_{3/2}$	1 923.31
O (8)	$1s^22s^22p^4$	$^3P_2$	0
		$^3P_1$	15.85
		$^3P_0$	22.65
		$^1D_2$	1 586.77
F (9)	$1s^22s^22p^5$	$^2P_{3/2}$	0
		$^2P_{1/2}$	40.40
	$1s^22s^22p^43s$	$^4P_{5/2}$	10 240.65

Source: From C. E. Moore, "Atomic Energy Levels," *National Bureau of Standards Circular* **467**, Vols. I–III (1949, 1952, 1958).

15.7 MOLECULAR ROTATION AND VIBRATION

In Section 15.5, we noted that in the simple internal model for a molecule, the rigid rotator, harmonic oscillator, and electronic level contributions to the internal mode wave equation are separable and can be solved and evaluated independently. We also noted that these solutions are quite difficult mathematically and are not discussed here. Instead, we will simply present the results for the discrete energy state so that these contributions to thermodynamic properties can be included in subsequent chapters.

Consider the rigid rotation of a diatomic molecule comprised of atoms 1 and 2, as shown in Fig. 15.7. The moment of inertia I_ϵ of the molecule is

$$I_\epsilon = \sum_i m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2 = \frac{m_1 m_2}{m_1 + m_2} r_\epsilon^2 = m_r r_\epsilon^2 \tag{15.58}$$

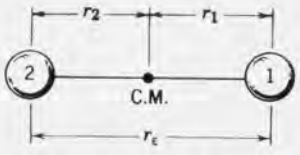


FIGURE 15.7 The coordinates of a diatomic rigid rotator.

Solution of the wave equation in the θ, ϕ directions for fixed r then yields the discrete rotational energy levels

$$\epsilon_r = \frac{h^2}{8\pi^2 I_r}\,\mathbf{j}(\mathbf{j}+1), \qquad \mathbf{j} = 0, 1, 2, 3, \ldots \tag{15.59}$$

where it is also found that these levels are degenerate. The degeneracy $\mathbf{g}_r$ is given by

$$\mathbf{g}_r = 2\mathbf{j} + 1 \tag{15.60}$$

In a similar manner, solution of the wave equation in the r direction for harmonic oscillation yields the discrete vibrational energy states

$$\epsilon_v = h\nu_e(\mathbf{v} + \tfrac{1}{2}) = hc\omega_e(\mathbf{v} + \tfrac{1}{2}), \qquad \mathbf{v} = 0, 1, 2, 3, \ldots \tag{15.61}$$

which are not degenerate.

The molecular constants r_e and ω_e for various molecules, as determined from spectroscopic data, are listed in Table A.19.1.

15.8 THE PAULI EXCLUSION PRINCIPLE

In this section we discuss the symmetry nature of wave functions and the Pauli exclusion principle.

For simplicity, let us consider two quantum states i and j, having energies ϵ_i and ϵ_j, respectively. Now suppose that there are two identical particles 1 and 2, one in each of the states i, j. This pair may be two electrons, two protons, and so forth. The total energy of the system, then, is

$$\epsilon = \epsilon_i + \epsilon_j$$

and we have a situation referred to as exchange degeneracy, since the system has the same energy whether particle 1 is in state i and particle 2 is in state j, or vice versa. The system wave functions describing these two possibilities can be written as the product of the single-particle wave functions, neglecting interactions,

$$\Psi_i(1)\Psi_j(2)$$

or

$$\Psi_i(2)\Psi_j(1)$$

The first combination is the product of the single-particle functions (including spin coordinates) for particle 1 in state i, particle 2 in state j. The second is the product of the functions for particle 2 in state i, particle 1 in state j. Obviously, both must satisfy the combined or system wave equation describing the two-particle system. We have a problem, though, in that either of these system functions considers that the two particles can be distinguished from one another, so that we can tell which particle is in which quantum state. Such a function would, of course, be unacceptable, for a basic hypothesis of quantum mechanics is that the particles are identical and indistinguishable. This difficulty is resolved when we realize that linear combinations of these functions must also satisfy the wave equation. We have two choices, then, for a system wave function—a symmetric function

$$\Psi_S = \Psi_i(1)\Psi_j(2) + \Psi_i(2)\Psi_j(1) \tag{15.62}$$

or an antisymmetric function

$$\Psi_A = \Psi_i(1)\Psi_j(2) - \Psi_i(2)\Psi_j(1) \tag{15.63}$$

The sign of the symmetric system wave function remains the same upon interchange of the coordinates of the two identical particles, but the antisymmetric system function changes sign if the particles are interchanged.

For any system of a pair of identical particles, either Eq. 15.62 or Eq. 15.63 must be valid (neglecting interaction). The important point is that both cannot be valid, because then their linear combination would also necessarily be valid, and we would be back to our original, unacceptable functions.

From experimentally observed behavior, particles with half-integral spin—electrons, protons, nuclei of odd mass number, for example—are found to have only antisymmetric states and wave functions. Particles with integral spin—photons, nuclei of even mass number—have only symmetric states and wave functions.

It is not difficult to construct symmetric or antisymmetric system functions from single-particle functions for a system of more than two quantum states and more than two identical particles. We realize immediately, however, that it is impossible to construct an antisymmetric function from a collection of single-particle functions if any two of the single-particle functions (that is, quantum states) are identical. In such a case these two states could be exchanged with no effect on the system function. We recognize this statement as one form of the Pauli exclusion principle presented earlier: no two electrons in an atom can simultaneously have an identical set of quantum numbers. Thus, we find that this statement is equivalent to the wave mechanical statement that the system wave function is antisymmetric. This, then, is the Pauli exclusion principle. For the electrons in an atom, it is commonly stated as follows. The wave function for any atom must be antisymmetric in all the electrons, since interchange of the coordinates of any pair must result in a sign change of the system function. We also note that the Pauli exclusion principle says nothing about any two particles that are not identical, as, for example, a proton and an electron, or about particles having symmetric wave functions.

To summarize, there are two classes of particles. For those that have antisymmetric system functions and are, therefore, subject to the Pauli exclusion principle, more than one particle is never allowable in a quantum state simultaneously. For those having symmetric system functions, however, there is no such restriction. We see that it will therefore be necessary to develop two statistical models to represent the possible distributions of particles among the various quantum states. This will be considered in the following chapter.

PROBLEMS

15.1 Consider the Bohr theory of the hydrogen atom. The proportionality constant C in the Coulomb potential has the value 8.98×10^9 J m/C^2.

(a) Show that the radii of the Bohr orbits are proportional to $\mathbf{n}^2$. Calculate the radius of the ground level orbit.

(b) Develop an expression for the change in energy corresponding to any change of $\mathbf{n}$ to $\mathbf{n}'$.

15.2 (a) In 1885, Balmer correlated hydrogen spectral data from the visible and near-ultraviolet region according to the expression

$$\nu = c\mathscr{R}\left(\frac{1}{2^2} - \frac{1}{\mathbf{n}^2}\right), \qquad \mathbf{n} = 3, 4, 5, \ldots$$

where $\mathscr{R}$ (called the Rydberg constant) has the value 10 968 mm^{-1}. Using the results of Problem 15.1 and Planck's relation, calculate the theoretical value of $\mathscr{R}$ according to Bohr's theory.

(b) The Lyman series for H in the far-ultraviolet region is expressed by the relation

$$\nu = c\mathscr{R}\left(\frac{1}{1^2} - \frac{1}{\mathbf{n}^2}\right), \qquad \mathbf{n} = 2, 3, 4, \ldots$$

Calculate the energy levels for H for both the Lyman and the Balmer series, and compare the results with Fig. 15.4. What is the ionization energy for atomic hydrogen?

15.3 A certain spectral series for singly ionized helium (He^+) is correlated by the formula

$$\nu = 4c\mathscr{R}\left(\frac{1}{(\mathbf{n}')^2} - \frac{1}{\mathbf{n}^2}\right)$$

where $\mathscr{R}$ has the value 10 972 mm^{-1}, nearly the same as the Rydberg constant of Problem 15.2. Discuss this expression in terms of the Bohr theory.

15.4 Explanation of the photoelectric effect was one of the early successes of quantum mechanics. For a given metal, it is found that light of less than a certain threshold frequency will not stimulate emission of electrons from the surface. Above this threshold frequency, the maximum kinetic energy of emitted electrons is directly proportional to frequency and independent of the intensity of the incident light. As explained by the quantum theory, the maximum kinetic energy of an emitted electron is the energy received from a photon of radiation minus an amount φ expended in escaping from the metal. For cesium, φ, called the work function, has the value 3.044×10^{-19} J. Show that light in the visible region of the spectra (400–700 nm) stimulates photoelectron emission in cesium.

15.5 Consider an α particle (the nucleus of a He^4 atom) traveling with a kinetic energy of 10^{-12} J. What is the de Broglie wavelength associated with this particle?

15.6 Suppose that the position of an electron moving in the x-direction is known to within 0.01 mm. What is the order of magnitude of uncertainty in the velocity of the electron? If the particle is an α particle instead of an electron, how is the result changed?

15.7 Verify that Eq. 15.37 is a solution of the Schrödinger wave equation for translational energy, Eq. 15.25.

15.8 Consider an electron gas confined in a volume of 1000 mm^3. Determine the spacing of adjacent translational energy states at the level where all three quantum numbers are 10 and at the level where all three quantum numbers are 10 000.

15.9 Repeat Problem 15.8 for

(a) Diatomic hydrogen.
(b) Diatomic chlorine.

15.10 Assuming that the contributions of translational and internal modes are independent (Eqs. 15.43 and 15.44), show that the Schrödinger wave equation applied to the molecule can be separated into the two parts, Eqs. 15.45 and 15.46.

15.11 Discuss the first 18 elements of the periodic table (hydrogen through argon) in terms of their respective ground level electron configurations.

15.12 Show that the rotational energy as given by Eq. 15.59 can be expressed in the form

$$\frac{\epsilon}{hc} = \frac{0.016\,863}{\dfrac{M_1 M_2}{M_1 + M_2} r_e^2} \mathbf{j}(\mathbf{j} + 1)$$

where r_e is in nanometers and ϵ/hc is in reciprocal millimeters.

15.13 (a) Calculate the spacing of rotational energy levels for diatomic hydrogen for the first five values of **j**. Compare the results with the spacings of Problem 15.9. (Use molecular constants from Table A.19.)

(b) Repeat the calculation for diatomic chlorine.

15.14 (a) Calculate the spacing of vibrational levels for diatomic hydrogen. Compare the result with the spacings of Problems 15.9 and 15.13.

(b) Repeat the calculation for diatomic chlorine.

15.15 (a) The first excited electronic level for diatomic hydrogen is 9017 mm^{-1} above the ground level. Compare this spacing with those of the rotational and vibrational levels.

(b) Repeat the calculation for diatomic chlorine, for which the first electronic level is 1815 mm^{-1} above the ground level.

15.16 In this chapter we have been concerned with the stationary states of particles, and consequently we have considered the time-independent Schrödinger wave equation. The general time-dependent Schrödinger equation is

$$\left(\frac{h^2}{8\pi^2 m}\right)\nabla^2\Psi - \Phi\Psi = \left(\frac{h}{2\pi i}\right)\frac{\partial\Psi}{\partial t}$$

Consider this equation applied to the x-direction only, for convenience. Using the procedures followed in Section 15.3, show that, if the potential energy Φ is not a function of time, the general wave function Ψ is separable to

$$\Psi(x, t) = \Psi(x)\varphi(t)$$

with two resulting expressions, one the relation

$$\varphi(t) = e^{-(2\pi i/h)\epsilon t}$$

and the other the time-independent Schrödinger equation, Eq. 15.17.

16

MOLECULAR DISTRIBUTIONS AND MODELS

In the previous chapter, the subject of quantum mechanics was introduced, with emphasis on determining the sets of discrete quantum states available for occupancy by the particles comprising a system. We now examine the nature of the distribution of particles among these quantum states. This matter requires some background in mathematical probability and statistics, the concepts of distributions of particles among available states, and the basic statistical models of thermodynamic analysis. All these topics are covered in the present chapter.

16.1 INTRODUCTION

We recall from Section 2.6 that the microscopic view of thermodynamic systems requires a detailed consideration of the energy associated with the particles making up the system. We discussed the various modes or general types of energy storage by molecules, without regard for specific values of energy allowable to the molecules in any of these modes. In Chapter 15 we studied this matter in detail and found the sets of quantum states available to the molecules.

In our analysis we will continue to consider only systems of independent particles, electrons, atoms, molecules, photons, and so on. Thus, we may speak of the energy of any individual particle without concern for the influence of other particles in the system. Solution of the wave equation for a particular energy mode (as, for example, translation in Eq. 15.42) yields a set of discrete quantum states available for occupancy by the individual particles. These quantum states should be considered part of the physical system, and not as properties of the particles. In general, the number of quantum states available is much larger than the number of particles, so that at any instant the majority of states are not occupied. Each quantum state is identifiable by a unique set of quantum numbers (such as 1, 4, 7 or 4, 1, 7 for translation), and has associated with it a specific value of energy. By this we mean that any particle occupying a certain quantum state must necessarily possess the energy and other characteristics of that state.

Again, using translational energy, Eq. 15.42, as an example, we note that for a given substance (which fixes the particle mass m) the quantum state energies are

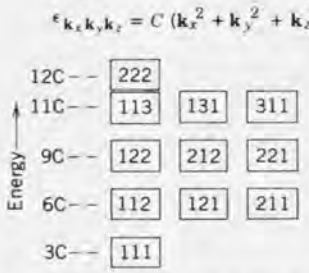


FIGURE 16.1 Translational quantum states.

fixed by specification of the system boundary parameters (volume, in the case of translation). If the boundary parameters are changed, then the energy value of each quantum state changes accordingly, quite irrespective of whether the state is occupied by a particle. It may be useful to imagine this set of quantum states as a group of boxes, with those at different heights or levels having correspondingly different values of energy. The lowest several quantum states for translation are shown in Fig. 16.1, with the set of translational quantum numbers identifying each of the states.

The basic problem in thermodynamics is the manner in which a fixed number of particles with a given total energy tend to distribute themselves among the available quantum states. In general, many of these quantum states have common values of associated energy, so that they can be conveniently grouped according to energy levels. For example, in Fig. 16.1 quantum states 112, 121, and 211 have exactly the same value of energy. And as stated in Chapter 15, the number of quantum states at each energy value or level is termed the degeneracy of that level. Thus, the analysis of particle distributions is commonly made over degenerate energy levels instead of over the individual quantum states. Such analysis becomes extremely complex, because in general we are concerned with systems containing billions of particles and even larger numbers of quantum states. Therefore, we must rely on certain statistical and averaging techniques in our calculations. To develop the appropriate analytical models and techniques, we need to introduce the fundamental concepts and terminology of mathematical probability and statistics, and particularly to examine a number of basic combinatorial problems.

16.2 MATHEMATICAL PROBABILITY

The subject of mathematical probability has a long history, having been developed formally over the past 300 years. Although we all have an intuitive feeling for this subject, there are many seemingly simple problems in which intuition may lead us astray. This is commonly due to a misinterpretation of the possible outcomes of a test or experiment. For example, suppose we toss a pair of fairly weighted coins simultaneously and inquire about the probability that both will come up heads. It is perhaps a natural mistake to list the possible outcomes of this experiment as two heads, two tails, and one head and one tail. We would then be led to assign

a probability of $\frac{1}{3}$ to each of these outcomes. If this experiment is actually performed a number of times, however, it will soon become apparent that the relative frequencies of the outcomes just listed approach the values $\frac{1}{4}$, $\frac{1}{4}$, and $\frac{1}{2}$. The reason for this apparent paradox is quite simple. There are four true outcomes to this experiment: H–H, T–T, H–T, T–H. Having no information to lead us to believe that these outcomes are not equally likely, we assign a probability of $\frac{1}{4}$ to each. (The last two correspond to one head and one tail, so that this probability becomes $\frac{1}{2}$.)

This simple example leads to a formal definition of the mathematical probability of an event as the limiting value of the relative frequency of occurrence of that event when the experiment is repeated a large number of times. Frequently, it is possible to calculate probabilities a priori (by recognizing all the possible outcomes), so that it is unnecessary to actually perform the experiment. For such cases, it is convenient to state the definition of probability as follows.

If there are N mutually exclusive, equally likely outcomes of an experiment, M of which result in a certain event A, then the probability of A is given by the ratio M/N. That is,

$$P(A) = M/N \tag{16.1}$$

The term mutually exclusive means that no two of the N outcomes can occur simultaneously. This term will be discussed later in this section.

This probability can be represented pictorially by setting up a sample space as shown in Fig. 16.2. Each of the possible outcomes of an experiment is represented by a point (or unit area) in the space S, which is set up with a uniform point density. The outcomes favorable to event A fall inside area A and those resulting in other events fall elsewhere in the total area S. Thus, in accordance with our definition, the probability of event A is the ratio of area A to the total area S.

Consistent with our definition of probability are the following:

$$\begin{aligned} P(A) &= 0 \text{ constitutes an impossibility} \\ P(A) &= 1 \text{ constitutes a certainty} \end{aligned} \tag{16.2}$$

In general, then, for any random event A,

$$0 \leqslant P(A) \leqslant 1 \tag{16.3}$$

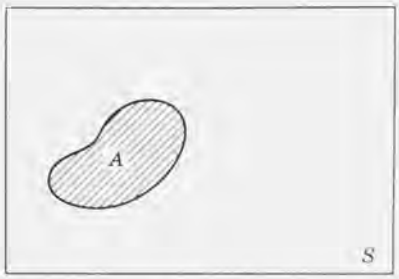


FIGURE 16.2 Outcomes of an experiment favorable to event A.

This discussion has concerned only simple probability. It does not include situations in which we have information about the experiment before it is conducted. This information, which will have some influence on our probability predictions, may be in the form of a restriction placed on the outcome, or it may concern the results of trials already completed.

Let us assume that event B depends in some manner on another event A. Of importance in such an instance is the conditional probability of B, denoted by the symbol $P(B/A)$, which is to be read as the probability of B given the fact that A has occurred. To clarify the difference between simple and conditional probabilities, consider the possible results of an experiment as shown in Fig. 16.3. It is apparent that

$$P(A) = \frac{\text{area } A}{\text{area } S}, \qquad P(B) = \frac{\text{area } B}{\text{area } S}$$

If we are given the information that A has occurred, then it is known that the result is a point somewhere inside the boundaries of A. The only portion of this area in which event B can occur is the intersection, labeled AB. Thus, we conclude that the conditional probability is given by

$$P(B/A) = \frac{\text{area } AB}{\text{area } A}$$

That is, the information conveyed to us has enabled us to reevaluate the probability that B will occur, which can be seen by comparing the area ratios.

Related to this discussion is the topic of the compound probability AB, that is, the probability that both A and B will occur. From Fig. 16.3 we note that the area of intersection is AB, so that in accordance with the definition of probability,

$$P(AB) = \frac{\text{area } AB}{\text{area } S}$$

It follows from our discussion and from the products of area ratios that

$$P(AB) = P(A) \times P(B/A) \tag{16.4}$$

and it is similarly apparent that

$$P(AB) = P(B) \times P(A/B) \tag{16.5}$$

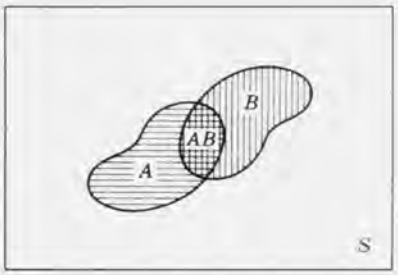


FIGURE 16.3 Representation of the intersection of two events.

Two other definitions are of interest at this point, those of independent events and mutually exclusive events. Event B is said to be independent of event A if

$$P(B/A) = P(B) \tag{16.6}$$

It follows from Eqs. 16.4 and 16.5 that event A must be independent of event B, according to a similar equation. Two events A and B are said to be mutually exclusive if they do not intersect, that is, if

$$P(AB) = 0 \tag{16.7}$$

This requirement was used in connection with the definition of probability according to Eq. 16.1.

EXAMPLE 16.1

A standard deck of playing cards consists of thirteen cards in each of four suits. Two suits are red (hearts and diamonds) and two are black (clubs and spades). Each suit contains the cards 2, 3, 4, . . . , 10, J, Q, K, A. Two cards are drawn from a well-shuffled deck and placed face down on the table.

1. Without looking at either card, determine the probability that the second card drawn is an ace.
2. Suppose the first card drawn is turned over and found to be an ace. How does this knowledge influence the prediction of part 1?
3. What is the probability that both cards drawn are aces?

Solution

1. We are concerned here only with the second card drawn from the deck. The fact that one other card has already been placed apart from the remainder of the deck has no influence on our prediction regarding the second, since we do not know what the first card is. That is, no information was conveyed by the first draw. Thus, the second card could equally well be any of the cards in the deck, so $N = 52$. Of these, four cards would give the desired event B, the draw of an ace on the second draw,

$$P(B) = P(\text{ace}) = M/N = 4/52 = 1/13$$

2. In this instance we have received the information that the card of interest to us cannot possibly be the ace that was drawn first, but it could be any of the remaining 51. The number resulting in the desired event B has also been reduced by 1, for one of the four aces is gone. Let event A be the draw of an ace on the first draw; then event B is still the draw of an ace on the second draw. Event A tells us that there are only 51 possibilities, of which 3 are favorable to event B. Then the probability of event B given event A, $P(B/A)$, is

$$P(B/A) = P(\text{ace/one ace already drawn}) = 3/51 = 1/17$$

3. Defining events A and B as in part 2, we note that

$$P(A) = 4/52 = 1/13$$
$$P(B/A) = 3/51 = 1/17$$

Therefore, from Eq. 16.4, the probability that both cards are aces is

$$P(AB) = P(A) \times P(B/A) = 1/13 \times 1/17 = 1/221$$

16.3 PERMUTATIONS, COMBINATIONS, AND REPEATED TRIALS

In the preceding section, we have calculated probabilities in situations for which it was not difficult to determine the number of possible outcomes, either through intuitive reasoning or by direct counting. It is important at this point to develop analytical means for evaluating more complex situations.

Let us define a permutation of a group of objects as any specific arrangement or ordering of the members of the group. For example, consider the three letters ABC. There are six arrangements or permutations of the three letters:

$$\begin{array}{lll} ABC & BAC & CAB \\ ACB & BCA & CBA \end{array}$$

It is a simple matter to list all the possibilities here, but suppose we asked for the number of permutations of all the letters in the alphabet? It would be an extremely tedious, if not a hopeless, task to attempt to list all the possibilities.

In an effort to develop formulas for calculating permutations, let us analyze what has been done in listing the arrangements of the three letters ABC. In writing down any arrangement, there are three choices for the first letter, either A, B, or C. After this decision has been made, however, there are only two letters remaining and therefore two possible choices for the second member of the arrangement. Once the second letter has been selected, there is but one letter remaining and therefore only a single choice for the third letter in the arrangement. Thus, we find that there are

$$3 \times 2 \times 1 = 6$$

possible arrangements or permutations of the group of three letters. Looking at this problem in terms of sampling, we might alternatively say that it is possible to pick six distinguishable samples of three letters from this group.

By extending this analysis to increasingly more complex examples, we conclude that, for N objects, there are N choices for the first member of any arrangement, $N - 1$ choices for the second, . . . , and one for the Nth, so that the number of permutations of N objects considered as a group, ${}_N\mathscr{P}_N$, is

$${}_N\mathscr{P}_N = N(N-1)(N-2)\cdots 3 \times 2 \times 1 = N! \tag{16.8}$$

In the symbol used for the number of permutations, the subscript N before the symbol $\mathscr{P}$ denotes the number of objects in the group. The subscript N after the symbol specifies that all N objects were considered together, or we might say that the sample consisted of N objects. We have also introduced the factorial symbol $N!$, which is defined as the product of all integers from 1 to N. It is of interest to note that

$$N \times (N-1)! = N! \tag{16.9}$$

Consequently, Eq. 16.9 for $N = 1$ defines

$$0! = 1 \tag{16.10}$$

Up to this point, we have been concerned only with the possible arrangements of all the objects making up the group. Suppose we consider now the possibility of picking only a portion of the group. For example, the number of permutations of two letters from the group of four letters $ABCD$ is given by

AB	BA	CA	DA
AC	BC	CB	DB
AD	BD	CD	DC

or a total of 12. Analyzing the process, we find that there are four choices for the first letter and three for the second, giving the total number of possible arrangements

$$4 \times 3 = 12$$

as we found by direct listing.

Extending this reasoning to the general case, we may think of this process as the number of ways of picking a sample of M objects out of a group of N without replacement ($M \leqslant N$) or, in other words, the number of permutations of N objects taken M at a time without repetition. There are N choices for the first object, $N - 1$ choices for the second, . . . , and $N - M + 1$ choices for the Mth object. Therefore,

$${}_N\mathscr{P}_M = N(N-1)(N-2)\cdots(N-M+2)(N-M+1) \tag{16.11}$$

where the symbol ${}_N\mathscr{P}_M$ is read as the number of permutations of N objects taken M at a time.

Equation 16.11 can be converted to a more useful form by using the factorial expression

$$N! = N(N-1)\cdots(N-M+1) \times (N-M)! \tag{16.12}$$

Comparing Eq. 16.11 and Eq. 16.12, we have

$${}_N\mathscr{P}_M = \frac{N!}{(N-M)!} \tag{16.13}$$

We see that, for $M = N$, Eq. 16.13 reduces to Eq. 16.8 (since $0! = 1$), and the two are found to be consistent.

Equation 16.13 may be viewed in the following manner. Of the $N!$ permutations of N objects, there are $(N - M)!$ permutations of the $N - M$ objects remaining after M have been selected. Therefore, the number of permutations when only M are selected from the group of N, ${}_N\mathscr{P}_M$, is given by

$$(N-M)! \times {}_N\mathscr{P}_M = {}_N\mathscr{P}_N$$

In these considerations, we have not allowed repetition of symbols or, in terms of sampling, the sampling has been made without replacement. Suppose that repetition (or replacement) had been permitted. Now, for the problem of selecting two letters from the group $ABCD$, there would be four choices for the first, and four

for the second, or

$$4 \times 4 = 4^2 = 16$$

possible ways of choosing two of the four letters. In addition to the twelve outcomes given previously, there would now also be the four doubles AA, BB, CC, DD. In general, the number of ways of picking a sample of M objects from a group of N with replacement, or the number of permutations of N objects taken M at a time with repetition, is

$$_N\mathscr{P}_{M(\text{rep})} = N^M \tag{16.14}$$

instead of that given by Eq. 16.13.

There are other aspects to be considered. Suppose that, for a sample of M objects selected from a group of N, we are not interested in the order of the objects within the sample drawn. For example, in the problem of selecting two letters from the group $ABCD$, if order is not considered, there are only the six pairs,

$$\begin{array}{lll} AB & BC & CD \\ AC & BD & \\ AD & & \end{array}$$

instead of the twelve given previously. That is, all such pairs as AB and BA are no longer considered different. Since we are now interested only in selections of objects rather than arrangements, we use the terminology "number of combinations" instead of "number of permutations." For the preceding problem the number of combinations of four objects taken two at a time is 6. In a manner similar to our explanation following Eq. 16.13, we conclude that, to discount the order within the sample, the number of combinations of four letters taken two at a time should be the number of permutations of four objects taken two at a time divided by the 2! permutations of the two objects selected. Then the number of combinations is given by

$$\frac{(4!/2!)}{2!} = \frac{4!}{2!2!} = 6$$

as found earlier by counting.

The number of combinations of N objects taken M at a time (that is, the number of ways of choosing a sample of M objects from a group of N objects when the order within the sample is not to be considered) is given by

$$_N\mathscr{C}_M = \frac{_N\mathscr{P}_M}{M!} = \frac{N!}{M!(N-M)!} \tag{16.15}$$

Since the order within the sample of M is not to be considered, the number of combinations is given by the number of permutations of N objects taken M at a time divided by $M!$, the number of permutations of the M objects within the sample.

EXAMPLE 16.2

In how many ways can two cards be drawn from a standard 52-card deck, if (1) order is not considered and (2) order is considered?

Solution

1. If the order is not considered, then, from Eq. 16.15, there are

$$_{52}\mathscr{C}_2 = \frac{52!}{2!(52-2)!} = \frac{52 \times 51}{2} = 1326$$

different pairs that can be drawn.

2. If order is considered, then, from Eq. 16.13, there are

$$_{52}\mathscr{P}_2 = \frac{52!}{(52-2)!} = 52 \times 51 = 2652$$

possible outcomes, exactly twice that of part 1. Each of the pairs of part 1 must be considered as two separate pairs to account for their ordering. That is, 10H–6C is different from 6C–10H, where H and C refer to hearts and clubs.

The preceding example raises questions about which quantity is of more practical interest, permutations or combinations. This is a problem that must be faced in every analysis and one that should not be taken lightly. The only answer to be given is that each case is individual, and each time we must ask ourselves whether or not ordering is of importance. For example, in one form of the card game of poker, each player is dealt five cards before the game begins. The order in which the five cards in a hand were dealt to a player is of no significance, for the only thing of importance is the resulting group. On the other hand, in another form of the same game, each player is dealt only two cards at the beginning and receives the third, fourth, and the fifth individually at later times during the course of the game. Then the order in which the cards are received is certainly of concern to a player, for he or she is given additional information with each card and must attempt to reevaluate the chances for eventually winning the game. At the end of the game, the ordering has no effect on determining who is the winner, but order does influence the players during the game. A player who did not look at any of these cards until he or she had received all five would obviously be at a tremendous disadvantage in the long run. We can all, no doubt, think of many additional illustrations in which ordering within a sample or group is either of primary concern or of no importance whatsoever. There are also, of course, many complex situations in which such a decision is not at all obvious.

A combinatorial problem that will be of particular interest to us in analyzing molecular distributions follows from Eq. 16.15. Suppose that we are concerned with dividing a group of N distinguishable objects, not into groups of M and $N - M$, but into a large number of groups, with M_1 objects in group 1, M_2 objects in group 2, . . . , M_k objects in group k, where

$$\sum_{k=1}^{k} M_k = N$$

and where the order of objects within each of the k groups is not considered. The number of combinations $_N\mathscr{C}_{M_1,M_2,\ldots,M_k}$ can be deduced from a repeated application

of Eq. 16.15 to each of the groups $1, 2, \ldots, k-1$, with the result

$$N\mathcal{C}_{M_1, M_2, \ldots, M_k} = \frac{N!}{M_1!M_2! \ldots M_k!} = \frac{N!}{\prod_k (M_k!)} \tag{16.16}$$

The symbol $\prod_k$ in Eq. 16.16 will be used extensively to denote the continued product over all values of k.

Let us now utilize the results of this section to evaluate probabilities in repeated trials. We consider an experiment with two outcomes, success or failure. A success may be the appearance of heads in the toss of a coin. Therefore, the appearance of tails constitutes a failure. Or, in tossing a die, the appearance of a 3 may be the success, but then that of any of the five other numbers is considered a failure. For any trial, let the probability of success be p. Then the probability of failure is $1 - p$. For N trials, the probability of achieving N successes is p^N, since the trials are independent. Similarly, the probability that all N trials will result in failures is $(1 - p)^N$. It follows that the probability of achieving M successes immediately followed by $N - M$ failures is

$$p^M \times (1 - p)^{N-M}$$

The probability for M successes and $N - M$ failures in any specific order is also given by this expression, since the outcome of each of the N trials is specified as being a success or a failure. However, it may be possible to achieve M successes in N trials in more than one way, and usually we are not interested in the order in which the success appears during the experiment, but only in the final number of successes. Thus, we should multiply the probability of achieving M successes one way by the number of ways M successes out of N can occur without regard for order (the number of combinations of N objects taken M at a time). Consequently, it follows from Eq. 16.15 that the probability $P(M)$ of achieving M successes in any unspecified order out of N trials is

$$P(M) = \frac{N!}{M!(N - M)!} (p)^M (1 - p)^{N-M} \tag{16.17}$$

EXAMPLE 16.3

A fairly weighted coin is tossed six times in succession. What is the most probable number of heads? What is the probability of the most probable number?

Solution

The probability of obtaining heads on any single toss is 1/2. From Eq. 16.17 for $N = 6$,

$$P(M) = \frac{6!}{M!(6 - M)!} \left(\frac{1}{2}\right)^M \left(\frac{1}{2}\right)^{6-M}$$

where M is the number of heads. If all the possible values of M are evaluated, the probabilities are

M	$P(M)$
0	0.015625
1	0.09375
2	0.234375
3	0.3125
4	0.234375
5	0.09375
6	0.015625

The most probable number of heads is 3, which has a probability of 0.3125.

16.4 DISTRIBUTION FUNCTIONS, MEAN VALUES, AND DEVIATIONS

Suppose that we analyze the results of the preceding section, and in particular discuss Example 16.3 in detail. The number of heads, M, obtained in the six-coin-toss experiment may be viewed as a variable, one that may take on only the discrete values 0, 1, 2, . . . , 6. If we performed this experiment a great many times, we would expect the results to be distributed with a relative frequency close to the calculated values of $P(M)$. If these values are plotted on a histogram, the probabilities are symmetric about the most probable result, three heads, as shown in Fig. 16.4.

The function $P(M)$ may also be called a distribution function, and the distribution specified by Eq. 16.17 is called the binomial distribution. When the probability

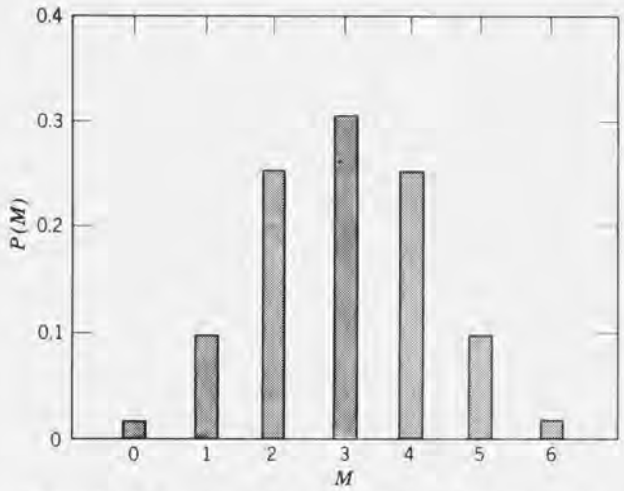


FIGURE 16.4 Histogram showing the results of Example 16.3.

function is used for this purpose, the distribution function is said to be normalized, since

$$\sum_M P(M) = 1 \tag{16.18}$$

Suppose that the six-coin-toss experiment is performed R times, where R is a very large number. The number of times that M heads will appear is $R \times P(M)$. The average number of heads occurring per trial, $\langle M \rangle$, which is also called the arithmetic mean value, is the sum of $M \times R \times P(M)$ over all values of M, with the total divided by the number of experiments R. That is,

$$\langle M \rangle = \frac{1}{R} \sum_M M \times R \times P(M) = \sum_M M \times P(M) \tag{16.19}$$

so that the mean value of M is independent of the number of trials, assuming that the number is sufficiently large. It can be shown by using Eq. 16.19 that the mean value of M for Example 16.3 is 3.0, the same as the most probable result.

In a similar manner, we could determine the mean value of the quantity M^2, which is designated $\langle M^2 \rangle$ and is found to be

$$\langle M^2 \rangle = \sum_M M^2 \times P(M) \tag{16.20}$$

a quantity that will be of interest to us. Note that the brackets indicate the mean value of the entire quantity inside them. For Example 16.3, the mean value of M^2 is found by Eq. 16.20 to be 10.50, which we note is not the same as the quantity $\langle M \rangle^2$.

Mean values such as those given by Eq. 16.19 or Eq. 16.20 supply some information but do not indicate the shape of the distribution. For this reason, it is necessary to have some knowledge about deviations from the mean value. We consider two such deviations here. The first is the average deviation from the mean value, which is given by

$$\langle M - \langle M \rangle \rangle = \sum_M (M - \langle M \rangle) \times P(M) = \sum_M M \times P(M) - \langle M \rangle \times \sum_M P(M)$$

Using Eq. 16.18 and Eq. 16.19 and the fact that $\langle M \rangle$ is a constant, this equation reduces to

$$\langle M - \langle M \rangle \rangle = \langle M \rangle - \langle M \rangle = 0 \tag{16.21}$$

which is consistent with the definition of the mean value. Thus, this deviation is of no help to us in describing the shape of the distribution. The second deviation to be examined is the mean-square deviation, also called the variance, σ^2, which can be expressed as

$$\begin{aligned}
\sigma^2 &= \langle (M - \langle M \rangle)^2 \rangle = \sum_M (M - \langle M \rangle)^2 \times P(M) \\
&= \sum_M (M^2 - 2M\langle M \rangle + \langle M \rangle^2) \times P(M) \\
&= \sum_M M^2 \times P(M) - 2\langle M \rangle \sum_M M \times P(M) + \langle M \rangle^2 \sum_M P(M)
\end{aligned}$$

Substituting Eqs. 16.18, 16.19, and 16.20 into this equation yields

$$\sigma^2 = \langle (M - \langle M \rangle)^2 \rangle = \langle M^2 \rangle - 2\langle M \rangle \times \langle M \rangle + \langle M \rangle^2 = \langle M^2 \rangle - \langle M \rangle^2 \tag{16.22}$$

A term commonly used in statistics is the standard deviation, σ, the square root of the variance given in Eq. 16.22. For Example 16.3, the variance is found from Eq. 16.22 to be

$$\sigma^2 = 10.50 - (3.0)^2 = 1.50$$

and the standard deviation is the square root of this number.

Figure 16.5 demonstrates the significance and usefulness of the standard deviation, σ. Both distributions have the same mean value $\langle M \rangle$. However, the distribution in Fig. 16.5*a* has a small value of σ, whereas that shown in Fig. 16.5*b* has a large σ. Thus, the standard deviation (or variance), together with the mean value, gives a meaningful description of the distribution in a variable.

We must keep in mind that, in the majority of practical applications, the approach is necessarily the opposite of that considered so far in this section. Commonly, the a priori probabilities and distribution functions are not known, and the role of statistics thus lies in the analysis of a set of experimental data, in terms of calculated mean values and standard deviations. In such analyses, the probabilities in Eqs. 16.19, 16.20, and 16.22 are simply the observed relative frequencies of occurrence, in accordance with our original definition of probability.

Of particular interest to us is the case in which the overall range of the discrete variable M is very large compared to the unit change in the variable, and in which the probability distribution function $P(M)$ changes by only a small amount for a unit change in the variable. We may approximate M very closely by a continuous variable x and $P(M)$ by a continuous function $P(x)$. This representation, shown in Fig. 16.6, may be viewed as the limiting case of a histogram like that of Fig. 16.4.

Now, for a continuous variable, the probability that the variable will have a value in the small interval between x and $x + dx$ is, as shown in Fig. 16.6,

$$P(x)\,dx$$

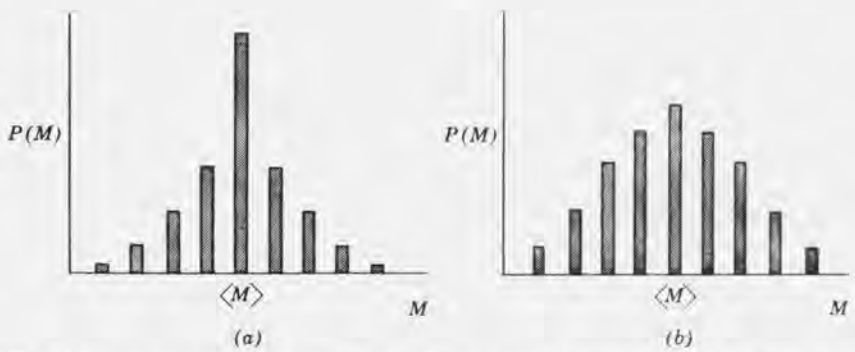


FIGURE 16.5 Histograms for distributions with different standard deviations. (*a*) Small value of σ; (*b*) large value of σ.

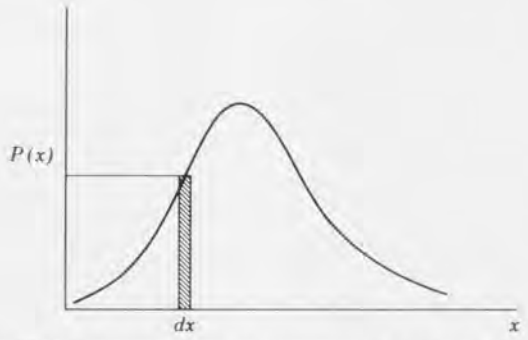


FIGURE 16.6 Representation of a continuous distribution function.

and, since the probability is used as the distribution function, the distribution is said to be normalized. That is, when it is integrated over all possible values of x,

$$\int P(x)\,dx = 1 \tag{16.23}$$

Equation 16.23 may be viewed as the limiting case of Eq. 16.18 as the intervals between discrete values of the variable become progressively smaller (relative to the range) and the distribution function are assumed to be continuous. In a similar manner, the limiting case of Eq. 16.19 for the mean value of the variable is given by

$$\langle x \rangle = \int xP(x)\,dx \tag{16.24}$$

and, similarly, the subsequent three expressions are

$$\langle x^2 \rangle = \int x^2 P(x)\,dx \tag{16.25}$$

$$\langle x - \langle x \rangle \rangle = 0 \tag{16.26}$$

$$\sigma^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \tag{16.27}$$

These expressions are all analogous to those previously derived, of course, but we now have the obvious mathematical advantage of being able to work with integrals instead of summations. It will be very important for us to understand the conditions under which summations of functions of discrete variables can accurately be approximated by the integration of continuous functions. (This constitutes one of the fundamental differences between quantum mechanics and classical mechanics.) For our purposes, this question can be illustrated as follows. Consider some function $f(j)$, where j is an integer, and the function is such that $f(j)$ changes only very slightly from j to $j + 1$. In addition, the range of summation over j is from zero to infinity, and the function is such that $f(j) \to 0$ for large j. The question then becomes whether the approximation

$$\sum_{j=0}^{\infty} f(j) = \sum_{j=0}^{\infty} f(j)\,\Delta j \approx \int_0^{\infty} f(x)\,dx \tag{16.28}$$

is valid. A powerful mathematical tool to apply in providing an answer to this question is the Euler–Maclaurin summation theorem, which is given in Table A.18.

16.5 MOLECULAR DISTRIBUTIONS AND MODELS

As was mentioned briefly in Section 16.1, the basic problem in statistical thermodynamics is the analysis of molecular distributions among degenerate energy levels (quantum states grouped according to values of energy) at conditions in which the system energy and the total number of particles are fixed. This is a difficult problem and is further complicated by the question of an appropriate molecular model. To avoid encountering all the complicating factors at once, let us begin by analyzing an extremely simplified system.

Consider a certain energy mode and substance for which the appropriate system boundary parameter fixes the set of available quantum states shown in Fig. 16.7. This set of available states may be represented in terms of the degenerate levels $\epsilon_j = 0, 1, 2$ energy units with corresponding degeneracies $\mathbf{g}_j = 2, 2, 2$. We now consider the thermodynamic state with two identical particles that, according to quantum mechanics, are indistinguishable, and a system energy of two energy units. We assume that each of the six quantum states is equally likely for each of the two particles, which is a fundamental hypothesis of statistical mechanics.

We now define a system macrostate as a given distribution of "number of particles" among energy levels, without concern for further detail at the microscopic level (for example, we do not know whether a particle at level 1 is in quantum state 11 or 12). Thus, a macrostate is specified solely by a list of values N_j; in our simple example this means a set of the three numbers N_0, N_1, and N_2. Our first question, then, concerns the number of macrostates possible in this system. We recognize that the only macrostates allowable are those that satisfy the two system constraints

$$N = \sum_j N_j = 2$$

$$U = \sum_j N_j \epsilon_j = 2$$

It is easily found that there are only two possible macrostates, which we label A and B. These macrostates are shown in Table 16.1. If we were to observe the system at any instant, it would necessarily be found in one or the other of these two macrostates, because of the particle and energy restrictions that were imposed in the specification of the thermodynamic state. Our next question concerns the relative probabilities of each of the two macrostates. To answer this we must examine the system in greater detail at a particle or microscopic level. In macrostate A, for example, one of the particles is in energy level 0 and the other particle is in energy level 2. Since the particles are assumed to be indistinguishable from each other, this situation can encompass four different microscopic configurations: 01, 21 (state

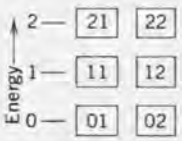


FIGURE 16.7 Set of quantum states.

TABLE 16.1 Number of Particles in Each Energy Level

Energy Level ϵ_j	Macrostate A	Macrostate B
2	1	0
1	0	2
0	1	0

01 occupied by a particle and state 21 occupied by a particle); 01, 22; 02, 21; and 02, 22.

Consequently, it is useful to define another term, the microstate. A microstate is an exact specification of the microscopic distribution of particles among available quantum states. Thus, a microstate gives total and complete knowledge of the particle configuration, consistent with the model to be used. Each of the four specifications listed is therefore a microstate corresponding to macrostate A. We will in general use the symbol w to denote the number of microstates consistent with a given macrostate. Thus, in our example,

$$w_A = 4$$

When we proceed in a similar manner to list the microstates corresponding to macrostate B, however, we encounter a difficulty noted earlier in Section 15.8, that there are two classes of particles. Those having antisymmetric system wave functions are subject to the Pauli exclusion principle and are not allowed to have more than one particle in a quantum state simultaneously. Conversely, there is no such restriction for those particles having symmetric system wave functions. This question did not come up in evaluating macrostate A, because the two particles were at different energy levels. Now, however, we find it necessary to develop two statistical molecular models, one or the other of which will be appropriate for any given substance. The first is for particles subject to the Pauli exclusion principle, that is, those with half-integral spin—electrons, protons, nuclei of odd mass number, for example. This is called the Fermi–Dirac model. In this model, macrostate B can occur from only one microstate, 11, 12. We find, therefore that

$$w_{B(\mathrm{F-D})} = 1$$

The second model is for particles with integral spin—protons, nuclei of even mass number, for example. This is called the Bose–Einstein model. In this model, macrostate B can occur from three microstates: 11, 12; 11, 11; and 12, 12. We find that

$$w_{B(\mathrm{B-E})} = 3$$

The assumption of equal probabilities for individual quantum states for a given particle is consistent with the assumption that the individual system microstates are equally likely to be observed at any given instant. In this context, w is a measure of the relative probabilities of the various macrostates, and for this reason is

commonly termed the thermodynamic probability of the macrostate. Since w_A is larger than w_B for either molecular model, we conclude that macrostate A in either case is the most probable macrostate for this system at the given conditions. The mathematical probabilities for both macrostates can be found by normalization over all microstates as

$$P(A) = \frac{w_A}{w_{\text{total}}} = \frac{4}{5}$$

$$P(B) = \frac{w_B}{w_{\text{total}}} = \frac{1}{5} \qquad \text{for the F–D model}$$

or

$$P(A) = \frac{w_A}{w_{\text{total}}} = \frac{4}{7}$$

$$P(B) = \frac{w_B}{w_{\text{total}}} = \frac{3}{7} \qquad \text{for the B–E model}$$

where w_{total} represents the total number of microstates for all possible macrostates. We find that the results are not the same, which is of course not surprising or inconsistent because only one of the models is appropriate for any given substance.

Let us now complicate the situation slightly by considering the set of available quantum states shown in Fig. 16.8. The thermodynamic state is, as before, two identical particles and a system energy of two energy units. The macrostates are still the same as those we found previously, macrostates A and B. However, the microstates for each are now more numerous and are as listed in Table 16.2. The mathematical probabilities of observing macrostate A or macrostate B are now found to be

$$P(A) = \frac{9}{12}$$

$$P(B) = \frac{3}{12} \qquad \text{for the F–D model}$$

or

$$P(A) = \frac{9}{15}$$

$$P(B) = \frac{6}{15} \qquad \text{for the B–E model}$$

depending on which molecular model is appropriate for the given substance.

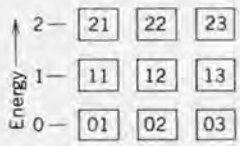


FIGURE 16.8 Set of quantum states.

TABLE 16.2 All Microstates Corresponding to the Two Macrostates

Macrostate *A* (F–D and B–E)	Macrostate *B* (F–D)	Macrostate *B* (B–E)
01, 21	11, 12	11, 12
01, 22	11, 13	11, 13
01, 23	12, 13	12, 13
02, 21		11, 11
02, 22		12, 12
02, 23		13, 13
03, 21		
03, 22		
03, 23		

When we apply these ideas to more complicated, realistic systems, we need to be able to evaluate situations in which the degeneracies at each energy level are not just two or three, but are instead very large numbers. Thus, we find it necessary to develop analytical formulas to calculate the number of microstates consistent with any given macrostate. In doing so, we first consider the two quantum statistical models, assuming identical and indistinguishable particles, one with a maximum of one particle per quantum state (Fermi–Dirac statistics) and the other with no restriction on the number of particles per quantum state (Bose–Einstein statistics). In each case we assume that a set of energy levels ϵ_j, with degeneracies $\mathbf{g}_j$, is available to the particles making up the system. There are N particles in the system, which has an energy of U.

FERMI–DIRAC STATISTICS

The Fermi–Dirac model assumes that the identical particles making up the system are indistinguishable from one another, and that there is a maximum of one particle per quantum state. Thus, for any macrostate, $N_j \leq \mathbf{g}_j$ for each energy level. Of the N particles in the system, for a given macrostate there are N_1 particles in level 1, N_2 in level 2, and so on. Since we cannot distinguish which particles are in which levels but only the numbers in each, the only factor to be considered is the number of ways that the N_j particles at each level can be distributed among the $\mathbf{g}_j$ states of that level, where $N_j \leq \mathbf{g}_j$. The indistinguishability of the particles complicates the analysis somewhat. If the particles were distinguishable, the number of ways of placing N_j particles in the $\mathbf{g}_j$ states would be given by Eq. 16.13 as

$$\frac{\mathbf{g}_j!}{(\mathbf{g}_j - N_j)!}$$

since there are $\mathbf{g}_j$ choices for the first particle, $\mathbf{g}_j - 1$ choices for the second, . . . , $\mathbf{g}_j - N_j + 1$ choices for the N_j^{th}, as in the analysis of the combinatorial problem. We can use this result if we divide it by the $N_j!$ permutations of the N_j particles to remove effectively their distinguishability from one another. Then the expression

becomes

$$\frac{\mathbf{g}_j!}{(\mathbf{g}_j - N_j)!N_j!}$$

Therefore, the thermodynamic probability for a given macrostate is the product of this factor over all levels; that is, for the Fermi–Dirac statistical model,

$$\mathrm{w} = \prod_j \frac{\mathbf{g}_j!}{(\mathbf{g}_j - N_j)!N_j!} \tag{16.29}$$

BOSE–EINSTEIN STATISTICS

The Bose–Einstein statistical model assumes, as does Fermi–Dirac statistics, that the particles are indistinguishable; but in this model there is no restriction on the number of particles per quantum state. As in the Fermi–Dirac model, we are concerned only with the number of ways that the N_j particles at each level can be distributed among the $\mathbf{g}_j$ states of that level. This turns out to be a very difficult question to answer for the assumed behavior, one which is best handled by resorting to a schematic example.

Let us consider a group of $\mathbf{g}_j$ boxes represented by the symbols $B_1, B_2, B_3, \ldots, B_{\mathbf{g}_j}$, and a group of N_j objects to be placed in the boxes. For the moment we assume the objects to be distinguishable from one another and represent them accordingly as $0_1, 0_2, 0_3, \ldots, 0_{N_j}$. Now consider any arrangement of the list of these $\mathbf{g}_j + N_j$ symbols that is completely arbitrary except that the list begins with the symbol B_1, for example,

$$B_1 \quad 0_2 \quad 0_7 \quad 0_5 \quad B_5 \quad B_3 \quad 0_4 \quad B_6 \quad 0_1 \quad 0_9 \ldots.$$

Let us read this arrangement of symbols as specifying the following particular distribution of objects in boxes: Box 1 contains objects 2, 7, 5 (in that order); box 5 is empty; box 3 contains object 4; box 6 contains objects 1, 9; and so on. After the symbol B_1, there are $(\mathbf{g}_j + N_j - 1)!$ permutations or arrangements of the $\mathbf{g}_j + N_j - 1$ symbols, and consequently this number of possible lists beginning with B_1. However, $(\mathbf{g}_j - 1)!$ Of these lists correspond to the same numbered objects in the same order placed in the same numbered boxes, if the relative positions of the $(\mathbf{g}_j - 1)$ B's (with their following 0's) are shifted. One such shift would be

$$B_1 \quad 0_2 \quad 0_7 \quad 0_5 \quad B_3 \quad 0_4 \quad B_5 \quad B_6 \quad 0_1 \quad 0_9 \ldots.$$

which gives exactly the same distribution as the preceding list. Therefore, the $(\mathbf{g}_j + N_j - 1)!$ lists are reduced by the factor $(\mathbf{g}_j - 1)!$ Now, recall that the objects are in reality identical and indistinguishable, so we are concerned only that there are any three objects in no specific order in box 1, no objects in box 5, any single object in 3, and so on. Thus, the number of lists of interest to us must be further reduced by the factor $N_j!$ permutations of the N_j objects. Consequently, the number of ways of placing the N_j indistinguishable objects in the $\mathbf{g}_j$ boxes with no restriction on the number per box is

$$\frac{(\mathbf{g}_j + N_j - 1)!}{(\mathbf{g}_j - 1)!N_j!}$$

This factor represents the number of ways of placing the N_j particles at each energy level in the $\mathbf{g}_j$ states at that level for the assumptions of this model. Consequently, the thermodynamic probability of a given macrostate is the product over all levels; that is, for the Bose–Einstein statistical model,

$$\mathrm{w} = \prod_j \frac{(\mathbf{g}_j + N_j - 1)!}{(\mathbf{g}_j - 1)! N_j!} \tag{16.30}$$

These general results, Eqs. 16.29 and 16.30, can be used to calculate the thermodynamic probabilities for the two simple examples discussed earlier, or for the more complicated situations in which the degeneracies are very large numbers. Many degeneracies are so large that for any energy level,

$$\mathbf{g}_j \gg N_j \tag{16.31}$$

Let us examine Eqs. 16.29 and 16.30 for this special case. Since

$$\frac{\mathbf{g}_j!}{(\mathbf{g}_j - N_j)!} = \mathbf{g}_j(\mathbf{g}_j - 1)(\mathbf{g}_j - 2) \cdots (\mathbf{g}_j - N_j + 1)$$

and each term on the right-hand side is approximately equal to $\mathbf{g}_j$, we find that Eq. 16.29 reduces to

$$\mathrm{w} = \prod_j \frac{\mathbf{g}_j(\mathbf{g}_j - 1) \cdots (\mathbf{g}_j - N_j + 1)}{N_j!} \approx \prod_j \frac{\mathbf{g}_j^{N_j}}{N_j!}$$

In a similar manner, since

$$\frac{(\mathbf{g}_j + N_j - 1)!}{(\mathbf{g}_j - 1)!} = \mathbf{g}_j(\mathbf{g}_j + 1)(\mathbf{g}_j + 2) \cdots (\mathbf{g}_j + N_j - 1)$$

and each term on the right-hand side is approximately equal to $\mathbf{g}_j$, we find that Eq. 16.30 reduces to

$$\mathrm{w} = \prod_j \frac{\mathbf{g}_j(\mathbf{g}_j + 1) \cdots (\mathbf{g}_j + N_j - 1)}{N_j!} \approx \prod_j \frac{\mathbf{g}_j^{N_j}}{N_j!}$$

In other words, in the special case in which Eq. 16.31 is valid, both quantum statistical molecular models converge to a common form

$$\mathrm{w} = \prod_j \frac{\mathbf{g}_j^{N_j}}{N_j!} \tag{16.32}$$

which is called the Boltzmann molecular model.

The molecular model expressed by Eq. 16.32 is often referred to as the "corrected" Boltzmann model, a consequence of correcting the statistical model developed from classical statistical mechanics to account for the indistinguishability of the particles. In this text we will simply call it the Boltzmann model, and recognize that this model is in fact an approximation to both of the quantum statistical models when Eq. 16.31 is valid. Let us now calculate the thermodynamic probabilities as predicted by this model for our two previous examples. In the first example, in which all the

degeneracies were 2, we find, from Eq. 16.32, that

$$w_A = \left(\frac{2^1}{1!}\right)\left(\frac{2^0}{0!}\right)\left(\frac{2^1}{1!}\right) = 4$$

$$w_B = \left(\frac{2^0}{0!}\right)\left(\frac{2^2}{2!}\right)\left(\frac{2^0}{0!}\right) = 2$$

We find that this model does predict the correct value of 4 for macrostate A, but the value for B should have been either 1 (for F–D) or 3 (for B–E) instead of 2.

Similarly, in the second example, in which all the degeneracies were 3, the Boltzmann model predicts

$$w_A = \left(\frac{3^1}{1!}\right)\left(\frac{3^0}{0!}\right)\left(\frac{3^1}{1!}\right) = 9$$

$$w_B = \left(\frac{3^0}{0!}\right)\left(\frac{3^2}{2!}\right)\left(\frac{3^0}{0!}\right) = \frac{9}{2} = 4.5$$

Again, the result is correct for A, but the value for B should have been either 3 (for F–D) or 6 (for B–E) instead of 4.5. Of course, we should not expect the Boltzmann model to be accurate for these examples, since the condition specified in Eq. 16.31 is certainly not met. We note that the Boltzmann model gives a value for thermodynamic probability in between those for the two quantum statistical models, and that it is somewhat closer, on a percentage basis, in the second example for which the degeneracies are larger.

Extending these conclusions, it seems reasonable that if the degeneracies of each energy level were larger, say 20, then the Boltzmann model should give a closer approximation to both of the quantum statistical models. In this case, for macrostate A, all three models, Eqs. 16.29, 16.30, and 16.32, give the value

$$w_A = 400$$

and for macrostate B, Eq. 16.29 gives the value

$$w_{B(F-D)} = 190$$

and Eq. 16.30 gives the value

$$w_{B(B-E)} = 210$$

The approximation of Eq. 16.32 gives the value

$$w_B = 200$$

which once again is in between the other two models, and in this case is accurate to approximately 5 percent for either one. Further extending the example to the point at which the degeneracy of each energy level is 200, we find that all the numbers are much larger and the Boltzmann approximation is now accurate to approximately 0.5 percent for either of the quantum statistical molecular models.

PROBLEMS

16.1 A box contains five white balls and three black balls. What is the probability that the second ball drawn from the box is white, if

(a) The color of the first is not known?
(b) The first is white?

16.2 There are ten coins in a box: four pennies, three nickels, two dimes, and one quarter. One coin is drawn out, and its denomination is not disclosed.

(a) What is the probability that the second coin drawn will be a nickel?
(b) If it is now learned that the first coin drawn is not a penny, what is the probability that the second will be a nickel?

16.3 In a certain manufacturing process it is known from previous experience that 70 percent of the finished parts are of acceptable quality.

(a) If two parts are selected at random, what is the probability that at least one will be acceptable?
(b) How many parts must one select to be 99 percent sure that at least one of them will be acceptable?

16.4 A system comprises electrical components, each of which is 99.99 percent reliable. If any component fails, the system fails. Find the probability that the system will operate properly, if the system is made up of

(a) Ten components.
(b) Five hundred components. (Use the binomial series.)

16.5 When we examine trials involving two events A and B, it is frequently of interest to determine the probability that either A or B or both A and B will occur. Show that this probability is given by the expression

$$P(A \text{ and/or } B) = P(A) + P(B) - P(AB)$$

16.6 Two types of missiles are fired at a target. Type A has a probability of 0.3 of scoring a hit, and type B a probability of 0.6. What is the probability that the target will be hit?

16.7 (a) How many seven-digit telephone numbers are there, if the only restriction is that the first digit cannot be a 0 or a 1?
(b) How many license plates can be made using two letters followed by four digits? By using three letters followed by three digits? By using six digits?

16.8 How many three-letter words can be constructed from the letters in the alphabet if no repetition of letters is allowed? How many combinations of letters taken three at a time are there? Explain why these results are different.

16.9 Find the number of ways that four pennies, three nickels, two dimes, and one quarter can be arranged in a line.

16.10 A shipment of 50 manufactured parts has been received from the factory. It has been decided that if 10 percent are defective, the shipment should be returned. Instead of testing all the parts, however, a sample will be taken and, if every part in the sample is reliable, the entire shipment will be accepted without further tests. Evaluate this

testing procedure if the sample consists of

(a) Five parts.
(b) Ten parts.

16.11 A fairly weighted coin is tossed ten times. Calculate the probabilities for each of the possible numbers of heads. How are these probabilities affected if the coin is weighted to land heads 60 percent of the time?

16.12 Five distinguishable balls are dropped at random into three boxes. What is the probability that three balls will be in the first box, two in the second, and zero in the third, if there is no limit on the number per box?

16.13 The experiment of Problem 16.12 is repeated with indistinguishable balls. Is the probability the same?

16.14 As a simple preliminary to the problem of mixing two substances, consider the following experiment. Box I contains two white balls, and box II contains two black balls. A ball is taken at random from box I and dropped into II, which gives an "intermediate result" of one ball in I and three in II. The trial is completed by taking a ball at random from II and dropping it in I. This two-step trial is to be repeated many times.

(a) Calculate the probabilities for each of the possible intermediate and final configurations for the first trial.
(b) Repeat part (a) for the second and third trials.
(c) What limits are approached as the number of trials becomes large?

16.15 Consider the example problem discussed briefly in Section 16.5, with energy levels of zero, one, and two units, each having a degeneracy of 20.

(a) Calculate the thermodynamic probability for each macrostate consistent with the thermodynamic state having two particles and a system energy of two units, assuming Fermi–Dirac statistics.
(b) Repeat part a assuming Bose–Einstein statistics.
(c) What is the accuracy of Boltzmann statistics as an approximation to the results of parts a or b?

16.16 Repeat Problem 16.15 for the case in which each degeneracy is 200 instead of 20.

16.17 Consider translational energy quantum states, as given by Eq. 15.42 and shown in Fig. 16.1. For the thermodynamic state with three particles and a system energy of $30C$ (where C is the proportionality constant shown in Fig. 16.1), determine the mathematical probability of the most probable macrostate, assuming Fermi–Dirac statistics.

16.18 Repeat Problem 16.17, but assume Bose–Einstein statistics.

16.19 A particular system has the available energy levels of zero, one, two, and three units, each with a degeneracy of 10. For the thermodynamic state of four particles and a system energy of three units, determine the thermodynamic probability of each of the possible macrostates, assuming Fermi–Dirac statistics and Bose–Einstein statistics.

16.20 Repeat Problem 16.19 for the thermodynamic state of eight particles and a system energy of six units.

16.21 Repeat Problem 16.20 for the situation in which energy levels of four, five, and six units are also available, in addition to those of zero, one, two, and three units.

16.22 Repeat Problem 16.19 for the thermodynamic state of twelve particles and a system energy of nine units.

16.23 Is the Boltzmann model a good approximation to either of the quantum statistical models for the situation of Problem 16.19? What if the degeneracy of each energy level is 100 instead of 10?

16.24 Determine the accuracy of the Boltzmann model in calculating the thermodynamic probabilities of the macrostates in Problem 16.20.

17

STATISTICAL MECHANICS AND THERMODYNAMICS

In the preceding chapter the concept of molecular distributions was developed by dealing with very simplified systems comprising a small number of independent particles and having a small number of available quantum states. Even so, it became necessary to develop analytical statistical models for the purpose of calculating the number of microstates corresponding to each macrostate of the system. In this chapter these results will be extended to the analysis of large-scale systems, for the ultimate purpose of determining thermodynamic properties and behavior.

We then consider the first and second laws of thermodynamics, as well as various thermodynamic properties, from a microscopic point of view. In so doing, we will relate the definitions of the properties and statements of the laws that are given in classical thermodynamics to the concepts and definitions of statistical thermodynamics, and thus demonstrate the added insight into the nature of physical processes that a microscopic point of view provides. In addition to discussing these quantities, we will develop expressions for thermodynamic properties of interest in terms of the partition function, so that the subsequent problem of evaluating properties will be focused on the determination of this quantity.

Since the developments of this chapter are based on the preceding chapter, we necessarily limit the discussion to systems of independent particles, and we will concentrate on systems for which the approximation of Boltzmann statistics is valid.

17.1 THE THERMODYNAMIC EQUILIBRIUM STATE

The basic problem in statistical thermodynamics is specifying the thermodynamic equilibrium state in terms of the appropriate independent variables. Consider as a thermodynamic system a gas enclosed in a rigid vessel, as shown in Fig. 17.1, with independent variables chosen to be U, V, and N. It is assumed that the gas is a pure substance, and the particles therefore identical, and also that the density is low, so that the particles may be considered independent. Specification of the volume V fixes the set of available quantum states, that is, a set of energy levels ϵ_j with corresponding degeneracies $\mathbf{g}_j$. Specification of the system mass N and energy U then places two constraints on the system macrostates (which are given by a set of numbers N_j). The only macrostates that are possible are those consistent

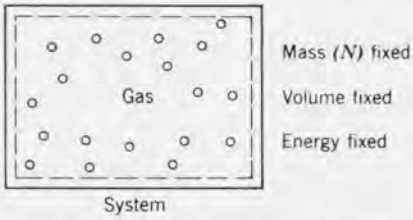


FIGURE 17.1 A thermodynamic system.

with the relations

$$N = \sum_j N_j \tag{17.1}$$

$$U = \sum_j N_j \epsilon_j \tag{17.2}$$

The concept of thermodynamic equilibrium assumes that all the macrostates (and microstates) consistent with these system constraints are accessible to the system, and it is a basic assumption of statistical mechanics that every microstate is equally likely. This means, then, that the macrostates are not equally likely. Since observed behavior at the macroscopic level in general varies with the macrostates, it is of interest to determine the relative probabilities of finding the system in its various macrostates. For this purpose it is necessary to use an appropriate statistical model and the corresponding expression for thermodynamic probability, as developed in Section 16.5.

We note that this problem is the same as that considered in Section 16.5, although here we assume a large-scale system, so that the numbers of particles N and energy levels ϵ_j (and their degeneracies $\mathbf{g}_j$ as well) are extremely large. Therefore, it is no longer possible to list directly the system macrostates, as was done in the earlier example. However, analyzing simple problems for which macrostates can be listed reveals that the thermodynamic probabilities of a small number of macrostates tend to dominate as the numbers N, ϵ_j, and $\mathbf{g}_j$ are made progressively larger, as is depicted schematically in Fig. 17.2. In statistical terminology, the distribution becomes very sharply peaked (a small standard deviation) about the mathematically

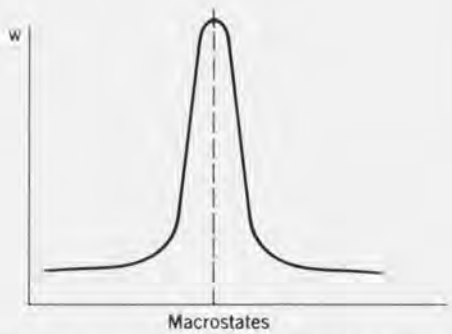


FIGURE 17.2 The thermodynamic probability for a large-scale system.

most probable macrostate. For the sizes of numbers corresponding to ordinary thermodynamic systems, this sharpness of distribution becomes extreme.

As a result of this behavior, we are able to draw a very important conclusion regarding the nature of thermodynamic equilibrium. Although we assume that all macrostates are accessible to the system, we conclude that a small number of these macrostates, clustered about the most probable, occur in such larger numbers of ways microscopically than do all the others that by comparison the number of ways in which the others occur is negligible. In other words, although equilibrium is recognized to be of a dynamic nature, with the system continually passing from one microstate to another, this characteristic is not observed at the macroscopic level, for essentially all the microstates assumed by the system correspond to macrostates that are nearly identical (within experimental limits). Small, short-term fluctuations from this group may be expected, but large or long-term fluctuations are extremely unlikely. Thus, in calculating the properties and behavior of a system at a condition of thermodynamic equilibrium, we may utilize the single mathematically most probable macrostate as representative of this small group of macrostates that actually occur.

For a given statistical molecular model (expressing thermodynamic probability for any given macrostate) the method of Lagrange undetermined multipliers enables us to determine analytically the most probable macrostate. Since the system is subject to two mathematical constraints, Eqs. 17.1 and 17.2, this result will be specified in terms of two undetermined multipliers, which must be evaluated by relating the mathematical results to the physical problem. At this point, we will simply determine the most probable macrostate in terms of the undetermined multipliers. We will carry through this mathematical procedure, assuming the approximation of Boltzmann statistics to be valid, so that the thermodynamic probability for a given macrostate is given by Eq. 16.32. For convenience, we rewrite this expression in logarithmic form:

$$\ln w = \ln\left(\prod_j \frac{\mathbf{g}_j^{N_j}}{N_j!}\right)$$

Since the logarithm of a product of quantities is equal to the sum of the logarithms, it follows that

$$\ln w = \sum_j (N_j \ln \mathbf{g}_j - \ln N_j!) \tag{17.3}$$

Now, assuming that N is very large and that the N_j's (for the levels that contribute significantly to w) are very large, we may accurately represent the factorials in Eq. 17.3 by Stirling's formula (Table A.18). Thus, Eq. 17.3 becomes

$$\ln w = \sum_j (N_j \ln \mathbf{g}_j - N_j \ln N_j + N_j) \tag{17.4}$$

To find the most probable macrostate, the maximum of w, we differentiate Eq. 17.4 with respect to N_j and set $d(\ln w)$ equal to zero. Since N and all the $\mathbf{g}_j$'s are constant, it follows that

$$d(\ln w) = \sum_j (\ln \mathbf{g}_j \, dN_j - \ln N_j \, dN_j - dN_j + dN_j) = 0 \tag{17.5}$$

Therefore, for the maximum of w,

$$d(\ln \mathrm{w}) = \sum_j \ln \frac{\mathbf{g}_j}{N_j}\, dN_j = 0 \tag{17.6}$$

However, from the system constraints, Eqs. 17.1 and 17.2,

$$dN = \sum_j dN_j = 0 \tag{17.7}$$

$$dU = \sum_j \epsilon_j\, dN_j = 0 \tag{17.8}$$

The most probable macrostate for Boltzmann statistics is given by Eq. 17.6, subject to the two constraints, constant N and U, that is, Eqs. 17.7 and 17.8. Consequently, the expression giving the maximum of w can be found by the method of Lagrange multipliers. Let us multiply Eq. 17.7 by some arbitrary value α, and Eq. 17.8 by some other constant β. Subtracting (for convenience) Eq. 17.6 from the sum of these gives the expression,

$$\sum_j \left(\ln \frac{N_j}{\mathbf{g}_j} + \alpha + \beta\epsilon_j \right) dN_j = 0 \tag{17.9}$$

The sum in Eq. 17.9 is taken over all energy levels, for example

$$j = 1, 2, 3, \ldots, J-1, J$$

or a total of J levels. However, only $J - 2$ of the N_j's are independent, because of the two restrictions. If the first two terms of the series in Eq. 17.9 are taken as the dependent terms, the multipliers α, β can then be selected for which the coefficients of dN_1 and dN_2 are identically zero. That is,

$$\ln \frac{N_1}{\mathbf{g}_1} + \alpha + \beta\epsilon_1 = 0 \tag{17.10}$$

$$\ln \frac{N_2}{\mathbf{g}_2} + \alpha + \beta\epsilon_2 = 0 \tag{17.11}$$

Since the remaining $J - 2$ variables are independent, $dN_3, dN_4, \ldots, dN_J$ can all be varied arbitrarily. Thus, the only way that Eq. 17.9 can be satisfied is for each of the coefficients to be identically zero, or

$$\ln \frac{N_j}{\mathbf{g}_j} + \alpha + \beta\epsilon_j = 0 \tag{17.12}$$

for all values of j. This is more conveniently written in the form

$$N_j = \mathbf{g}_j e^{-\alpha} e^{-\beta\epsilon_j} \tag{17.13}$$

This equation is called the Boltzmann distribution law, which specifies the most probable distribution of particles among energy levels. The distribution according to Eq. 17.13 is seen to be of an exponential form. Therefore, given values of the multipliers α, β, which remain to be determined, the general form of the distribution is that shown in Fig. 17.3. The shape of the curve depends considerably on the magnitudes of α and β.

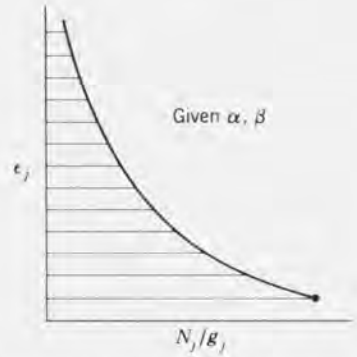


FIGURE 17.3 Exponential nature of the Boltzmann distribution function.

The molecular distribution for the most probable macrostate has been expressed in terms of the unknown multipliers α and β, according to Eq. 17.13. At this point, it is convenient to examine the relation between these parameters. If we substitute the distribution equation, Eq. 17.13, into the system mass constraint, Eq. 17.1, we have

$$N = \sum_j N_j = e^{-\alpha} \sum_j \mathbf{g}_j e^{-\beta \epsilon_j} \tag{17.14}$$

We note that the resulting expression can be used to eliminate α in terms of β and the basic energy state parameters ϵ_j, $\mathbf{g}_j$. Thus, the summation on the right side of Eq. 17.14 becomes of fundamental importance in statistical thermodynamics and is termed the partition function Z:

$$Z = \sum_j \mathbf{g}_j e^{-\beta \epsilon_j} \tag{17.15}$$

In words, the partition function is the summation over all energy levels j of the Boltzmann factor $e^{-\beta \epsilon_j}$ times the number of quantum states $\mathbf{g}_j$ at the level. Thus, the partition function could alternatively be expressed as the summation of the Boltzmann factor over all individual quantum states i,

$$Z = \sum_{i(\text{states})} e^{-\beta \epsilon_i} \tag{17.16}$$

if it is found more convenient to sum over individual states than over degenerate energy levels. It will also prove beneficial to our subsequent developments to recognize that the partition function is a fundamental thermodynamic property, expressable as

$$Z = Z(\beta, V) \tag{17.17}$$

because the available energy states are fixed and specified by the system boundary parameters (volume, for a simple compressible substance).

In terms of the definition of the partition function, Eq. 17.14 can be written as

$$e^{-\alpha} = \frac{N}{Z} \tag{17.18}$$

and, correspondingly, the distribution equation for the most probable macrostate, Eq. 17.13, can be written in the form

$$N_j = \frac{N}{Z}\mathbf{g}_j e^{-\beta\epsilon_j} \tag{17.19}$$

If this result is substituted into the system energy constraint, Eq. 17.2, we obtain

$$U = \sum_j N_j\epsilon_j = \frac{N}{Z}\sum_j \mathbf{g}_j\epsilon_j e^{-\beta\epsilon_j} \tag{17.20}$$

which includes a new summation that appears similar to that defining Z. Let us now differentiate Eq. 17.15, keeping in mind the functional relationship given by Eq. 17.17. It is found that

$$\left(\frac{\partial Z}{\partial \beta}\right)_V = -\sum_j \mathbf{g}_j\epsilon_j e^{-\beta\epsilon_j} \tag{17.21}$$

Substituting this into Eq. 17.20, we have

$$U = -\frac{N}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_V \tag{17.22}$$

This expression demonstrates the fundamental nature and importance of the partition function in statistical thermodynamics. We find that it is possible to express an important thermodynamic property U in terms of Z, so that evaluation of Z permits a direct calculation of the energy of a system at a given state.

Equation 17.22 is also useful at this point for identifying three areas of statistical thermodynamics that we wish to examine in the remainder of this text. These areas include (1) expression of other thermodynamic properties of interest in terms of the partition function; (2) identification of the multiplier β; and (3) evaluation of the partition function from the fundamental energy state parameters (which in general requires a solution of the wave equation, as discussed in Chapter 15). Before proceeding to these problems, however, we examine the first law and then entropy and the second law from a microscopic point of view.

17.2 THE FIRST LAW OF THERMODYNAMICS

Consider a thermodynamic system for which the first law of thermodynamics is given by Eq. 5.7. If kinetic and potential energy changes of the system as a whole are negligible, this equation reduces to

$$dU = \delta Q - \delta W \tag{17.23}$$

where the change in internal energy is given in terms of the two macroscopic energy-transfer quantities, namely heat transfer and work.

Let us now examine the change in internal energy of this system from a microscopic view. The energy of the system is given by Eq. 17.2:

$$U = \sum_j N_j\epsilon_j$$

It was found in Chapter 15 that the molecular energy values ϵ_j are fixed by specifying the system boundary parameter (V for a simple compressible substance). Therefore, we may write Eq. 17.2 in differential form as

$$\begin{aligned} dU &= \sum_j \epsilon_j \, dN_j + \sum_j N_j \, d\epsilon_j \\ &= \sum_j \epsilon_j \, dN_j + \sum_j N_j \left(\frac{d\epsilon_j}{dV} \right) dV \end{aligned} \tag{17.24}$$

where the second form emphasizes the dependency of ϵ_j on the boundary parameter V. We find that from the microscopic view the change in internal energy, Eq. 17.24, is expressed as the sum of two contributions, as in the macroscopic point of view, Eq. 17.23. The first contribution is the change brought about by a net redistribution of particles among the available energy levels. The second contribution is the change resulting from a shift in the magnitude of energy associated with each of the levels or groups of quantum states, this shift in turn being caused by a change in the system boundary parameters.

Let us now try to associate these two distinct contributions to Eq. 17.24 with the macroscopic quantities, work and heat transfer. For example, consider the work done when the system boundary of a simple compressible substance is allowed to move, as was analyzed in Section 4.3. If the driving force is only infinitesimally greater than that resisting the movement, the process will proceed very slowly and the system will pass through a series of equilibrium states. In such a reversible process, the work done at the moving boundary is given by Eq. 4.2:

$$\delta W_r = P \, dV$$

Note that the second term of Eq. 17.24 gives the change of energy associated with the volume change. We conclude that the second term of Eq. 17.24 and the macroscopic work both represent the energy change associated with the change in volume and are therefore equivalent. Equating the two, we have

$$\begin{aligned} \delta W_r &= -\sum_j N_j \, d\epsilon_j \\ &= -\sum_j N_j \left(\frac{d\epsilon_j}{dV} \right) dV \end{aligned} \tag{17.25}$$

In the general case, other thermodynamic driving forces and corresponding boundary parameters may be significant. Analysis of this possibility for the macroscopic view leads to Eq. 4.16, although from the microscopic view we recognize that the energy levels depend on whatever boundary parameters are important to the problem at hand. Therefore, in the general case, we again reach the conclusion that the identity of Eq. 17.25 is valid, although the second equality would have to be modified to account for the dependence of ϵ_j on all the boundary parameters.

Now by comparing Eqs. 17.23, 17.24, and 17.25, we conclude that the first term of Eq. 17.24 and the macroscopic heat transfer both correspond to the same effect, for a reversible process. That is,

$$\delta Q_r = \sum_j \epsilon_j \, dN_j \tag{17.26}$$

so that heat transfer can be visualized from the microscopic view as the energy change resulting in a net redistribution of particles among the available fixed energy levels.

To aid in the visualization of the quantities work and heat transfer, let us represent the change in energy resulting from two sequential processes as shown in Fig. 17.4. Figure 17.4*a* represents the equilibrium distribution in a system of some particular energy U. Consider first a reversible heat transfer to the system during a process in which there is no work; that is, the various boundary parameters such as volume are held constant. The energies of the various levels therefore remain fixed, and the increase in the energy of the system comes about solely from a net shifting of particles from lower levels to higher levels, as shown in Fig. 17.4*b*. Consider next a reversible adiabatic process in which work is put into the system, as for example by boundary movement. From the first law we conclude that the internal energy is increased. Taking a microscopic view, we see that the change in boundary parameters causes a shift in energy of the various levels, as shown in Fig. 17.4*c*. The increase in energy of the system comes from the shifting of the energy levels, and not from a net redistribution of particles among levels.

Although our example is an extremely simple one, the ability to visualize heat transfer or work on a microscopic scale should give us a further insight into the nature of these quantities, even if only for a reversible process. The nature of an irreversible process will be discussed in conjunction with the second law of thermodynamics in Section 17.4.

17.3 ENTROPY

Let us consider as a thermodynamic system two metal blocks that initially are at different temperatures. If these blocks are brought into thermal communication, they will gradually come to the same temperature, at a value intermediate to the two initial temperatures, by means of a spontaneous heat transfer. We say that in the final state the blocks have reached thermal equilibrium. The change occurred because of the initial imbalance in temperature, which is the driving force or

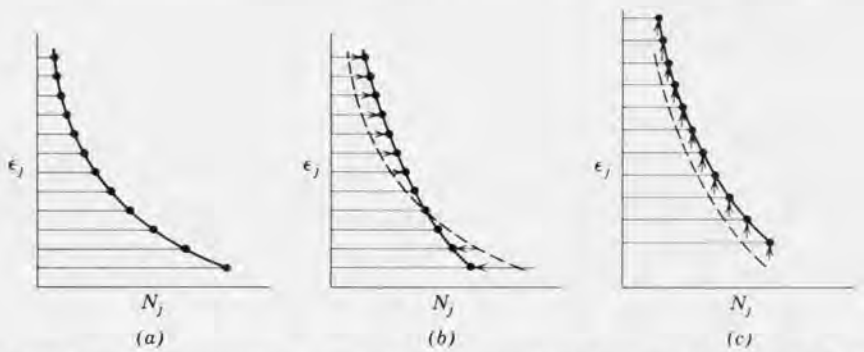


FIGURE 17.4 The microscopic viewpoint representation of the transfer of heat or work in a reversible process.

thermodynamic potential. If we also include other thermodynamic potentials (pressure, chemical potential, and so on), we say that a condition of thermodynamic equilibrium exists in a system when the system is at equilibrium with respect to all potentials. That is, there is no imbalance in any driving force, and consequently no tendency for any spontaneous change to occur. From the methods of classical thermodynamics, the equilibrium state of a system of a given mass, volume, and internal energy is the state of maximum entropy, as can be seen from the property relation, Eq. 8.5. Mathematically, this is stated as

$$dS_{U,V,m} = 0 \qquad \text{for an infinitesimal change}$$
$$\Delta S_{U,V,m} < 0 \qquad \text{for a finite change}$$

Let us now examine the system from a microscopic point of view. A particular macrostate or distribution d of particles among the various energy levels can occur in w_d ways, the thermodynamic probability for that macrostate. For an equilibrium state of the system of given V, N, U, all macrostates consistent with the system constraints are accessible or available to the system. Thus, the total number of microstates available to the system, w_{tot}, is the summation of w_d over all possible macrostates, or

$$w_{tot} = \sum_d w_d$$

On the other hand, we can also consider an inhibited state, one in which the system is restrained in some manner, at least temporarily, from reaching all possible macrostates (and microstates). The w_{tot} for such a state is some smaller number than that just given.

Comparing this microscopic view of the equilibrium state at fixed V, N, U with the classical concept, we conclude that the entropy should be directly related to the total number of microstates available to the system. We must keep in mind, however, that entropy is an extensive thermodynamic property; this statement means that if two independent systems are combined, their entropies are additive. If the entropy is directly proportional to $\ln w_{tot}$, this behavior will hold, since the total thermodynamic probabilities of two systems are multiplicative when the systems are combined. Finally, the constant of proportionality must have the units of energy per degree.

With these considerations in mind, we define entropy from the microscopic view by the expression

$$S = k \ln w_{tot} \tag{17.27}$$

where k is the Boltzmann constant.

The definition of S according to Eq. 17.27 has all the required characteristics of entropy discussed earlier. It remains to be shown that this definition is completely consistent with the classical definition of entropy from the second law of thermodynamics. Before proceeding to this demonstration, however, let us make a number of observations regarding Eq. 17.27. We note that there is an increase in entropy associated with a change from a given macroscopic state to a state that has a greater number of microscopic ways of occurring. In this sense, entropy can be considered a measure of disorder, randomness, or lack of information about the microscopic configuration of the particles making up the system. A perfectly

ordered system, with w_{tot} equal unity, corresponds to zero entropy and implies a complete knowledge of the microscopic state of the system.

Our principal concern in this text is with equilibrium states. Although all possible macrostates consistent with the constraints are available to the system, the most probable macrostate has a thermodynamic probability tremendously larger than all macrostates differing from it by a distinguishable amount. Thus, the thermodynamic equilibrium state may be represented for all practical purposes by the most probable macrostate, that is,

$$\ln w_{mp} \approx \ln w_{tot}$$

so that the entropy for an equilibrium state can be calculated from the expression

$$S = k \ln w_{mp} \tag{17.28}$$

In our consideration of equilibrium states, let us now express Eq. 17.28 in a more readily usable form. For Boltzmann statistics, the thermodynamic probability for any given macrostate is given by Eq. 16.32 which, in logarithmic form and with Stirling's formula for $N_j!$, is

$$\ln w = \sum_j N_j \left(\ln \frac{\mathbf{g}_j}{N_j} + 1 \right) \tag{17.29}$$

However, for the most probable macrostate, the ratio $\mathbf{g}_j/N_j$ can be eliminated by introducing the equilibrium distribution equation, Eq. 17.13. Substituting this into Eq. 17.29, we have

$$\begin{aligned} \ln w_{mp} &= \sum_j N_j \left[\ln \left(\frac{Z}{N} e^{\beta \epsilon_j} \right) + 1 \right] \\ &= \ln \frac{Z}{N} \sum_j N_j + \beta \sum_j N_j \epsilon_j + \sum_j N_j \\ &= N \ln \frac{Z}{N} + \beta U + N \end{aligned} \tag{17.30}$$

Therefore, the entropy of a system in an equilibrium state, Eq. 17.28, can be written in the form

$$S = k \ln w_{mp} = Nk \left(\ln \frac{Z}{N} + 1 \right) + k\beta U \tag{17.31}$$

Recognizing the functional dependencies of U and Z according to Eqs. 17.17 and 17.22, we note that Eq. 17.31 is of the form

$$S = S(N, \beta, V) \tag{17.32}$$

At this point, we do not know that the entropy, as defined conceptually by Eq. 17.27 and evaluated for an equilibrium Boltzmann system as Eq. 17.31, is the same function called entropy in classical thermodynamics. From the classical approach, entropy was defined for a reversible change of state by Eq. 8.2:

$$dS = \left(\frac{\delta Q}{T} \right)_{rev}$$

Let us now derive an expression for dS from the statistical point of view, by differentiating Eq. 17.31 at fixed N:

$$dS = k\left(\frac{N}{Z}\,dZ + \beta\,dU + U\,d\beta\right) \tag{17.33}$$

But from the definition of partition function, Eq. 17.15,

$$\frac{N}{Z}\,dZ = \frac{N}{Z}(-\beta)\sum_j \mathbf{g}_j e^{-\beta\epsilon_j}\,d\epsilon_j - \frac{N\,d\beta}{Z}\sum_j \mathbf{g}_j\epsilon_j e^{-\beta\epsilon_j} \tag{17.34}$$

If we assume the change to be reversible, however, the system passes through a sequence of equilibrium states, in such a manner that the equilibrium distribution equation, Eq. 17.13, must be valid at any point along the path. Substituting Eq. 17.13 into Eq. 17.34, we have, for the reversible process,

$$\frac{N}{Z}\,dZ = -\beta\sum_j N_{j\,\mathrm{mp}}\,d\epsilon_j - d\beta\sum_j N_{j\,\mathrm{mp}}\epsilon_j$$

Substituting Eqs. 17.2 and 17.25, we have

$$\frac{N}{Z}\,dZ = \beta\,\delta W_r - U\,d\beta \tag{17.35}$$

Now, substituting Eq. 17.35 into Eq. 17.33 and using the first law, Eq. 17.23, we have

$$\begin{aligned} dS &= k(\beta\,\delta W_r - U\,d\beta + \beta\,dU + U\,d\beta) \\ &= k\beta(\delta W_r + dU) \\ &= k\beta(\delta Q_r) \end{aligned} \tag{17.36}$$

From the previous expression and using Eq. 4.2 to represent the work term, we may write

$$dU = \frac{1}{k\beta}\,dS - P\,dV \tag{17.37}$$

This equation applies to a fixed quantity of mass. Let us add a term to allow for a mass variation, which results in

$$dU = \frac{1}{k\beta}\,dS - P\,dV + \mu\,dN \tag{17.38}$$

Here μ is called the chemical potential, which is the driving force causing a mass transfer. Now, since Eq. 17.38 is expressed in terms of the extensive properties U, S, V, and N, it may be integrated and then rearranged to the form

$$\begin{aligned} PV &= N\mu - U + \frac{1}{k\beta}S \\ &= N\mu - A \end{aligned} \tag{17.39}$$

in which

$$A = U - \frac{1}{k\beta}S \tag{17.40}$$

If we now differentiate Eq. 17.40 and substitute Eq. 17.38,

$$dA = dU - \frac{1}{k\beta} dS - S\, d\frac{1}{k\beta}$$

$$= -P\, dV + \mu\, dN - S\, d\frac{1}{k\beta} \tag{17.41}$$

In this form, we note that the quantity A is expressed as a function of V, N, and β, so that the chemical potential μ is recognized as

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{\beta,V} \tag{17.42}$$

To identify the right-hand side of Eq. 17.42, we rearrange Eq. 17.31 and use the definition of A from Eq. 17.40:

$$A = U - \frac{1}{k\beta} S = -\frac{N}{\beta}\left(\ln \frac{Z}{N} + 1\right) \tag{17.43}$$

Differentiating this expression, we obtain

$$N\mu = N\left(\frac{\partial A}{\partial N}\right)_{\beta,V} = -\frac{N}{\beta} \ln \frac{Z}{N} = A + \frac{N}{\beta} \tag{17.44}$$

Now, comparing Eqs. 17.39 and 17.44, we find that

$$PV = \frac{N}{\beta} \tag{17.45}$$

We are now in a position to identify the multiplier β from the two expressions, Eqs. 17.36 and 17.45. We note that if β is related to the classical concept of temperature as

$$\beta = \frac{1}{kT} \tag{17.46}$$

then, from Eq. 17.45,

$$PV = NkT \tag{17.47}$$

the ideal-gas equation of state, where the Boltzmann constant k is the universal gas constant divided by Avogadro's number, or

$$k = \frac{\overline{R}}{N_0} \tag{17.48}$$

It is logical to expect the ideal-gas model to be valid inasmuch as we originally assumed a system of independent particles, or no intermolecular potential energy, a situation that can be reasonable only for a gas of very low density. Now, in view of Eq. 17.46, we find from Eq. 17.36 that

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{rev}} \tag{17.49}$$

which is equivalent to the classical definition of entropy. We find that our concept of entropy as expressed by Eq. 17.27 does indeed have the required characteristics of entropy, as defined by classical thermodynamics.

Before we discuss the second law from the microscopic point of view, it is of interest to note that the function A defined by Eq. 17.40 is, using Eq. 17.46, the Helmholtz function as defined by Eq. 9.49, and the quantity μN is the Gibbs function as defined by Eq. 9.52.

17.4 THE SECOND LAW OF THERMODYNAMICS

We have discussed the quantities heat and work and have in the process examined the first law from a microscopic view. We now consider the second law of thermodynamics from a microscopic point of view, and again consider first the reversible process. We then examine the nature of irreversible processes from the microscopic view.

Suppose that a gas is contained in an insulated cylinder fitted with a frictionless piston, as shown in Fig. 17.5. The system initially has some known number of particles N, internal energy U, and volume V, and is assumed to exist at a condition of equilibrium. The pressure of the gas on the face of the piston is exactly balanced by the proper resisting force (including the contribution of ambient pressure on the back face of the piston). Now let the resisting force be reduced by an infinitesimal amount, which allows the piston to move very slowly toward the right. The gas will expand and, because the piston is moving slowly, the system will pass through a series of equilibrium states and undergo a reversible expansion. Since the cylinder is well insulated, we assume that no heat is transferred during the process.

From our discussion of the first law, we know that the energy change taking place in this system during the process described is due solely to a shifting of the energy levels and not to any net redistribution of particles among the levels. We note from Eq. 17.29 that, for the succession of equilibrium states the system passes through, the thermodynamic probability remains constant because there was no net redistribution of particles. Consequently, in accordance with our definition of entropy in Eq. 17.28, the entropy of the system remains constant during the process. The same conclusion is, of course, reached on the basis of classical thermodynamics, but the molecular point of view gives us another way of visualizing the concept of an isentropic process.

Let us now consider the opposite extreme, an irreversible expansion in which no work is done, as represented in Fig. 17.6. The tank is insulated, and a gas on the left side is restrained by a thin partition. The initial state of the gas is identical



FIGURE 17.5 *The reversible expansion of a gas.*

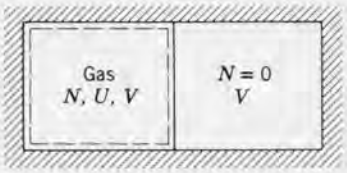


FIGURE 17.6 An irreversible expansion of a gas.

with that of the gas in the previous example: N particles, an internal energy U, and volume V. The equal volume on the other side of the partition in the tank is completely evacuated. If the partition is broken, the gas will expand to fill the entire volume. This expansion is irreversible and is certainly very different in nature from the reversible expansion examined previously.

If we analyze this process from a classical view, we are limited to a description of the system before the process and after the gas has again come to equilibrium at the end of the process. We do not know exactly what happened between these two end states, since the changes occurred very rapidly and the system was not at equilibrium. However, as in the first example, there is no heat transfer during the process because the tank is well insulated. Furthermore, in this process no work is done, since there was no resistance to the expansion, assuming that the hole in the partition was reasonably large compared to molecular dimensions. We therefore conclude from the first law that there is no change in internal energy during the process.

When we examine this process from a microscopic view, we cannot describe the series of states that the system passes through; this is the same difficulty that is encountered in an analysis from the macroscopic point of view. We are, however, able to make some interesting observations about the process. There is a change in volume, and consequently there will be a shift in the energy levels. Since no work was done during the process, Eq. 17.25, which applies to a reversible process, cannot in general be valid for the irreversible process as well. In addition, since the energy of the system remained constant, we conclude from Eq. 17.24 that there must have been some net redistribution of particles among levels during the process. Because there was no heat transfer, we conclude also that Eq. 17.26 is not in general valid for an irreversible process. (The heat transfer is given, however, by Eq. 17.26 for a process in which all the boundary parameters are fixed.) Consequently, our description of an irreversible process is quite limited in scope. We conclude that there is a general shifting of levels and of particles among levels, but we do not know the path followed—only the end states. However, the microscopic view gives us another means of regarding an irreversible process, and in this respect is very useful.

The microscopic point of view is even more useful and informative when we consider the second law for this process. Since the system is isolated from its surroundings (no energy transfer), from a classical view the second law of thermodynamics can be written, Eq. 8.16:

$$\Delta S_{\substack{\text{isolated} \\ \text{system}}} \geq 0$$

That is, the entropy change for an isolated system undergoing a spontaneous process will increase or, in the limit, for a completely reversible process, remain constant.

For an analysis from the microscopic view, let us imagine the system described in Fig. 17.6 at the instant after the partition has been broken, before the gas has begun to expand. It is possible, at least in theory, that at the moment that the partition is ruptured, none of the molecules in the vicinity of the hole is moving toward the partition, and consequently all the gas will remain on the left side of the container for a period of time. If the hole is extremely small, of molecular dimensions, this might seem reasonable, but it certainly is unacceptable to us if the hole is large, as we assumed previously. That is, although there is a probability that all the gas will remain on the left side, this probability is so small that we do not expect to observe this behavior in nature. Thus, it is overwhelmingly more probable that the gas will expand to fill the entire volume as the additional number of microstates becomes available to the system. Similarly, once the gas has filled the volume, there always exists the minute possibility that at some later time all the molecules will be found on the left side of the tank. But it is as unlikely that this condition will exist for any finite period of time as it is that the gas would have remained on the left side when the partition ruptured, for the number of microscopic states resulting in such a macroscopic configuration is infinitesimal compared to the total number of states available.

Since the total thermodynamic probability for the state associated with the gas filling the volume is much greater than that for the initial state of the gas on the left side of the tank, we find from Eq. 17.28 that the spontaneous process occurring when the partition breaks corresponds to an increase in entropy, which agrees, of course, with the classical statement of the second law. The microscopic approach is also very informative, however, because it gives a different view from which to examine the second law of thermodynamics and, in particular, a more meaningful concept of the thermodynamic equilibrium state and the property entropy. For any change of state of an isolated system (during which there is an increase in entropy), a larger number of microstates is made available to the system, as for example by the removal of some internal inhibition or restriction on the system.

We should always bear in mind that the second law of thermodynamics is our attempt to describe systematically certain aspects of phenomena that we observe in nature. However, the perspective of our description from the microscopic point of view is quite different from that of our description from the macroscopic point of view, and it provides very significant additional insight into the fundamental nature of the processes that give rise to the second law.

Before proceeding, we should mention that, although we have discussed only two specific examples, a completely reversible expansion and an irreversible one with no work output, there are any number of degrees of irreversibility between these extremes. For example, in the first example, if the resisting force on the piston is reduced by a finite amount, the process will proceed at a finite rate, and the system will not pass through a series of equilibrium states. The resulting process is irreversible to a certain extent, and the work done by the system on its surroundings will be some amount less than that for the reversible expansion. Therefore, the work and heat transfer are not in general given by Eqs. 17.25 and 17.26 since the process is not reversible, and the entropy will increase, although not as much as in a completely irreversible expansion.

Another factor causing irreversibilities is the mixing of two different substances. Consider an insulated tank containing two ideal gases A and B, initially separated by a partition as shown in Fig. 17.7. The number of molecules, N, of each gas is the same, and each gas initially occupies a volume V and is at temperature T. Gases A and B considered together constitute an isolated system, the entropy of which at the initial state 1 is

$$S_1 = S_{A1} + S_{B1} = k \ln w_{mp_{A1}} + k \ln w_{mp_{B1}} = k \ln(w_{mp_{A1}} \times w_{mp_{B1}}) \quad (17.50)$$

If the partition is now removed or broken, the two gases will gradually mix, and after a period of time the entire tank will be filled with a uniform mixture of A and B at a condition of equilibrium. The number of microstates consistent with the most probable macrostate in the mixture at state 2 will be the product of those for the two components as they exist in the mixture, and the entropy of the mixture is

$$S_2 = k \ln w_{mp_{AB2}} = k \ln(w_{mp_{A2}} \times w_{mp_{B2}}) \quad (17.51)$$

To determine the change in thermodynamic probability for A and B as a result of the mixing process, let us visualize the process in a manner similar to that used before. Immediately after the partition is removed, all the molecules of substance A are still on the left side of the tank and those of B on the right. Now there is certainly a possibility that A and B will remain for a period of time in this separated state, but we realize that, owing to the random motions of the molecules, the probability of the two gases mixing is much greater. That is,

$$\begin{aligned} w_{mp_{A2}} &> w_{mp_{A1}} \\ w_{mp_{B2}} &> w_{mp_{B1}} \end{aligned} \quad (17.52)$$

Using Eq. 17.52 to compare Eqs. 17.50 and 17.51, we find that the mixing process constitutes an increase in entropy, or

$$S_2 - S_1 > 0 \quad (17.53)$$

which is the result obtained from a classical analysis.

For this problem it is important to realize that if the same gas is initially on both sides of the partition, the preceding analysis is not valid. Once the partition is removed, we are no longer able to distinguish which molecules were initially on the left side and which were on the right. Consequently, the thermodynamic probability for the system after the partition is broken cannot be split into the probability associated with the molecules that started on the left side and the probability associated with those that started on the right side. The thermodynamic probability

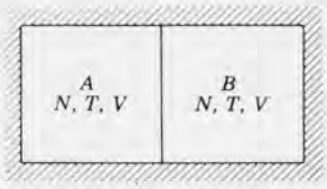


FIGURE 17.7 The mixing of two gases.

equals the product of the initial values of w for the two parts, and there is no change in entropy.

In this section we have discussed irreversibility resulting from unrestrained expansion (boundary movement at a finite rate resulting from a finite pressure difference) and that caused by mixing different substances. In general, any change driven by a finite imbalance in a thermodynamic potential is irreversible. Since the force resisting the change is a finite amount less than the driving force, the process occurs at a finite rate. Consequently, the system does not pass through a series of equilibrium states and the process is not reversible. Other examples of irreversibility, as discussed in Chapter 7, are processes involving friction, heat transfer through a finite temperature difference, and flow of electrical current through a finite resistance, which can similarly be examined from the microscopic point of view.

17.5 THERMODYNAMIC PROPERTIES

In earlier sections we developed a number of general equilibrium state equations for a system obeying the Boltzmann statistical model. These equations include Eq. 17.15 for the partition function, Eq. 17.19 for the equilibrium distribution, and Eq. 17.22 for internal energy, all from Section 17.1, and Eq. 17.31 for entropy, in Section 17.3. In that section we also demonstrated the general relationship between β and temperature, as given by Eq. 17.46. Because of this relation, we may now rewrite Eq. 17.15 as

$$Z = \sum_j \mathbf{g}_j e^{-\epsilon_j/kT} \tag{17.54}$$

Eq. 17.19 as

$$N_j = \frac{N}{Z} \mathbf{g}_j e^{-\epsilon_j/kT} \tag{17.55}$$

Eq. 17.22 as

$$U = \frac{NkT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_v = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_v \tag{17.56}$$

and Eq. 17.31 as

$$S = Nk\left(\ln \frac{Z}{N} + 1\right) + \frac{U}{T} \tag{17.57}$$

These four expressions now constitute the basic set or relations from which we will develop equations for other thermodynamic properties for Boltzmann systems.

The Helmholtz function A has been defined in Eq. 9.49, in connection with the second law of thermodynamics. We find from Eq. 17.43 that

$$A = U - TS = -NkT\left(\ln \frac{Z}{N} + 1\right) \tag{17.58}$$

Similarly, the Gibbs function is defined in Eq. 9.52. We find from Eqs. 17.44 and 17.58 that

$$G = N\mu = -NkT \ln \frac{Z}{N} \tag{17.59}$$

There is another development of interest concerning the equation of state. Suppose we consider a system in which the only significant boundary parameter is the volume. Then, for a small change occurring along a reversible path,

$$\delta W_r = P\,dV = -\sum_j N_j\,d\epsilon_j \tag{17.60}$$

But because the system passes through a series of equilibrium states, the equilibrium distribution equation, Eq. 17.55, may be substituted into Eq. 17.60, giving

$$P\,dV = -\frac{N}{Z}\sum_j \mathbf{g}_j e^{-\epsilon_j/kT}\,d\epsilon_j \tag{17.61}$$

Note that the summation in this equation is the same as that obtained by differentiating Z at constant temperature. If we do this,

$$dZ = -\frac{1}{kT}\sum_j \mathbf{g}_j e^{-\epsilon_j/kT}\,d\epsilon_j \tag{17.62}$$

we find that, at constant temperature,

$$P\,dV = \frac{NkT}{Z}\,dZ = NkT\,d\ln Z \tag{17.63}$$

Therefore, for a system at equilibrium,

$$P = NkT\left(\frac{\partial \ln Z}{\partial V}\right)_T \tag{17.64}$$

Because this development has been made for a system of independent particles, it follows that Eq. 17.64 must be identical with Eq. 17.47. A comparison of the two equations indicates that, for an ideal gas,

$$Z = V \times f(T) \tag{17.65}$$

An important consequence of Eq. 17.65 becomes evident if we use this equation in the evaluation of the internal energy from Eq. 17.56. Writing Eq. 17.65 in logarithmic form, we have

$$\ln Z = \ln V + \ln f(T)$$

It follows that

$$\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{d \ln f(T)}{dT}$$

Substituting this result into Eq. 17.56, we find

$$U = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V$$

$$U = NkT^2\left[\frac{d \ln f(T)}{dT}\right] = U(N, T) \tag{17.66}$$

We conclude that internal energy per unit mass will be expressed as some function of temperature only, and will not depend on volume (or pressure).

In practical applications, especially for tabulating the properties of a substance for use in thermodynamic calculations, it is convenient to write the equations for the various thermodynamic properties on a unit mole basis. Using Eq. 17.48 and the relation

$$n = \frac{N}{N_0} \tag{17.67}$$

we can write Eq. 17.47 as

$$P\bar{v} = \bar{R}T \tag{17.68}$$

which is, of course, the same as Eq. 3.1. Similarly, Eq. 17.56 becomes

$$\bar{u} = \frac{U}{n} = \bar{R}T^2\left(\frac{\partial \ln Z}{\partial T}\right)_V \tag{17.69}$$

We could write an equation for enthalpy in terms of the partition function. However, in practice, enthalpy is more easily calculated from its definition and Eq. 17.68 by

$$\bar{h} = \bar{u} + P\bar{v} = \bar{u} + \bar{R}T \tag{17.70}$$

In a similar manner, the specific heats $\bar{C}_v$ and $\bar{C}_p$ could be expressed in terms of the partition function, but they are more readily evaluated from their definitions. For the constant-volume specific heat, from Eqs. 5.14 and 17.66,

$$\bar{C}_{v0} = \left(\frac{\partial \bar{u}}{\partial T}\right)_v = \frac{d\bar{u}}{dT} \tag{17.71}$$

For the constant-pressure specific heat, from Eqs. 5.15, 17.66 and 17.70,

$$\bar{C}_{p0} = \left(\frac{\partial \bar{h}}{\partial T}\right)_p = \frac{d\bar{h}}{dT} \tag{17.72}$$

Equations for other thermodynamic properties discussed in this section are written on a mole basis, using Eqs. 17.48 and 17.67, as

$$\bar{s} = \frac{S}{n} = \bar{R}\left(\ln \frac{Z}{N} + 1\right) + \frac{\bar{u}}{T} \tag{17.73}$$

$$\bar{a} = \frac{A}{n} = -\bar{R}T\left(\ln \frac{Z}{N} + 1\right) \tag{17.74}$$

$$\bar{g} = \frac{G}{n} = -\bar{R}T \ln \frac{Z}{N} \tag{17.75}$$

PROBLEMS

17.1 Stirling's approximation for $N!$ (Appendix A.18) is used to determine the most probable macrostate in Section 17.1. Compare the value given by this expression with the correct value, for $N = 10$ and for $N = 50$.

17.2 The method of Lagrange undetermined multipliers is used to determine the most probable macrostate in Section 17.1. As a simple example of this technique, consider the following problem. A rectangle has a base x and height y, where $x + y = 8$. Use the method of Lagrange multipliers to find the values of x and y giving the maximum area.

17.3 A particular system has available energy levels of zero, one, and two units, and each of the energy levels has a degeneracy of 10^4. For the thermodynamic state of 2000 particles and system energy of 1000 units, find the most probable macrostate, assuming Boltzmann statistics.

17.4 A system contains 3000 particles and has an energy of 4100 units. There are three degenerate energy levels, of energies one, two, and three units, respectively. The degeneracies of the levels are large, equal numbers, much larger than the total number of particles in the system.

(a) One macrostate consistent with the given constraints is $N_1 = 2000$, $N_2 = 900$, $N_3 = 100$. Shifts of one particle from level 2 to 1 and one from 2 to 3 or shifts of one particle from level 1 to 2 and one from 3 to 2 represent small changes in both directions from the given macrostate. Calculate the ratio of thermodynamic probabilities for each of these small changes. Is the stated macrostate the equilibrium distribution that is consistent with the constraints?

(b) Determine analytically the equilibrium distribution for this system. Then use the particle-shifting procedure of part a to demonstrate that it is the equilibrium distribution.

17.5 What is the entropy of the system described in Problem 16.19? Is it reasonable to use the thermodynamic probability of the most probable macrostate for this calculation, as in the approximation of Eq. 17.28?

17.6 Repeat Problem 17.5 for the system described in Problem 16.20.

17.7 Calculate the entropy of the system described in Problem 17.3.

17.8 The entropy of 1 kmol of carbon dioxide gas is 213.794 kJ/K at 25°C, 100-kPa pressure. What is the thermodynamic probability of the most probable macrostate?

17.9 Consider 1 mol of a gas at room conditions, for which a typical value for $\ln w_{mp}$ is about 10^{25}. For developing Eq. 17.28 from Eq. 17.27, it is recognized that the most probable macrostate is not the only macrostate with a large thermodynamic probability, but is instead representative of a group of very similar macrostates. Suppose that there were 10^{10} macrostates with a value of w nearly as large as that for the most probable macrostate. Would it still be reasonable to use Eq. 17.28 for entropy?

17.10 The most probable macrostate in a thermodynamic system has been assumed to be extremely more likely than any macrostate differing from it by a distinguishable amount. For a volume V containing N particles at energy U, consider a macrostate d for which $N_j = N_{j\,mp} + \delta N_j$, where $|\delta N_j| \ll N_{j\,mp}$. Starting with Eq. 17.29, show

that the entropy for such a macrostate must be less than that corresponding to the most probable macrostate.

17.11 Consider 1 mol of gas having a macrostate d for which

$$\frac{|\delta N_j|}{N_{j\,\mathrm{mp}}} = 0.001 \text{ percent}$$

for every level j. Calculate the ratio of thermodynamic probabilities w_{mp}/w_d, and find the corresponding difference in entropies.

18

APPLICATIONS OF STATISTICAL THERMODYNAMICS

In Chapter 17, certain thermodynamic properties of interest were expressed as functions of the partition function, which is defined in terms of energy levels and their degeneracies. This partition function development is valid for systems obeying Boltzmann statistics, which is the approximation to both the Bose–Einstein and the Fermi–Dirac systems. The energies and degeneracies for the various energy modes had previously been evaluated in terms of the appropriate sets of quantum numbers in Chapter 15. In this chapter we proceed to use these results in considering various applications of statistical thermodynamics.

18.1 CONTRIBUTIONS TO THE PARTITION FUNCTION AND TO PROPERTIES

For Boltzmann statistics, the partition function has been expressed by Eq. 17.54:

$$Z = \sum_j \mathbf{g}_j e^{-\epsilon_j/kT}$$

Because the summation is to be made over all energy levels accessible to the molecule, it must include all the various modes of energy. It would prove convenient to separate this into summations over the individual energy modes. The degree to which such a separation can be carried depends on several factors (the substance and the range of temperature, for example), but in all cases we can separate the energy into translational and internal contributions in accordance with Eq. 15.43:

$$\epsilon = \epsilon_t + \epsilon_{\text{int}}$$

Since the corresponding wave functions Ψ (representing quantum states) are in such an instance multiplicative, as given by Eq. 15.44,

$$\Psi = \Psi_t \Psi_{\text{int}}$$

the component energy level degeneracies must also be multiplicative, or

$$\mathbf{g} = \mathbf{g}_t \mathbf{g}_{\text{int}} \tag{18.1}$$

Substituting Eqs. 15.43 and 18.1 into the partition function, Eq. 17.54, results in the separation

$$\begin{aligned} Z &= \sum_{\text{all } j} \mathbf{g}_{j_t}\mathbf{g}_{j\,\text{int}} \exp\left(-\frac{\epsilon_{j_t} + \epsilon_{j\,\text{int}}}{kT}\right) \\ &= \left[\sum_{j_t} \mathbf{g}_{j_t} \exp\left(-\frac{\epsilon_{j_t}}{kT}\right)\right]\left[\sum_{j\,\text{int}} \mathbf{g}_{j\,\text{int}} \exp\left(-\frac{\epsilon_{j\,\text{int}}}{kT}\right)\right] \\ &= Z_t Z_{\text{int}} \end{aligned} \tag{18.2}$$

where, by definition,

$$Z_t = \sum_{j_t} \mathbf{g}_{j_t} \exp\left(-\frac{\epsilon_{j_t}}{kT}\right) \tag{18.3}$$

$$Z_{\text{int}} = \sum_{j\,\text{int}} \mathbf{g}_{j\,\text{int}} \exp\left(-\frac{\epsilon_{j\,\text{int}}}{kT}\right) \tag{18.4}$$

Thus, the partition function can be written as the product of the translational partition function, Eq. 18.3, and of the internal partition function, Eq. 18.4. The first of these equations can be readily evaluated by using the expression for translational energy found from quantum mechanics in Chapter 15. The evaluation of the second equation usually proves more difficult, depending on the number of modes contributing internally (in general, rotational, vibrational, electronic) and the degree to which they can be separated from one another.

Having found that the partition function can be separated into a product having translational and internal modes of energy, let us now substitute Eq. 18.4 into our equations for the thermodynamic properties. From Eq. 17.69,

$$\begin{aligned} \bar{u} &= \overline{R}T^2\left[\frac{\partial \ln(Z_t Z_{\text{int}})}{\partial T}\right]_V \\ &= \overline{R}T^2\left(\frac{\partial \ln Z_t}{\partial T}\right)_V + \overline{R}T^2\left(\frac{\partial \ln Z_{\text{int}}}{\partial T}\right)_V \\ &= \bar{u}_t + \bar{u}_{\text{int}} \end{aligned} \tag{18.5}$$

We find that the internal energy can be calculated as a sum of contributions, the contribution which is due to translation,

$$\bar{u}_t = \overline{R}T^2\left(\frac{\partial \ln Z_t}{\partial T}\right)_V \tag{18.6}$$

and the contribution resulting from the internal modes,

$$\bar{u}_{\text{int}} = \overline{R}T^2\left(\frac{\partial \ln Z_{\text{int}}}{\partial T}\right)_V \tag{18.7}$$

The enthalpy of an ideal gas can now be found from Eq. 17.70 to be

$$\bar{h} = \bar{u} + P\bar{v} = \bar{u} + \overline{R}T = \bar{u}_t + \bar{u}_{\text{int}} + \overline{R}T$$

This can also be expressed as

$$\bar{h} = \bar{h}_t + \bar{h}_{\text{int}} \tag{18.8}$$

if the translational enthalpy is defined as

$$\bar{h}_t = \bar{u}_t + \bar{R}T \tag{18.9}$$

It is then noted that the internal contribution to enthalpy and internal energy are the same:

$$\bar{h}_{\text{int}} = \bar{u}_{\text{int}} \tag{18.10}$$

The $\bar{R}T$ term has been associated with the translation in Eq. 18.9. This can be justified from experimental observation for substances having no internal contributions. We might alternatively justify this by using the expression developed for pressure in Chapter 17, Eq. 17.64:

$$P = NkT\left(\frac{\partial \ln Z}{\partial V}\right)_T$$

We recall from our analysis of quantum mechanics that the internal modes are not functions of volume and consequently do not contribute anything to the pressure (or to $P\bar{v}$). From the definition of enthalpy, we then arrive at Eq. 18.10.

Expressions for specific heats can also be developed, but these quantities are most readily evaluated from their definitions, Eqs. 17.71 and 17.72, using Eqs. 18.5 to 18.10.

From Eqs. 17.73, 18.2, and 18.5, we find that the entropy can also be expressed as a sum of the contributions of translational and internal modes:

$$\bar{s} = \bar{R}\left(\ln \frac{Z_t Z_{\text{int}}}{N} + 1\right) + \frac{\bar{u}_t + \bar{u}_{\text{int}}}{T}$$

This can also be written as

$$\bar{s} = \bar{s}_t + \bar{s}_{\text{int}} \tag{18.11}$$

if the translational entropy is defined as

$$\bar{s}_t = \bar{R}\left(\ln \frac{Z_t}{N} + 1\right) + \frac{\bar{u}_t}{T} \tag{18.12}$$

and the internal contribution to this property is defined as

$$\bar{s}_{\text{int}} = \bar{R} \ln Z_{\text{int}} + \frac{\bar{u}_{\text{int}}}{T} \tag{18.13}$$

The factors N and unity are associated with the translational contribution, which agrees with observed data for substances lacking internal contributions.

In a similar manner, the Helmholtz function is given by

$$\bar{a} = \bar{a}_t + \bar{a}_{\text{int}} \tag{18.14}$$

with

$$\bar{a}_t = -\bar{R}T\left(\ln \frac{Z_t}{N} + 1\right) \tag{18.15}$$

$$\bar{a}_{\text{int}} = -\bar{R}T \ln Z_{\text{int}} \tag{18.16}$$

The Gibbs function is given by

$$\bar{g} = \bar{g}_t + \bar{g}_{\text{int}} \tag{18.17}$$

where

$$\bar{g}_t = -\bar{R}T \ln \frac{Z_t}{N} \tag{18.18}$$

$$\bar{g}_{\text{int}} = \bar{a}_{\text{int}} = -\bar{R}T \ln Z_{\text{int}} \tag{18.19}$$

18.2 TRANSLATION

In the preceding section, we performed a general separation of the partition function into translational and internal mode components. In subsequent sections of this chapter, we will discuss the thermodynamic properties for the various classes of gases—monatomic, diatomic, and polyatomic. Each of these classes differs in its number and types of internal modes, as mentioned in Chapter 2, and will be considered in turn in later sections. However, the expression for the translational energy as given by Eq. 15.42,

$$\epsilon_{\mathbf{k}_x,\mathbf{k}_y,\mathbf{k}_z} = \frac{h^2}{8mV^{2/3}}(\mathbf{k}_x^2 + \mathbf{k}_y^2 + \mathbf{k}_z^2)$$

is the same for each of these types of molecules. Thus, the equations of the present section will apply to all the classes of molecules. We need only be careful to use the total mass of the molecule (as found by summing the masses of the component atoms for molecules comprised of two or more atoms) for m in Eq. 15.42.

To use Eq. 15.42 to evaluate the translational partition function, we recall that this expression gives the energy of a particular quantum state and not a degenerate level of energy. Thus, the translational partition function can be calculated most directly by summing over all quantum or energy states, according to Eq. 17.16, instead of over all levels of energy as implied in Eq. 18.3. That is,

$$\begin{aligned} Z_t &= \sum_{j_t \text{ levels}} \mathbf{g}_{j_t} \exp\left(-\frac{\epsilon_{j_t}}{kT}\right) \\ &= \sum_{\mathbf{k}_x=1}^{\infty} \sum_{\mathbf{k}_y=1}^{\infty} \sum_{\mathbf{k}_z=1}^{\infty} \exp\left(-\frac{\epsilon_{\mathbf{k}_x,\mathbf{k}_y,\mathbf{k}_z}}{kT}\right) \end{aligned} \tag{18.20}$$

Now, substituting Eq. 15.42, which gives the energy of a state, into Eq. 18.20, we have

$$Z_t = \sum_{\mathbf{k}_x=1}^{\infty} \sum_{\mathbf{k}_y=1}^{\infty} \sum_{\mathbf{k}_z=1}^{\infty} \exp\left[-\frac{h^2}{8mV^{2/3}kT}(\mathbf{k}_x^2 + \mathbf{k}_y^2 + \mathbf{k}_z^2)\right]$$

Because the three functions and summations in $\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z$ are identical, an arbitrary subscript i can be used for each term, so that

$$Z_t = \left[\sum_{\mathbf{k}_i=1}^{\infty} \exp\left(-\frac{h^2}{8mV^{2/3}kT}\mathbf{k}_i^2\right)\right]^3 \tag{18.21}$$

The summation inside the brackets in this equation is of the form

$$\sum_{\mathbf{k}=1}^{\infty} e^{-r\mathbf{k}^2} = \sum_{\mathbf{k}=0}^{\infty} e^{-r\mathbf{k}^2} - 1$$

with r a constant. The summation on the right side is evaluated in terms of an integral using the Euler–Maclaurin summation theorem, Table A.18:

$$\sum_{\mathbf{k}=0}^{\infty} e^{-r\mathbf{k}^2} = \int_0^{\infty} e^{-r\mathbf{k}^2}\, d\mathbf{k} + \tfrac{1}{2}(1) - \tfrac{1}{12}(0) + \tfrac{1}{720}(0) + \cdots$$

Therefore, only the first two terms are different from zero and, on combining this expression with the previous one, we have

$$\sum_{\mathbf{k}=1}^{\infty} e^{-r\mathbf{k}^2} = \int_0^{\infty} e^{-r\mathbf{k}^2}\, d\mathbf{k} - \tfrac{1}{2}$$

To apply this equation to Eq. 18.21, we anticipate that Z_t will be a large number. The difference of $-\frac{1}{2}$ between the summation and integral will then be negligible. In other words, we are assuming that the translational energy levels are so closely spaced that the summation of Eq. 18.21 can be directly replaced by an integral. This will be found to be of general validity for translational energy in our applications, but the Euler–Maclaurin theorem gives us a means for justifying the approximation. Therefore

$$Z_t = \left[\int_0^{\infty} \exp\left(-\frac{h^2}{8mV^{2/3}kT}\,\mathbf{k}_i^2\right) d\mathbf{k}_i\right]^3$$

On performing this integration, we find that

$$Z_t = \left(\tfrac{1}{2}\sqrt{\pi}\sqrt{\frac{8mV^{2/3}kT}{h^2}}\right)^3 = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{18.22}$$

For the translational contributions to thermodynamic properties, it is convenient to write Eq. 18.22 in logarithmic form:

$$\ln Z_t = \ln V + \tfrac{3}{2}\ln\left(\frac{2\pi mk}{h^2}\right) + \tfrac{3}{2}\ln T \tag{18.23}$$

From Eq. 18.6,

$$\bar{u}_t = \bar{R}T^2\left(\frac{\partial \ln Z_t}{\partial T}\right)_V$$

the internal energy is

$$\bar{u}_t = \bar{R}T^2\left(\frac{3}{2T}\right) = \tfrac{3}{2}\bar{R}T \tag{18.24}$$

and from Eq. 18.9 the enthalpy is found to be

$$\bar{h}_t = \tfrac{3}{2}\bar{R}T + \bar{R}T = \tfrac{5}{2}\bar{R}T \tag{18.25}$$

The translational contribution to the constant-volume specific heat is found, from Eqs. 17.71 and 18.24,

$$\overline{C}_{v_t} = \frac{d\overline{u}_t}{dT} = \tfrac{3}{2}\overline{R} \tag{18.26}$$

and that to the constant-pressure specific heat is, from Eqs. 17.72 and 18.25,

$$\overline{C}_{p_t} = \frac{d\overline{h}_t}{dT} = \tfrac{5}{2}\overline{R} \tag{18.27}$$

From Eq. 18.12 the translational entropy is found to be

$$\overline{s}_t = \overline{R}\left(\ln\frac{Z_t}{N} + 1\right) + \tfrac{3}{2}\overline{R} = \overline{R}\left(\ln\frac{Z_t}{N} + \frac{5}{2}\right) \tag{18.28}$$

From Eqs. 18.22 and 17.68,

$$\frac{Z_t}{N} = \frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \left(\frac{2\pi m}{h^2}\right)^{3/2}\frac{(kT)^{5/2}}{P} \tag{18.29}$$

It will be useful to develop a working form of Eq. 18.29 by substituting numerical values for the various physical constants from Table A.20. This gives the expression

$$\begin{aligned}\frac{Z_t}{N} &= \left[\frac{2\pi \times 1.660\,565 \times 10^{-27}}{(6.626\,176 \times 10^{-34})^2}\right]^{3/2}\frac{(1.380\,662 \times 10^{-23})^{5/2}}{1000}\frac{M^{3/2}T^{5/2}}{P} \\ &= 2.594\,676\frac{M^{3/2}T^{5/2}}{P}\end{aligned} \tag{18.30}$$

in which M is the atomic or molecular weight, T the temperature in K, and P the pressure in kPa.

Similarly, the translational contributions to the Helmholtz and Gibbs functions are found from Eqs. 18.15 and 18.18, respectively, using Eq. 18.30 for the quantity Z_t/N.

EXAMPLE 18.1

Calculate the translational contributions to the enthalpy and entropy for helium at 25°C, 100 kPa.

Solution

From Eq. 18.25,

$$\overline{h}_t = \tfrac{5}{2}\overline{R}T = \tfrac{5}{2}(8.3144)(298.15) = 6197 \text{ kJ/kmol}$$

From Eq. 18.30,

$$\frac{Z_t}{N} = 2.594\,676\frac{(4.0026)^{3/2}(298.15)^{5/2}}{100} = 318\,921$$

From Eq. 18.28,

$$\bar{s}_t = \bar{R}\left(\ln \frac{Z_t}{N} + \frac{5}{2}\right) = 8.3144(12.673 + 2.5) = 126.152 \text{ kJ/kmol K}$$

18.3 AN ALTERNATIVE EVALUATION OF THE TRANSLATIONAL PARTITION FUNCTION

It was noted in Section 17.1 that the partition function defined by Eq. 17.15 in terms of a summation over degenerate levels of energy can alternatively be expressed as a sum over all individual quantum states, so that

$$Z = \sum_{j \text{ levels}} \mathbf{g}_j e^{-\epsilon_j/kT} = \sum_{i \text{ states}} e^{-\epsilon_i/kT}$$

The latter approach was used in Section 18.2 in evaluating the partition function for translation, since the translational energy as given by Eq. 15.42 is the energy of a quantum state, and not that of a degenerate level of energy. It is also desirable, however, to analyze this problem from the standpoint of energy levels, and to do so we must develop an expression for energy level degeneracy. That is, the number of individual quantum states (each specified by a set of integers $\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z$) having energy in an interval ϵ to $\epsilon + d\epsilon$ must be found.

Let us consider a three-dimensional space of coordinates $\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z$, a two-dimensional cross section of which is shown in Fig. 18.1. Each of the three variables is restricted to positive integral values, and a point in this $\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z$ space represents

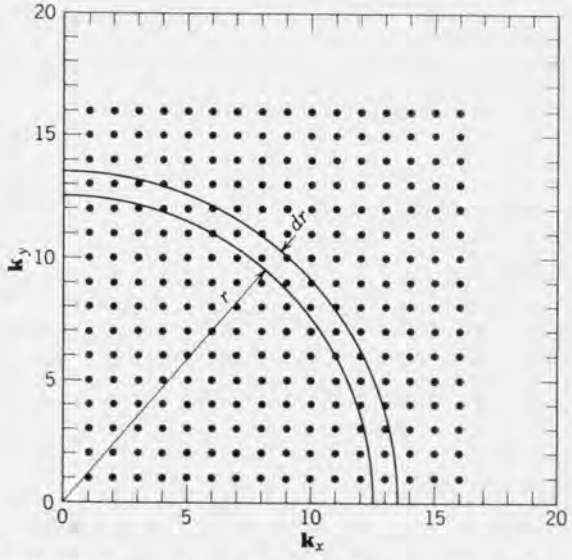


FIGURE 18.1 Cross section of the three-dimensional $\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z$ space.

a translational quantum state. The distance r of any point from the origin is given by

$$r = (\mathbf{k}_x^2 + \mathbf{k}_y^2 + \mathbf{k}_z^2)^{1/2} \tag{18.31}$$

We now restrict the discussion to the states (sets of $\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z$) for which r is large compared to unity, so that r can be treated as essentially continuous. (Translational states for which r is small constitute only a negligible fraction of the total number and can therefore be neglected here.) Thus, the number of states $\mathbf{g}_r$ in the spherical shell from r to $r + dr$ is

$$\mathbf{g}_r = \tfrac{1}{8}(4\pi r^2\, dr) \tag{18.32}$$

where the factor $\frac{1}{8}$ accounts for the restriction of $\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z$ to all positive values only.

The quantity of interest to us, however, is the number of states in an interval of energy ϵ to $\epsilon + d\epsilon$. From Eqs. 15.42 and 18.31,

$$\epsilon = \frac{h^2}{8mV^{2/3}}\, r^2 \tag{18.33}$$

and

$$d\epsilon = \frac{h^2}{8mV^{2/3}}\, 2r\, dr \tag{18.34}$$

Using Eqs. 18.33 and 18.34 in Eq. 18.32, we find that the number of states in the interval ϵ to $\epsilon + d\epsilon$ is

$$\mathbf{g}_\epsilon = \frac{4\pi mV}{h^3}\,(2m\epsilon)^{1/2}\, d\epsilon \tag{18.35}$$

If we use Eq. 18.35 (for the degeneracy) in Eq. 18.3 (for the translational partition function) and integrate from $\epsilon = 0$ to $\epsilon = \infty$, the equation is once again that given by Eq. 18.22. The details of the evaluation are left as an exercise.

18.4 THE MONATOMIC GAS

For any ideal gas, the contributions to partition function and to properties are those from translation and the internal modes. The translational contributions have already been evaluated in Section 18.2, and for a monatomic gas the only internal mode contribution is that of the electronic levels of the atom. By convention we take the ground electronic level energy as the reference state, that is,

$$\epsilon_{e0} = 0 \tag{18.36}$$

The internal partition function then becomes

$$Z_{\text{int}} = Z_e = \mathbf{g}_{e0} + \mathbf{g}_{e1} \exp\left(-\frac{\epsilon_{e1}}{kT}\right) + \mathbf{g}_{e2} \exp\left(-\frac{\epsilon_{e2}}{kT}\right) + \cdots \tag{18.37}$$

This can be evaluated by direct summation over the electronic terms as necessary.

Using the definitions

$$Z'_e = T\left(\frac{dZ_e}{dT}\right) = \sum_j \mathbf{g}_{e_j}\left(\frac{\epsilon_{e_j}}{kT}\right)\exp\left(-\frac{\epsilon_{e_j}}{kT}\right) \tag{18.38}$$

$$Z''_e = T\left(\frac{dZ'_e}{dT}\right) = \sum_j \mathbf{g}_{e_j}\left(\frac{\epsilon_{e_j}}{kT}\right)^2\exp\left(-\frac{\epsilon_{e_j}}{kT}\right) - Z'_e \tag{18.39}$$

we find from Eqs. 18.7, 18.10, 18.13, and 18.19 that the electronic contributions to properties are given by the following relations.

$$\bar{h}_e = \bar{u}_e = \bar{R}T\frac{Z'_e}{Z_e} \tag{18.40}$$

$$\bar{s}_e = \bar{R}\left(\ln Z_e + \frac{Z'_e}{Z_e}\right) \tag{18.41}$$

$$\bar{g}_e = \bar{a}_e = -\bar{R}T\ln Z_e \tag{18.42}$$

Differentiating Eq. 18.40, we find

$$\bar{C}_{p_e} = \bar{C}_{v_e} = \bar{R}\left[\frac{Z''_e + Z'_e}{Z_e} - \left(\frac{Z'_e}{Z_e}\right)^2\right] \tag{18.43}$$

EXAMPLE 18.2

1. Using values from Table 15.2, determine the fraction of atoms in each of the first three electronic levels for monatomic fluorine at 1000 K.
2. Calculate the internal energy, the constant-volume specific heat, and the entropy of monatomic fluorine at 1000 K, 100 kPa.

Solution

1. From the data for fluorine in Table 15.2, we have

Term	ϵ/hc, mm^{-1}	$\mathbf{g} = 2\mathbf{J} + 1$
$^2P_{2/3}$	0	4
$^2P_{1/2}$	40.40	2
$^4P_{5/2}$	10 240.65	6

Therefore, at 1000 K,

$$\frac{\epsilon_{e1}}{kT} = \left(\frac{\epsilon_{e1}}{hc}\right)\left(\frac{hc}{k}\right)\frac{1}{T} = 40.40(14.3879)\left(\frac{1}{1000}\right) = 0.5813$$

Similarly,

$$\frac{\epsilon_{e2}}{kT} = 10\,240.65(14.3879)\left(\frac{1}{1000}\right) = 147.2$$

so that the electronic partition function is, from Eq. 18.37,

$$Z_e = 4 + 2 \times e^{-0.5813} + 6 \times e^{-147.2} = 5.118$$

From the distribution equation, Eq. 17.55,

$$\frac{N_{e_j}}{N} = \frac{\mathbf{g}_{e_j} \exp(-\epsilon_{e_j}/kT)}{Z_e}$$

and the fraction of particles in the electronic ground level is

$$\frac{N_{e0}}{N} = \frac{\mathbf{g}_{e0}(1)}{Z_e} = \frac{4}{5.118} = 0.782$$

Similarly, the fraction of particles in the first excited level is

$$\frac{N_{e1}}{N} = \frac{\mathbf{g}_{e1} \exp(-\epsilon_{e1}/kT)}{Z_e} = \frac{2 \times e^{-0.5813}}{5.118} = 0.218$$

For the second excited level, we find

$$\frac{N_{e2}}{N} = \frac{\mathbf{g}_{e2} \exp(-\epsilon_{e2}/kT)}{Z_e} = \frac{6 \times e^{-147.2}}{5.118} \approx 0$$

2. A negligible fraction of the fluorine atoms are in the second and higher excited levels, so we need consider only the ground and first excited levels as contributing to properties. let us evaluate the translational contributions. From Eq. 18.24

$$\bar{u}_t = \tfrac{3}{2}\overline{R}T = \tfrac{3}{2}(8.3144)(1000) = 12\,472 \text{ kJ/kmol}$$

From Eq. 18.26,

$$\overline{C}_{v_t} = \tfrac{3}{2}\overline{R} = \tfrac{3}{2}(8.3144) = 12.472 \text{ kJ/kmol K}$$

For the entropy contribution, using the working form of the translational entropy expression, Eq. 18.30, we have

$$\ln \frac{Z_t}{N} = \ln\left[2.594\,676 \frac{(18.9984)^{3/2}(1000)^{5/2}}{100}\right]$$
$$= 18.034$$

Therefore, from Eq. 18.28,

$$\bar{s}_t = \overline{R}\left(\ln \frac{Z_t}{N} + \frac{5}{2}\right) = 8.3144(18.034 + 2.5) = 170.728 \text{ kJ/kmol K}$$

For the electronic contributions, it is convenient to construct a table like the accompanying one, using

$$y_j = \frac{\epsilon_{e_j}}{kT}$$

ϵ_{e_j} mm^{-1}	$\mathbf{g}_{e_j}$	y_j	e^{-y_j}	$\mathbf{g}_{e_j} e^{-y_j}$	$\mathbf{g}_{e_j} y_j e^{-y_j}$	$\mathbf{g}_{e_j} y_j^2 e^{-y_j}$
0	4	0	1	4.0	0	0
40.40	2	0.5813	0.559	1.118	0.650	0.378
10 240.65	6	147.2	~0	~0	~0	~0
				$Z_e = 5.118$	$Z'_e = 0.650$	$Z''_e + Z'_e = 0.378$

The summations for Z_e, Z'_e, $Z''_e + Z'_e$ follow from Eqs. 18.37 to 18.39. From Eq. 18.40,

$$\bar{u}_e = \bar{R}T\frac{Z'_e}{Z_e} = 8.3144(1000)\left(\frac{0.650}{5.118}\right) = 1056 \text{ kJ/kmol}$$

From Eq. 18.43,

$$\bar{C}_{v_e} = \bar{R}\left[\frac{Z''_e + Z'_e}{Z_e} - \left(\frac{Z'_e}{Z_e}\right)^2\right]$$
$$= 8.3144\left[\frac{0.378}{5.118} - \left(\frac{0.650}{5.118}\right)^2\right] = 0.480 \text{ kJ/kmol K}$$

From Eq. 18.41,

$$\bar{s}_e = \bar{R}\left(\ln Z_e + \frac{Z'_e}{Z_e}\right)$$
$$= 8.3144\left(\ln 5.118 + \frac{0.650}{5.118}\right) = 14.631 \text{ kJ/kmol K}$$

Therefore, the values of the properties to be determined are

$$\bar{u} = \bar{u}_t + \bar{u}_e = 12\,472 + 1056 = 13\,528 \text{ kJ/kmol}$$
$$\bar{C}_{v0} = \bar{C}_{v_t} + \bar{C}_{v_e} = 12.472 + 0.480 = 12.952 \text{ kJ/kmol K}$$
$$\bar{s} = \bar{s}_t + \bar{s}_e = 170.728 + 14.631 = 185.359 \text{ kJ/kmol K}$$

It is of interest to note that for the very common case in which only the ground electronic level is significant, the partition function Z_e reduces to the degeneracy of the ground level, and both Z'_e and Z''_e are zero. Consequently, the electronic level contributions $\bar{h}_e$, $\bar{u}_e$, $\bar{C}_{p_e}$, and $\bar{C}_{v_e}$ are all zero, whereas $\bar{s}_e$, $\bar{g}_e$, and $\bar{a}_e$ are zero only if the ground level degeneracy is unity.

18.5 THE MAXWELL–BOLTZMANN VELOCITY DISTRIBUTION

In this section we reconsider the monatomic ideal gas from the point of view of classical mechanics, so that, assuming ground electronic level, all the energy is the familiar translational kinetic energy, $\frac{1}{2}m\mathbf{V}^2$. For this model the energy is conveniently expressed in terms of velocity components as

$$\epsilon_{\mathbf{V}_x\mathbf{V}_y\mathbf{V}_z} = \tfrac{1}{2}m(\mathbf{V}_x^2 + \mathbf{V}_y^2 + \mathbf{V}_z^2) \tag{18.44}$$

which is the energy corresponding to a particular set of velocity components $\mathbf{V}_x$, $\mathbf{V}_y$, and $\mathbf{V}_z$. Actually, we should more properly state that the energy expressed by Eq. 18.44 is for a specified interval $\mathbf{V}_x$, $\mathbf{V}_y$, $\mathbf{V}_z$ to $\mathbf{V}_x + \Delta\mathbf{V}_x$, $\mathbf{V}_y + \Delta\mathbf{V}_y$, $\mathbf{V}_z + \Delta\mathbf{V}_z$. We then note that $\mathbf{g}_{\mathbf{V}_x\mathbf{V}_y}\mathbf{V}_y$ is the number of quantum states in this interval $\Delta\mathbf{V}_x$, $\Delta\mathbf{V}_y$, $\Delta\mathbf{V}_z$. If we now interpret this interval as corresponding to the energy level j in the

most probable macrostate equation, Eq. 17.55, we find that

$$\Delta N_{\mathbf{V}_x\mathbf{V}_y\mathbf{V}_z} = \frac{N}{Z_t}\, \mathbf{g}_{\mathbf{V}_x\mathbf{V}_y\mathbf{V}_z} e^{-\epsilon_{\mathbf{V}_x\mathbf{V}_y\mathbf{V}_z}/kT} \tag{18.45}$$

in which $\Delta N_{\mathbf{V}_x\mathbf{V}_y\mathbf{V}_z}$ is the number of particles in the given velocity component interval.

To develop Eq. 18.45 into a useful form, we must be able to evaluate the degeneracy $\mathbf{g}_{\mathbf{V}_x\mathbf{V}_y\mathbf{V}_z}$, and for this purpose we must introduce the concept of a phase space. A single point in this phase space specifies the state, both location and momentum, of a particle. We simplify this discussion by considering only one dimension x, for which the phase space would be two dimensions, x and $m\mathbf{V}_x$. We speak of a point in this two-dimensional space, but realize that we must in fact deal with a unit area $\Delta x\, \Delta m\mathbf{V}_x$ of some minimum size, in accordance with the Heisenberg uncertainty principle. This principle, discussed in detail in Chapter 15, establishes a minimum fundamental uncertainty in any simultaneous measurement of position and momentum, as

$$(\Delta x\, \Delta m\mathbf{V}_x)_{\min} \sim h \tag{18.46}$$

in which h is Planck's constant. This then fixes the unit cell size in our phase space, so that a given interval $\mathbf{V}_x$ to $\mathbf{V}_x + \Delta\mathbf{V}_x$ is described as shown in Fig. 18.2.

Our interest is in the number of cells in the specified interval $\mathbf{V}_x$ to $\mathbf{V}_x + \Delta\mathbf{V}_x$ without regard for the location of the particle within the tank, that is, $\Delta x \to X$. Thus, the number of cells or quantum states in this range is the area of this region of the phase space divided by the unit area, or

$$\mathbf{g}_{\mathbf{V}_x} = \frac{mX\ \Delta\mathbf{V}_x}{h} \tag{18.47}$$

It follows readily that in our three-dimensional problem, a similar argument involving a six-dimensional phase space with unit cell volume of h^3 leads to the

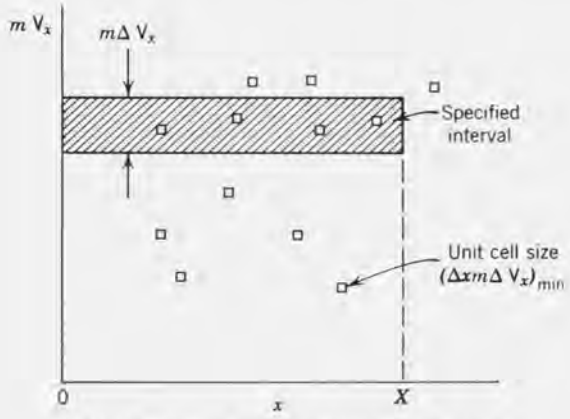


FIGURE 18.2 A two-dimensional phase space.

conclusion that

$$g_{\mathbf{V}_x\mathbf{V}_y\mathbf{V}_z} = \frac{m^3 V}{h^3}\,\Delta\mathbf{V}_x\,\Delta\mathbf{V}_y\,\Delta\mathbf{V}_z \tag{18.48}$$

Let us now substitute Eqs. 18.44 and 18.48 into the most probable macrostate equation, Eq. 18.45, and also utilize Eq. 18.22 for the translational partition function. Rearranging, we have

$$\frac{\Delta N_{\mathbf{V}_x,\mathbf{V}_y,\mathbf{V}_z}}{N} = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m}{2kT}(\mathbf{V}_x^2 + \mathbf{V}_y^2 + \mathbf{V}_z^2)\right]\Delta\mathbf{V}_x\,\Delta\mathbf{V}_y\,\Delta\mathbf{V}_z \tag{18.49}$$

If we now let the velocity interval become very small, the limit is, in differential form,

$$\frac{dN_{\mathbf{V}_x,\mathbf{V}_y,\mathbf{V}_z}}{N} = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m}{2kT}(\mathbf{V}_x^2 + \mathbf{V}_y^2 + \mathbf{V}_z^2)\right]d\mathbf{V}_x\,d\mathbf{V}_y\,d\mathbf{V}_z \tag{18.50}$$

which is termed the Maxwell–Boltzmann velocity distribution equation.

Instead of using the vector velocity components, we often find the scalar magnitude of velocity or speed of the particles, given by

$$\mathbf{V} = |(\mathbf{V}_x^2 + \mathbf{V}_y^2 + \mathbf{V}_z^2)^{1/2}| \tag{18.51}$$

more convenient. It is helpful to think of the components $\mathbf{V}_x$, $\mathbf{V}_y$, $\mathbf{V}_z$ as the cartesian coordinates of a point on the surface of a sphere of radius $\mathbf{V}$, as shown in Fig. 18.3. Using spherical coordinates, the velocity components can be expressed by

$$\begin{aligned} \mathbf{V}_x &= \mathbf{V}\sin\theta\cos\phi \\ \mathbf{V}_y &= \mathbf{V}\sin\theta\sin\phi \\ \mathbf{V}_z &= \mathbf{V}\cos\theta \end{aligned} \tag{18.52}$$

It is important to keep in mind that, although the components $\mathbf{V}_x$, $\mathbf{V}_y$, $\mathbf{V}_z$ can have values from $-\infty$ to $+\infty$, the scalar $\mathbf{V}$ can have values only from 0 to $+\infty$. To

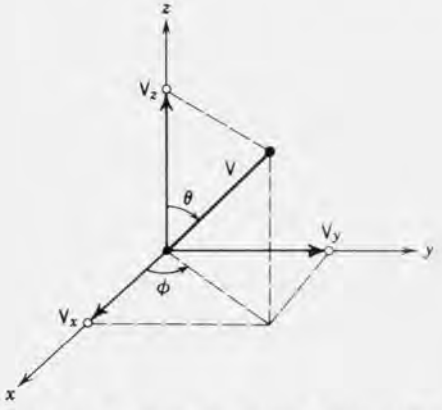


FIGURE 18.3 The cartesian and spherical coordinate systems.

write Eq. 18.50 in terms of $\mathbf{V}$, we note that an integral over $d\mathbf{V}_x\, d\mathbf{V}_y\, d\mathbf{V}_z$ in cartesian coordinates is replaced in spherical coordinates by the integral over $\mathbf{V}^2 \sin\theta\, d\theta\, d\phi\, d\mathbf{V}$. Consequently, Eq. 18.50 can be written as the fraction of particles in the interval $\mathbf{V}, \theta, \phi$ to $\mathbf{V} + d\mathbf{V}, \theta + d\theta, \phi + d\phi$ as

$$\frac{dN_{\mathbf{V}\theta\phi}}{N} = \left(\frac{m}{2\pi kT}\right)^{3/2} \mathbf{V}^2 e^{-m\mathbf{V}^2/2kT} \sin\theta\, d\theta\, d\phi\, d\mathbf{V} \tag{18.53}$$

which is an alternative form of the Maxwell–Boltzmann velocity distribution equation.

Frequently, we are concerned with molecular speeds but not with orientation. That is, we would like to know the fraction of particles in the interval $\mathbf{V}$ to $\mathbf{V} + d\mathbf{V}$ and with any θ, ϕ. This distribution is obtained by integrating Eq. 18.53 over all values of θ and ϕ, and takes the form

$$\begin{aligned}\frac{dN_{\mathbf{V}}}{N} &= \int_{\phi}\int_{\theta} \frac{dN_{\mathbf{V}\theta\phi}}{N} \\ &= \left(\frac{m}{2\pi kT}\right)^{3/2} \mathbf{V}^2 e^{-m\mathbf{V}^2/2kT}\, d\mathbf{V} \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} \sin\theta\, d\theta\, d\phi \\ &= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \mathbf{V}^2 e^{-m\mathbf{V}^2/2kT}\, d\mathbf{V}\end{aligned} \tag{18.54}$$

A number of useful results can be obtained through integrating this expression, or Eq. 18.50.

The fraction of particles having an x-component velocity between some $\mathbf{V}_x$ and $\mathbf{V}_x + d\mathbf{V}_x$ and any value of $\mathbf{V}_y, \mathbf{V}_z$ can be found by integrating Eq. 18.50 over all possible values of $\mathbf{V}_y$ and $\mathbf{V}_z$. This yields

$$\begin{aligned}\frac{dN_{\mathbf{V}_x}}{N} &= \int_{\mathbf{V}_y}\int_{\mathbf{V}_z} \frac{dN_{\mathbf{V}_x\mathbf{V}_y\mathbf{V}_z}}{N} \\ &= \left(\frac{m}{2\pi kT}\right)^{3/2} \left\{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \exp\left[-\frac{m}{2kT}(\mathbf{V}_x^2 + \mathbf{V}_y^2 + \mathbf{V}_z^2)\right] d\mathbf{V}_y\, d\mathbf{V}_z\right\} d\mathbf{V}_x \\ &= \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{m}{2kT}\mathbf{V}_x^2\right) d\mathbf{V}_x\end{aligned} \tag{18.55}$$

A plot of this function is shown in dimensionless form in Fig. 18.4. It is apparent that the component velocity is symmetrical in the $\pm x$-direction with a maximum at zero. The average value of $\mathbf{V}_x$ is given by

$$\langle \mathbf{V}_x \rangle = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_{-\infty}^{+\infty} \mathbf{V}_x \exp\left(-\frac{m}{2kT}\mathbf{V}_x^2\right) d\mathbf{V}_x = 0 \tag{18.56}$$

The integral is zero because of the symmetry displayed in Fig. 18.4.

Let us return now to the velocity distribution as expressed by Eq. 18.54. The most probable speed $\mathbf{V}_{mp}$ is that corresponding to the maximum of that function found from

$$\frac{d}{d\mathbf{V}}\left(\frac{dN_{\mathbf{V}}}{N\, d\mathbf{V}}\right) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \mathbf{V} \exp\left(-\frac{m\mathbf{V}^2}{2kT}\right)\left(2 - \frac{m\mathbf{V}^2}{kT}\right) = 0 \tag{18.57}$$

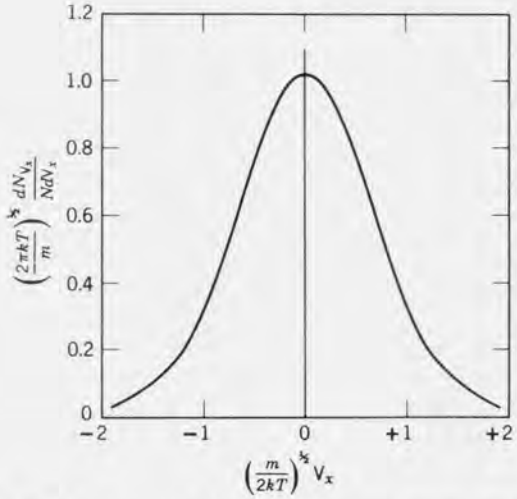


FIGURE 18.4 *x*-component, Maxwell–Boltzmann velocity distribution.

so that

$$\mathbf{V}_{\text{mp}} = \left(\frac{2kT}{m}\right)^{1/2} \tag{18.58}$$

On the other hand, the mean speed is given by

$$\begin{aligned}\langle \mathbf{V} \rangle &= \int_0^\infty \mathbf{V}\left(\frac{dN_{\mathbf{V}}}{N\, d\mathbf{V}}\right) d\mathbf{V} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty \mathbf{V}^3 \exp\left(-\frac{m\mathbf{V}^2}{2kT}\right) d\mathbf{V} \\ &= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left[2\left(\frac{kT}{m}\right)^2\right] = \left(\frac{8kT}{\pi m}\right)^{1/2}\end{aligned} \tag{18.59}$$

or

$$\langle \mathbf{V} \rangle = 1.1284\mathbf{V}_{\text{mp}} \tag{18.60}$$

Similarly, the mean-square speed is

$$\begin{aligned}\langle \mathbf{V}^2 \rangle &= \int_0^\infty \mathbf{V}^2\left(\frac{dN_{\mathbf{V}}}{N\, d\mathbf{V}}\right) d\mathbf{V} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty \mathbf{V}^4 \exp\left(-\frac{m\mathbf{V}^2}{2kT}\right) d\mathbf{V} \\ &= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left[\frac{3\sqrt{\pi}}{8}\left(\frac{2kT}{m}\right)^{5/2}\right] = \frac{3kT}{m}\end{aligned} \tag{18.61}$$

Thus, the mean kinetic energy and, consequently, the internal energy are

$$\frac{U}{N} = \tfrac{1}{2}m\langle \mathbf{V}^2 \rangle = \tfrac{3}{2}kT \tag{18.62}$$

in agreement with the value given by Eq. 18.24. The root-mean-square speed is

$$\langle \mathbf{V}^2 \rangle^{1/2} = 1.2248\mathbf{V}_{\text{mp}} \tag{18.63}$$

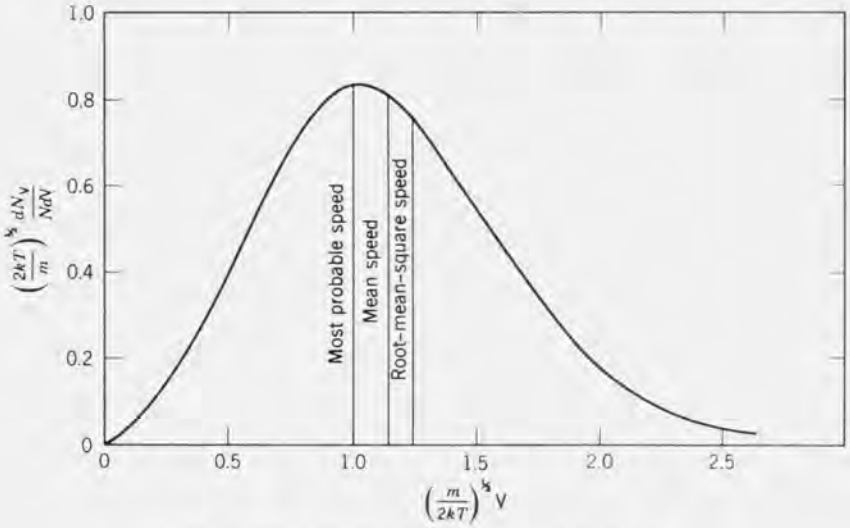


FIGURE 18.5 Maxwell–Boltzmann speed distribution.

If we now plot the speed distribution of Eq. 18.54, as in Fig. 18.5, we see that the distribution is asymmetric and tends toward zero for large **V**. The values given in Eqs. 18.58, 18.60, and 18.63 are also indicated in this figure.

EXAMPLE 18.3

1. Calculate the most probable speed, the mean speed, and the root-mean-square speed for helium at 0°C.
2. Plot the speed distribution for helium, $(dN_{\mathbf{V}}/N\,d\mathbf{V})$, versus **V** at 0 and 200°C.

Solution

1. From Table A.17, the mass of the helium atom is

$$m = 1.66 \times 10^{-27} \times (4.003) = 6.645 \times 10^{-27}\ \text{kg}$$

From Eq. 18.58, the most probable speed at 0°C is

$$\mathbf{V}_{\text{mp}} = \left(\frac{2kT}{m}\right)^{1/2} = \left[\frac{2(1.380\,66 \times 10^{-23})273.15}{6.645 \times 10^{-27}}\right]^{1/2}$$
$$= 1064\ \text{m/s}$$

From Eq. 18.61, the mean or average speed is

$$\langle \mathbf{V} \rangle = 1.1284 \times (1064) = 1201\ \text{m/s}$$

and, from Eq. 18.63, the root-mean-square speed is

$$\langle \mathbf{V}^2 \rangle^{1/2} = 1.2248 \times (1064) = 1303\ \text{m/s}$$

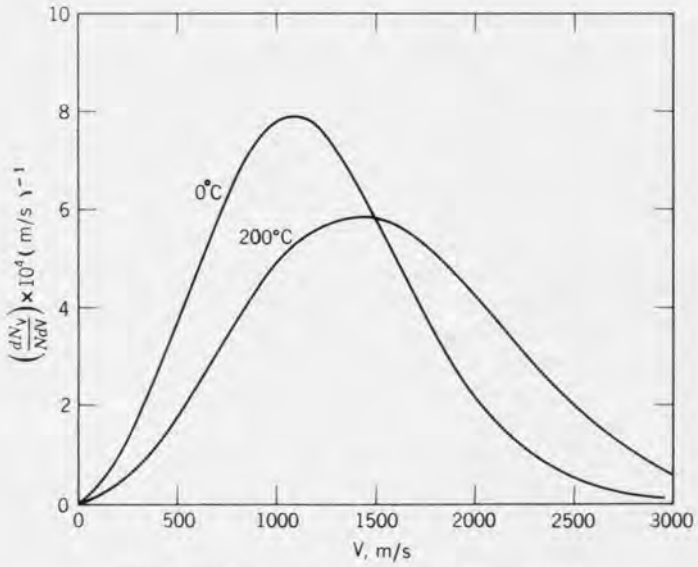


FIGURE 18.6 *Speed distributions for Example 18.3.*

2. From Eqs. 18.54 and 18.58,

$$\frac{dN_{\mathbf{V}}}{N\, d\mathbf{V}} = \frac{4}{\sqrt{\pi}\mathbf{V}_{\text{mp}}}\left(\frac{\mathbf{V}}{\mathbf{V}_{\text{mp}}}\right)^2 \exp\left(-\frac{\mathbf{V}}{\mathbf{V}_{\text{mp}}}\right)^2$$

At 0°C,

$$\frac{dN_{\mathbf{V}}}{N\, d\mathbf{V}} = 0.002\,12\left(\frac{\mathbf{V}}{1064}\right)^2 \exp\left(-\frac{\mathbf{V}}{1064}\right)^2$$

At 200°C,

$$\mathbf{V}_{\text{mp}} = 1064 \times \left(\frac{473.15}{273.15}\right)^{1/2} = 1400 \text{ m/s}$$

and

$$\frac{dN_{\mathbf{V}}}{N\, d\mathbf{V}} = 0.001\,61\left(\frac{\mathbf{V}}{1400}\right)^2 \exp\left(-\frac{\mathbf{V}}{1400}\right)^2$$

Plots of these distributions are shown in Fig. 18.6. We note that, as the temperature is increased, the distribution becomes broader, for more atoms shift to the higher energy levels (higher velocities). There is, of course, an increase in the internal energy of the gas.

18.6 FREE MOLECULAR FLOW

In this section we examine a class of problems involving molecular flow, which is readily analyzed using the techniques developed in the present chapter.

Let us consider a vessel containing a gas in a certain thermodynamic state N, V, T. One wall of the vessel contains a hole, so that molecules of the gas can flow out of the vessel. If this hole is large relative to molecular dimensions, a certain portion of the molecules striking the hole can be expected to collide with other molecules and be deflected. If, however, the hole is sufficiently small, nearly every molecule striking the hole may be expected to pass freely through. The characteristics of these two types of flow can be expected to be quite different.

Our interest here is in the second, the free molecular flow, for which we focus our attention on two questions. How many particles strike the hole in a given time, and what constitutes a sufficiently small hole for the reasonable assumption of free molecular flow? To answer the first question, we may develop an analysis for a monatomic ideal gas contained in a box of dimensions X, Y, Z, as shown in Fig. 18.7. Consider the atoms striking the wall perpendicular to the x-axis at distance $x = X$ during an interval of time Δt. An atom with a given x-component of velocity $\mathbf{V}_x$ and any $\mathbf{V}_y$, $\mathbf{V}_z$ must lie within a distance $\mathbf{V}_x\,\Delta t$ of the wall at the beginning of the time interval (and consequently within a fraction $\mathbf{V}_x\,\Delta t/X$ of the total volume) to strike that wall during the interval. The number of atoms in the entire box with this particular x-component velocity is denoted by $dN_{\mathbf{V}_x}$, and the number of these atoms striking the X wall during a unit interval is

$$\frac{\mathbf{V}_x\,\Delta t}{X}\,dN_{\mathbf{V}_x}\,\frac{1}{\Delta t}$$

Here we are concerned not with the number of particles of this component striking the entire X wall (area YZ) but only with those striking a certain area A on that wall. Therefore, this number is

$$\frac{\text{Number of atoms with } \mathbf{V}_x \text{ striking } A}{\text{second}} = \frac{\mathbf{V}_x\,\Delta t}{X}\,dN_{\mathbf{V}_x}\,\frac{1}{\Delta t}\,\frac{A}{YZ}$$

$$= \frac{\mathbf{V}_x A}{V}\,dN_{\mathbf{V}_x}$$

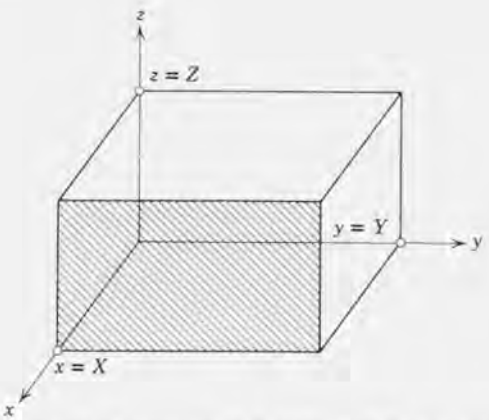


FIGURE 18.7 A box of dimensions X, Y, Z confining a monatomic ideal gas.

If we now assume that the Maxwell–Boltzmann velocity distribution is valid and substitute Eq. 18.55 for $dN_{\mathbf{V}_x}$, we have

$$\frac{\text{Number of atoms with } \mathbf{V}_x \text{ striking } A}{\text{second}} = \frac{NA}{V}\left(\frac{m}{2\pi kT}\right)^{1/2} \mathbf{V}_x \exp\left(-\frac{m\mathbf{V}_x^2}{2kT}\right) d\mathbf{V}_x$$

We then integrate this expression over all values of $\mathbf{V}_x$ with which molecules can strike this area from inside,

$$\begin{aligned}\frac{\text{Total number of atoms striking } A}{\text{second}} &= \frac{NA}{V}\left(\frac{m}{2\pi kT}\right)^{1/2}\int_0^\infty \mathbf{V}_x \exp\left(-\frac{m\mathbf{V}_x^2}{2kT}\right) d\mathbf{V}_x \\ &= \frac{1}{4}\frac{N}{V} A\left(\frac{8kT}{\pi m}\right)^{1/2} = \frac{1}{4}\frac{N}{V} A\langle \mathbf{V}\rangle \end{aligned} \tag{18.64}$$

We find that the number of particles striking the hole depends on the number density N/V of particles inside the vessel and on their mean speed $\langle \mathbf{V}\rangle$ as given by Eq. 18.59, in addition to the size of the hole.

Regarding the second question, we must determine the mean free path Λ of a molecule, that is, its average distance traveled between collisions. We first recognize that during a time Δt, a molecule travels an average distance equal to $\langle \mathbf{V}\rangle \Delta t$. Thus, the problem becomes one of finding the average number of collisions suffered by a molecule during Δt. Since only an order of magnitude of Λ is required for our purposes, we will not analyze this problem in detail, but merely attempt to justify the equation expressing it. If we consider the molecules as rigid spheres of diameter σ, each molecule presents a target size or collision cross section of $\pi\sigma^2$ to other molecules of the same diameter. The average number of collisions should be proportional to this value, and also to the number density of particles and to their average speeds. Therefore, the mean free path becomes

$$\Lambda = \frac{\langle \mathbf{V}\rangle \Delta t}{C(N/V)\langle \mathbf{V}\rangle \pi\sigma^2 \Delta t} = \frac{1}{C(N/V)\pi\sigma^2} \tag{18.65}$$

Using the Maxwell–Boltzmann velocity distribution, Eq. 18.53, and analyzing the characteristics of relative motion of particles in a system, we find the value of the constant in Eq. 18.65 to be $C = \sqrt{2}$.

EXAMPLE 18.4

Calculate the mean free path for nitrogen at 30°C, 100-kPa pressure. Use a molecular diameter $\sigma = 0.4$ nm.

Solution

From Eq. 17.47,

$$\frac{N}{V} = \frac{P}{kT} = \frac{100 \times 10^3}{1.380\,66 \times 10^{-23} \times 303.15} = 2.389 \times 10^{25}\,\frac{1}{\text{m}^3}$$

In addition,

$$\pi\sigma^2 = \pi(0.4 \times 10^{-9})^2 = 5.027 \times 10^{-19}\ \text{m}^2$$

Therefore, from Eq. 18.65,

$$\Lambda = \frac{1}{\sqrt{2}(N/V)\pi\sigma^2} = \frac{1}{\sqrt{2}(2.389 \times 10^{25})(5.027 \times 10^{-19})}$$
$$= 5.89 \times 10^{-8} \text{ m} = 58.9 \text{ nm}$$

We are now in a position to state that if the hole in the vessel wall is considerably larger than the mean free path of the molecules inside the vessel, the flow can be expected to be of the ordinary macroscopic, or bulk-flow type. If the hole is considerably smaller, say an order of magnitude, than Λ, the flow can be expected to be of the free molecule type, as given by Eq. 18.64. Between these extremes, the problem becomes more difficult and, for the most part, empirical in nature.

18.7 THE DIATOMIC GAS

The evaluation of thermodynamic properties of diatomic gases is approached in the same manner as for monatomic gases. The translational contributions to the thermodynamic properties are again given by the equations developed in Section 18.2. Evaluation of the internal contributions for diatomic gases is much more difficult than for monatomic gases, however, since a diatomic molecule has rotational and vibrational energies in addition to the electronic states.

For diatomic gas, we use the internal model discussed in Section 15.5, consisting of independent rigid rotation and harmonic oscillation, and here we further assume that all the molecules are in the ground electronic level. Thus, the internal mode contribution to the energy is, from Eq. 15.47,

$$\epsilon_{\text{int}} = \epsilon_r + \epsilon_v + \epsilon_{e0}$$

The component wave functions (and, therefore, energy level degeneracies) for this model are multiplicative, as in Eq. 15.48. By convention, the energy of the ground electronic level, ϵ_{e0}, is taken as zero, but we include the term here as a reminder that the degeneracy of this level must be accounted for in our calculations.

Before we proceed, we must consider the reference state or "zero-of-energy." We have already noted that the vibrational energy is written with respect to the minimum point on the potential curve, which is shown in Fig. 18.8. (In the vicinity of the minimum point, the assumption of a harmonic oscillator is a good one.) Thus, when $\mathrm{v} = 0$, the ground vibrational state energy, ϵ_{v0} is given by the equation

$$\epsilon_{v0} = \tfrac{1}{2}h\nu_i \tag{18.66}$$

Since it is more convenient to calculate vibrational contributions with respect to the ground vibrational state, we write Eq. 15.47 in the form

$$\epsilon_{\text{int}} = \epsilon_r + (\epsilon_v - \epsilon_{v0}) + \epsilon_{v0} + \epsilon_{e0} \tag{18.67}$$

One other point to be considered in selecting the energy reference state is that the reference must be made consistent with that for monatomic gases. This is particularly important in the analysis of chemical reactions, as will be found in Section

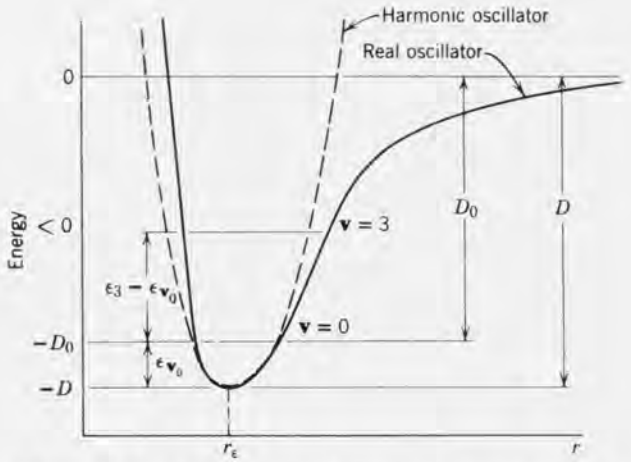


FIGURE 18.8 The zero-energy reference for a diatomic molecule.

18.11. So that the two will be consistent, we should select for the zero-of-energy of the diatomic molecule the energy at which the molecule is dissociated to the monatomic form, and the separation r of the atoms is so large that they are effectively no longer joined together. Therefore, as is evident from Fig. 18.8, ϵ_{int} relative to this base is given by the expression

$$\epsilon_{\text{int}} = \epsilon_r + (\epsilon_v - \epsilon_{v0}) + \epsilon_{v0} + \epsilon_{e0} - D = \epsilon_r + (\epsilon_v - \epsilon_{v0}) + \epsilon_{e0} - D_0 \quad (18.68)$$

in terms of the observed dissociation energy of the molecule, D_0.

Equation 18.4 gives an expression for the internal partition function in terms of the various internal modes of energy. Substituting Eq. 18.68 into Eq. 18.4, we have

$$\begin{aligned} Z_{\text{int}} &= \sum_{\text{all } j} \mathbf{g}_{r_j} \mathbf{g}_{v_j} \mathbf{g}_{e0} \exp\left[-\frac{\epsilon_{r_j} + (\epsilon_{v_j} - \epsilon_{v0}) + \epsilon_{e0} - D_0}{kT} \right] \\ &= Z_r Z_v Z_{e0} Z_{\text{chem}} \end{aligned} \quad (18.69)$$

The rotational partition function Z_r in Eq. 18.69 is

$$Z_r = \sum_{r_j} \mathbf{g}_{r_j} \exp\left(\frac{-\epsilon_{r_j}}{kT} \right) \quad (18.70)$$

It was found in Chapter 15 that the vibrational energy levels are nondegenerate. Therefore, $\mathbf{g}_v$ is unity for all levels, and the vibrational partition function Z_v with respect to the ground vibrational state energy ϵ_{v0} is

$$Z_v = \sum_{v_j} \exp\left[\frac{-(\epsilon_{v_j} - \epsilon_{v0})}{kT} \right] \quad (18.71)$$

Since the ground electronic level energy ϵ_{e0} is by convention taken as zero, the partition function Z_{e0} for the ground electronic level is

$$Z_{e0} = \mathbf{g}_{e0} \exp\left(\frac{-\epsilon_{e0}}{kT} \right) = \mathbf{g}_{e0} \quad (18.72)$$

Finally, we define the chemical partition function Z_{chem} in terms of the dissociation energy D_0 by the relation

$$Z_{\text{chem}} = \exp\left(\frac{D_0}{kT}\right) \tag{18.73}$$

If Eq. 18.69 is written in logarithmic form, we have

$$\ln Z_{\text{int}} = \ln Z_r + \ln Z_v + \ln Z_{e0} + \ln Z_{\text{chem}} \tag{18.74}$$

From this equation, it is apparent that each of the four terms has a contribution to the thermodynamic properties as given by Eqs. 18.7, 18.10, 18.13, 18.16, and 18.19 for $\bar{u}$, $\bar{h}$, $\bar{s}$, $\bar{a}$, and $\bar{g}$, respectively. These contributions will be evaluated in turn.

ROTATION

We now use the results of quantum mechanics to evaluate the rotational partition function, as defined by Eq. 18.70, and subsequently the rotational contributions to thermodynamic properties. Substituting the expressions for energy (Eq. 15.59) and rotational level degeneracy (Eq. 15.60) into Eq. 18.70, we have

$$Z_r = \sum_{j=0}^{\infty} (2\mathbf{j} + 1) \exp\left[-\frac{h^2}{8\pi^2 I_e kT}\mathbf{j}(\mathbf{j} + 1)\right] \tag{18.75}$$

Let us assume that the rotational energy levels are spaced sufficiently close together that the summation in this expression can be replaced directly by an integral. If we also change variable according to the relation

$$y^2 = \mathbf{j}(\mathbf{j} + 1)$$

Eq. 18.75 becomes

$$Z_r = \int_0^{\infty} 2y \exp\left(-\frac{h^2}{8\pi^2 I_e kT} y^2\right) dy = \frac{8\pi^2 I_e kT}{h^2} = \frac{T}{\theta_r} \tag{18.76}$$

where the constant θ_r is defined by

$$\theta_r = \frac{h^2}{8\pi^2 I_e k} \tag{18.77}$$

and, having the units of temperature, is termed the characteristic rotational temperature.

There is one additional factor that must be considered in the evaluation of the rotational partition function for homonuclear molecules (for example, N_2, O_2, H_2, and so on). Since the two atoms making up the molecule are identical, the molecule can be rotated through 180° and the new configuration will be indistinguishable from the original one. To correct for this double counting, we introduce a symmetry number σ into the result, so that the correct expression for the rotational partition function is

$$Z_r = \frac{T}{\sigma\theta_r} \tag{18.78}$$

in which $\sigma = 1$ for heteronuclear molecules and $\sigma = 2$ for homonuclear molecules. The argument used here in introducing the symmetry number is admittedly somewhat artificial and incomplete. The complete explanation justifying this number is based on the symmetry characteristics of the molecular wave function and, being a rather complete and advanced subject in itself, will not be examined in this text.

For the rotational contributions to thermodynamic properties, we rewrite Eq. 18.78 in logarithmic form:

$$\ln Z_r = \ln T - \ln \sigma\theta_r \tag{18.79}$$

Then, on applying Eq. 18.7,

$$\bar{u}_{\text{int}} = \bar{R}T^2\left(\frac{\partial \ln Z_{\text{int}}}{\partial T}\right)_v$$

to the rotation, we find that

$$\bar{u}_r = \bar{R}T^2\left(\frac{1}{T}\right) = \bar{R}T \tag{18.80}$$

Similarly, it follows from Eq. 18.10 that

$$\bar{h}_r = \bar{u}_r = \bar{R}T \tag{18.81}$$

When Eqs. 18.80 and 18.81 are differentiated with respect to temperature, it follows from the definitions of the specific heats that

$$\bar{C}_{v_r} = \bar{C}_{p_r} = \bar{R} \tag{18.82}$$

The rotational contribution to entropy can be found by applying Eq. 18.13,

$$\bar{s}_{\text{int}} = \bar{R} \ln Z_{\text{int}} + \frac{\bar{u}_{\text{int}}}{T}$$

to the rotation. The equation is

$$\bar{s}_r = \bar{R}\left(\ln \frac{T}{\sigma\theta_r} + 1\right) \tag{18.83}$$

The rotational contributions to Helmholtz and Gibbs functions are found from Eqs. 18.16 and 18.19,

$$\bar{a}_r = \bar{g}_r = -\bar{R}T \ln \frac{T}{\sigma\theta_r} \tag{18.84}$$

EXAMPLE 18.5

Calculate the rotational partition function and the rotational contributions to internal energy and entropy for diatomic nitrogen at 500 K.

Solution

From Table A.19.1 for N_2,

$$r_e = 0.109\,76 \text{ nm}$$

The mass of a single nitrogen atom is

$$m_N = 1.6606 \times 10^{-27}(14.0067) = 23.259 \times 10^{-27}\ \text{kg}$$

or one-half the mass of the diatomic molecule. The reduced mass is found from Eq. 15.58:

$$m_r = \frac{m_N m_N}{m_N + m_N} = \frac{m_N}{2} = 11.63 \times 10^{-27}\ \text{kg}$$

Then, from Eq. 15.58,

$$I_\varepsilon = m_r r_\varepsilon^2 = 11.63 \times 10^{-27}(0.109\,76 \times 10^{-9})^2 = 0.1401 \times 10^{-45}\ \text{kg m}^2$$

The characteristic rotational temperature θ_r is found from Eq. 18.77:

$$\theta_r = \frac{h^2}{8\pi^2 I_\varepsilon k} = \frac{(6.626\,18 \times 10^{-34})^2}{8\pi^2(0.1401 \times 10^{-45})(1.380\,66 \times 10^{-23})} = 2.875\ \text{K}$$

Because diatomic nitrogen is a homonuclear molecule (two N atoms), the symmetry number σ is 2. The rotational partition function can be found from Eq. 18.78:

$$Z_r = \frac{T}{\sigma\theta_r} = \frac{500}{2(2.875)} = 87.0$$

The internal energy of rotation is, from Eq. 18.80,

$$\bar{u}_r = \bar{R}T = 8.3144(500) = 4157\ \text{kJ/kmol}$$

The rotational entropy is calculated from Eq. 18.83:

$$\bar{s}_r = \bar{R}(\ln Z_r + 1) = 8.3144(\ln 87.0 + 1) = 45.446\ \text{kJ/kmol K}$$

The expression for the rotational partition function for a rigid rotator as given by Eq. 18.78 was obtained under the assumption that the rotational energy levels are very closely spaced. In other words, the temperature must be much greater than the characteristic rotational temperature, θ_r. When this is not true, it is necessary to evaluate the rotational partition function by direct summation, over as many rotational levels as necessary, and then to calculate the contributions to the thermodynamic properties in a manner equivalent to that followed for electronic contributions in Section 18.4.

VIBRATION

For the vibrational partition function in our simple internal model, we assume that the molecule behaves as a harmonic oscillator. The vibrational energy is given by Eq. 15.61. In the vibrational partition function (Eq. 18.71), the energy is that with respect to the ground state $\mathbf{v} = 0$, which is

$$\epsilon_v - \epsilon_{v0} = h\nu_\varepsilon \mathbf{v} \tag{18.85}$$

where $\mathbf{v}$ is the vibrational quantum number. Substituting Eq. 18.85 into the vi-

brational partition function (Eq. 18.71), we obtain

$$Z_v = \sum_{v=0}^{\infty} \exp\left(-\frac{hv_\varepsilon}{kT}\,v\right) \tag{18.86}$$

Unlike the translational and rotational energies, the vibrational energy levels are so widely spaced that it is not possible to replace the summation in Eq. 18.86 by an integral, even if the Euler–Maclaurin summation theorem is used. It is noted, however, that this expression is given by

$$Z_v = \sum_{v=0}^{\infty} \exp\left(-\frac{hv_\varepsilon}{kT}\,v\right) = \frac{1}{1-e^{-\theta_v/T}} = \frac{1}{1-e^{-x}} \tag{18.87}$$

where the characteristic vibrational temperature, θ_v, is defined as

$$\theta_v = \frac{hv_\varepsilon}{k} = \frac{hc\omega_\varepsilon}{k} \tag{18.88}$$

and

$$x = \frac{\theta_v}{T} \tag{18.89}$$

In the evaluation of the vibrational contributions to thermodynamic properties, it is convenient to express Eq. 18.87 in the logarithmic form:

$$\ln Z_v = -\ln(1-e^{-\theta_v/T}) = -\ln(1-e^{-x}) \tag{18.90}$$

The internal energy contribution is found from Eq. 18.7:

$$\bar{u}_{\text{int}} = \bar{R}T^2\left(\frac{\partial \ln Z_{\text{int}}}{\partial T}\right)_V$$

Since the partition function Z_v to be used in this expression is evaluated with respect to the ground vibrational state energy ϵ_{v0}, it follows that the molal energy calculated from the equation will be that with respect to the molal ground state energy $\bar{u}_{v0}$, which equals $N_0\epsilon_{v0}$. Therefore, from Eqs. 18.7 and 18.90, we find

$$\bar{u}_v - \bar{u}_{v0} = \bar{R}T^2\left[-\frac{e^{-x}}{1-e^{-x}}\left(-\frac{x}{T}\right)\right] = \bar{R}T\left(\frac{x}{e^x-1}\right) \tag{18.91}$$

Similarly, using Eq. 18.10, we have

$$\bar{h}_v - \bar{u}_{v0} = \bar{u}_v - \bar{u}_{v0} = \bar{R}T\left(\frac{x}{e^x-1}\right) \tag{18.92}$$

Differentiating Eqs. 18.91 and 18.92, we obtain

$$\bar{C}_{v_v} = \bar{C}_{p_v} = \bar{R}\left[\frac{x^2e^x}{(e^x-1)^2}\right] \tag{18.93}$$

The entropy contribution is found directly from Eq. 18.13:

$$\bar{s}_{\text{int}} = \bar{R}\ln Z_{\text{int}} + \frac{\bar{u}_{\text{int}}}{T}$$

It is easily shown that this expression is independent of the zero-point energy $\bar{u}_{v0}$. Therefore, substituting Eqs. 18.90 and 18.91 into Eq. 18.13, we have

$$\bar{s} = \bar{R}\left[-\ln(1 - e^{-x}) + \frac{x}{e^x - 1}\right] \tag{18.94}$$

It also follows from Eqs. 18.16 and 18.19 that

$$\bar{a}_v - \bar{u}_{v0} = \bar{g}_v - \bar{g}_{v0} = \bar{R}T[\ln(1 - e^{-x})] \tag{18.95}$$

EXAMPLE 18.6

Calculate the specific heat $\bar{C}_{p0}$ for diatomic iodine at 0°C.

Solution

The translational, rotational, and vibrational contributions to the specific heat must all be considered. The translational contribution is found from Eq. 18.27:

$$\bar{C}_{p_t} = \tfrac{5}{2}\bar{R} = \tfrac{5}{2}(8.3144) = 20.786 \text{ kJ/kmol K}$$

For rotation, it is found from the values in Table A.19.2 that, for diatomic iodine,

$$\theta_r = 0.054 \text{ K}$$

Therefore, at $T = 273.15$ K, we find that $T \gg \theta_r$; hence, the rotational partition function is accurately given by Eq. 18.78 and, correspondingly, the specific-heat contribution is given by Eq. 18.82:

$$\bar{C}_{p_r} = \bar{R} = 8.314 \text{ kJ/kmol K}$$

Now we determine the vibrational contribution. We use the value of ω_e from Table A.19.1 to calculate the characteristic vibrational temperature from Eq. 18.88:

$$\theta_v = \frac{hc}{k}\omega_e = 14.3879(21.45) = 308.6 \text{ K}$$

Therefore,

$$x = \frac{\theta_v}{T} = \frac{308.6}{273.15} = 1.130$$

The value for $\bar{C}_{p_v}$ can now be found from Eq. 18.93:

$$\bar{C}_{p_v} = \bar{R}\left[\frac{x^2 e^x}{(e^x - 1)^2}\right] = 8.3144(0.9001) = 7.484 \text{ kJ/kmol K}$$

Adding the translational, rotational, and vibrational contributions, we find, for the specific heat $\bar{C}_{p0}$,

$$\bar{C}_{p0} = \bar{C}_{p_t} + \bar{C}_{p_r} + \bar{C}_{p_v} = 20.786 + 8.314 + 7.484 = 36.584 \text{ kJ/kmol K}$$

GROUND ELECTRONIC LEVEL AND CHEMICAL ENERGY

Since the electronic energy in the ground electronic level is by convention assigned the value zero, only the ground level degeneracy is significant for electronic contributions in the simple internal model for the diatomic gas. In logarithmic form, the electronic partition function (Eq. 18.72) is

$$\ln Z_e = \ln \mathbf{g}_{e0} = \text{constant} \tag{18.96}$$

It therefore follows from Eqs. 18.7 and 18.10 and the definitions of $\overline{C}_v$ and $\overline{C}_p$ and that

$$\overline{u}_e = \overline{h}_e = \overline{C}_{v_e} = \overline{C}_{p_e} = 0 \tag{18.97}$$

However, there is an electronic contribution to entropy as given by Eq. 18.13, from which we find

$$\overline{s}_e = \overline{R} \ln \mathbf{g}_{e0} \tag{18.98}$$

For the Helmholtz and Gibbs functions we have, from Eq. 18.19,

$$\overline{a}_e = \overline{g}_e = -\overline{R}T \ln \mathbf{g}_{e0} \tag{18.99}$$

Note that $\overline{s}_e$, $\overline{a}_e$, and $\overline{g}_e$ are zero only if the ground electronic level degeneracy is unity.

Finally, we must determine the contribution of the chemical energy to thermodynamic properties. As noted earlier, we have selected the zero-of-energy for the molecule as the dissociated state, so that the reference state will be consistent with that chosen previously for a monatomic substance. This selection introduces a constant value of $-D_0$ into the internal mode energy of the molecule, with a resulting contribution to the thermodynamic properties. Therefore, in accordance with Eq. 18.73,

$$\ln Z_{\text{chem}} = \frac{D_0}{kT} = \frac{N_0 D_0}{\overline{R}T} = -\frac{\overline{h}^0_{f0}}{\overline{R}T} \tag{18.100}$$

where $\overline{h}^0_{f0}$ is the enthalpy of formation of the molecule at absolute-zero temperature and is by definition

$$\overline{h}^0_{f0} = -N_0 D_0 \tag{18.101}$$

With the molecule in the ground electronic level, the enthaply of formation is a negative number, since the energy of the dissociated molecule has been selected as zero, as discussed with reference to Fig. 18.8.

From Eqs. 18.7 and 18.10,

$$\overline{h}_{\text{chem}} = \overline{u}_{\text{chem}} = \overline{R}T^2\left(+\frac{\overline{h}^0_{f0}}{\overline{R}T^2}\right) = \overline{h}^0_{f0} \tag{18.102}$$

which is a constant. Therefore,

$$\overline{C}_{v\,\text{chem}} = \overline{C}_{p\,\text{chem}} = 0 \tag{18.103}$$

It also follows from Eq. 18.13 that

$$\bar{s}_{\text{chem}} = \bar{R}\left(-\frac{\bar{h}^0_{f0}}{\bar{R}T}\right) + \frac{\bar{u}_{\text{chem}}}{T} = 0 \tag{18.104}$$

Since $\bar{s}_{\text{chem}}$ is zero, we find from Eqs. 18.19 and 18.104 that

$$\bar{a}_{\text{chem}} = \bar{g}_{\text{chem}} = \bar{h}^0_{f0} \tag{18.105}$$

The relation between the enthalpy of formation as defined by Eq. 18.101 and that used in Chapters 13 and 14 in the study of chemical reactions is examined in Section 18.11, and in the problems at the end of this chapter.

18.8 THE POLYATOMIC GAS

Translational contributions to properties for polyatomic gases are evaluated the same way as those to properties for the monatomic and diatomic species, by using the total mass of the molecule and the equations of Section 18.2. The evaluation of internal modes proves to be a difficult task, however, even though we assume the simple internal model: rigid rotator, harmonic oscillator, ground electronic level. The first question to be faced concerns the number of degrees of freedom for the molecule. Consider a molecule comprised of a atoms, for which the total number of degrees of freedom of motion must equal $3a$. Since each molecule has three directions of translational motion, this leaves a total of $3a - 3$ degrees of freedom for the rotational and vibrational modes. We must now divide our discussion of polyatomic molecules into two parts according to structure, linear and nonlinear, for which the behavior and, consequently, the thermodynamic properties are different.

As examples of linear molecules, consider CO_2 and N_2O, the structures of which are as shown in Fig. 18.9. In either structure the moment of inertia about the axis joining the three nuclei is negligibly small, and the remaining two moments are equal, the same as for diatomic molecules. Therefore, the rotational behavior of a linear polyatomic molecule is the same as determined in Section 18.7. The partition function is found from Eq. 18.78, and the characteristic rotational temperature is given by Eq. 18.77. Rotational contributions to properties are found from Eqs. 18.80 to 18.84, as before. Evaluation of the equilibrium point moment of inertia I_ε, which is required in Eq. 18.77, is somewhat more complicated for the polyatomic gas. For the linear polyatomic molecule, I_ε is given by the relation

$$I_\varepsilon = \sum_{i=1}^{a} m_i r_i^2 \tag{18.106}$$



FIGURE 18.9 The alignment of two linear polyatomic molecules.

where r_i is the equilibrium distance of atom i from the center of mass of the molecule. This equilibrium distance r_i is defined by the expression

$$\sum_{i=1}^{a} m_i r_i = 0 \tag{18.107}$$

It is also necessary to know the symmetry number σ for the molecule. This number requires a knowledge of the structure of the molecule, as is seen from Fig. 18.9.

Since the linear molecule has but two rotational degrees of freedom, there are $3a - 5$ degrees of freedom remaining for vibration of the molecule. The contributions of these $3a - 5$ vibrational modes can be considered as being independent in the simple model, and the vibration can be assumed harmonic for each mode. Thus, we have $3a - 5$ contributions of vibrational partition function, as given in the terms of Eq. 18.87. The $3a - 5$ characteristic vibrational temperatures θ_v are given in terms of the normal frequencies or wave numbers, as in Eq. 18.88. Two or more of these modes may have the same frequency, depending on the molecule. Contributions to properties from these modes are given by Eqs. 18.91 to 18.95 for each of the $3a - 5$ vibrational modes of the molecule. We should keep in mind that there is a $\frac{1}{2}hv_e$ zero-point contribution for each of the vibrational modes, which by convention is included in the chemical energy term. These zero-point terms add a constant value to $\bar{u}$, $\bar{h}$, $\bar{a}$, and $\bar{g}$, but of course not to $\bar{s}$, $\overline{C}_{p0}$, and $\overline{C}_{v0}$ for the molecule.

Ground electronic level contributions to properties are found, as for diatomic substances, by using Eqs. 18.97 to 18.99.

EXAMPLE 18.7

Calculate the entropy of carbon dioxide at 1200 K, 100-kPa pressure.

Solution

From Table A.19.1 for CO_2, the C–O distances are 0.1160 nm, and the vibrational wave numbers are

$$\omega_1 = 138.49 \text{ mm}^{-1}$$
$$\omega_2 = 66.73 \text{ (two modes)}$$
$$\omega_3 = 234.93$$

For the ground electronic level, $\mathbf{g}_{e0} = 1$.

In solving this problem, we consider in turn the translational, rotational, vibrational, and electronic modes and find the entropy contribution of each mode. We consider first the translational contribution to entropy. From Eq. 18.30 at 1200 K, 100 kPa,

$$\frac{Z_t}{N} = 2.594\,676 \frac{M^{3/2}T^{5/2}}{P}$$
$$= 2.594\,676 \frac{(44.01)^{3/2}(1200)^{5/2}}{100}$$
$$= 3.7789 \times 10^8$$

The translational entropy is, from Eq. 18.28,

$$\bar{s}_t = \bar{R}\left(\ln \frac{Z_t}{N} + \frac{5}{2}\right) = 8.3144(19.75 + 2.5) = 184.996 \text{ kJ/kmol K}$$

Next, we consider the rotational contribution. From Eq. 18.103, the center of mass is at the center of the C atom. Therefore, $r_C = 0$, $r_O = \pm 0.1160$ nm, and, using Eq. 18.102, we have

$$I_r = \sum_i m_i r_i^2 = 2(16.0 \times 1.6606 \times 10^{-27})(0.1160 \times 10^{-9})^2$$
$$= 0.7150 \times 10^{-45} \text{ kg m}^2$$

From Eq. 18.77,

$$\theta_r = \frac{h^2}{8\pi^2 I_r k} = \frac{(6.626\,18 \times 10^{-34})^2}{8\pi^2(0.715 \times 10^{-45})(1.380\,66 \times 10^{-23})} = 0.563 \text{ K}$$

The rotational partition function is found from Eq. 18.78:

$$Z_r = \frac{T}{\sigma\theta_r} = \frac{1200}{2(0.563)} = 1065.7$$

The resulting contribution to entropy is, from Eq. 18.83,

$$\bar{s}_r = \bar{R}(\ln Z_r + 1) = 8.3144(\ln 1065.7 + 1) = 66.277 \text{ kJ/kmol K}$$

Regarding the vibrational contribution, there are four vibrational degrees of freedom, two of which have the same frequency. Thus,

$$\theta_{v1} = \frac{hc}{k}\omega_1 = 14.3879(138.49) = 1993 \text{ K}$$
$$\theta_{v2} = 14.3879(66.73) = 960 \text{ K (double)}$$
$$\theta_{v3} = 14.3879(234.93) = 3380 \text{ K}$$

and

$$x_1 = \frac{\theta_{v1}}{T} = \frac{1993}{1200} = 1.66$$
$$x_2 = \frac{\theta_{v2}}{T} = \frac{1960}{1200} = 0.80 \text{ (double)}$$
$$x_3 = \frac{\theta_{v3}}{T} = \frac{3380}{1200} = 2.82$$

Using Eq. 18.94 for each of the four vibrational modes, we find the vibrational entropy to be

$$\bar{s}_v = \bar{R}\sum_i \left[-\ln(1 - e^{-x_i}) + \frac{x_i}{e^{x_i} - 1}\right]$$
$$= 8.3144[(0.2109 + 0.3897) + 2(0.5966 + 0.6528) + (0.0615 + 0.1787)]$$
$$= 27.767 \text{ kJ/kmol K}$$

From Eq. 18.98, the electronic contribution is

$$\bar{s}_e = \bar{R} \ln \mathbf{g}_{e0} = 0$$

Therefore, the entropy of CO_2 at 1200 K, 100 kPa, is found by summing the various contributions. The result is

$$\bar{s} = \bar{s}_t + \bar{s}_r + \bar{s}_v + \bar{s}_e = 184.996 + 66.277 + 27.767 + 0$$
$$= 279.040 \text{ kJ/kmol K}$$

It is of interest to compare this result with the value listed in Table A.12, at the same temperature and pressure. The value in Table A.12 is 279.390 kJ/kmol K, which was calculated using a more sophisticated internal model that included correction terms and excited electronic terms. Nevertheless, the simple internal model approach used in Example 18.7 gives a very close approximation.

In our discussion and in Example 18.7, we have found that the calculation of thermodynamic properties for linear polyatomic molecules is very similar to that for diatomic molecules, at the same time noting that the contributions of the multiple vibrational modes make the properties much more temperature-dependent. The vast majority of polyatomic molecules are not linear, however, and determination of the properties for such molecules becomes much more complicated. A simple example of a nonlinear molecule is water, which was discussed briefly in Section 2.6. This type of molecule has three significant and contributing degrees of freedom for rotation, instead of only two as linear molecules have. We will not analyze the rotational contributions of nonlinear molecules in this text, but we do point out that three rotational degrees of freedom instead of two mean that the $\bar{R}$ contribution to rotational specific heat is one and a half times that of the linear molecule. Rotational contributions to entropy are more difficult because rotation is a function of the three principal moments of inertia, which may or may not be equal to one another, depending on the structure of the particular molecule. The rotational symmetry number may also be difficult to determine, especially for complex molecules. Vibrational contributions to properties of nonlinear molecules are determined in the same manner as for linear molecules, keeping in mind that there are only $3a - 6$ independent modes remaining for vibration for these molecules instead of $3a - 5$.

18.9 THE ELECTRON GAS IN A METAL

In this section we consider the conduction electrons in a metal as an example of a substance in a condition for which the Boltzmann approximation is not a reasonable statistical model. It was noted in Section 16.5 that when $N_j \ll \mathbf{g}_j$ for all energy levels, both the quantum statistical models, Bose–Einstein and Fermi–Dirac, reduce to a common approximate form, which is called the Boltzmann model. Using this approximate model, we then developed the equilibrium state distribution, which led to Eq. 17.13. Notice from this equation that in order for N_j to be much less than $\mathbf{g}_j$, it is necessary for e^{α} to be a very large number, which becomes an

alternative specification for the validity of the Boltzmann approximate model. Whenever e^{α} is not large compared with unity, however, the appropriate quantum statistical model, the Fermi–Dirac model in this case, must be employed in its general form. Conduction electrons in a metal have sufficient energy to move quite freely through the lattice of positive ions. Because forces between the electrons are relatively small, we assume that it is reasonable to treat the collection of free electrons in a metal as a system of independent particles, which we term the electron gas.

Before we analyze the electron gas, it is necessary to discuss certain aspects of the general behavior of a Fermi–Dirac system—the most probable macrostate or equilibrium distribution and low-temperature behavior. Rewriting Eq. 16.29 in logarithmic form and using Stirling's approximation for the factorials, we have

$$\ln w = \sum_j [\mathbf{g}_j \ln \mathbf{g}_j - (\mathbf{g}_j - N_j) \ln(\mathbf{g}_j - N_j) - N_j \ln N_j] \tag{18.108}$$

Now, as in previous developments, we differentiate Eq. 18.108 and set the result equal to zero, subject to two constraints, the fixed number of particles and the fixed system energy. Then, by the method of undetermined multipliers, the most probable macrostate is found to be

$$N_j = \frac{\mathbf{g}_j}{e^{\alpha} e^{\beta \epsilon_j} + 1} \tag{18.109}$$

As in the earlier developments, we then find that

$$\beta = \frac{1}{kT}, \qquad \alpha = -\frac{\mu}{kT} \tag{18.110}$$

Substituting gives

$$N_j = \frac{\mathbf{g}_j}{e^{(\epsilon_j - \mu)/kT} + 1} \tag{18.111}$$

Let us now examine the behavior of a Fermi–Dirac system at very low temperature. As the temperature is decreased, particles move into the lower energy levels, but, because of the Pauli exclusion principle, there can be no more than one particle per quantum state. Thus, as the temperature approaches absolute zero, the ground energy level becomes filled with $\mathbf{g}_0$ particles, the first level above that by $\mathbf{g}_1$ particles, and so on. Therefore, in the limiting case, absolute-zero temperature, the particles would assume the lowest possible energy states, but could not all crowd into the ground level. This behavior can be seen by examining the distribution equation, Eq. 18.111, at low temperature. As the temperature approaches zero, the chemical potential μ approaches a zero-point value μ_0. For all the energy levels for which ϵ_j is less than μ_0,

$$\lim_{T \to 0} (e^{(\epsilon_j - \mu_0)/kT}) = e^{-\infty} = 0$$

so that, for these levels,

$$\lim_{T \to 0} \left(\frac{N_j}{\mathbf{g}_j} \right) = 1 \tag{18.112}$$

That is, all these levels are completely filled. On the other hand, for the levels for which ϵ_j is greater than μ_0,

$$\lim_{T \to 0} (e^{(\epsilon_j - \mu_0)/kT}) = e^{+\infty}$$

and

$$\lim_{T \to 0} \left(\frac{N_j}{\mathbf{g}_j} \right) = 0 \tag{18.113}$$

That is, all energy levels above an energy equal to μ_0 are empty at absolute zero. This limiting distribution for Fermi–Dirac statistics at absolute-zero temperature is depicted in Fig. 18.10. The separating value of energy μ_0, below which all levels are filled and above which all levels are empty at absolute-zero temperature, is known as the Fermi energy.

We also note that, as the temperature is increased, some particles shift into the higher energy levels, and the distribution changes to that shown by the broken line in Fig. 18.10. As the temperature continues to increase, the upper portion of the distribution curve approaches the exponential function predicted by Boltzmann statistics.

We are now in a position to discuss the electron gas as a model of the conduction electrons in a metal. Let us begin by doing so in the limiting case, at absolute-zero temperature, for which it would be of interest to evaluate the Fermi energy μ_0. It will therefore be necessary to determine the number of quantum states available at all levels of energy less than μ_0. The number of translational states in an interval of energy ϵ to $\epsilon + d\epsilon$ has been given previously by Eq. 18.35:

$$\mathbf{g}_{\epsilon \text{ trans}} = \frac{4\pi m V}{h^3} (2m\epsilon)^{1/2} \, d\epsilon$$

Because this expression considers translation only, this result must be multiplied by a factor of 2 for the electron gas to account for electron spin degeneracy. That

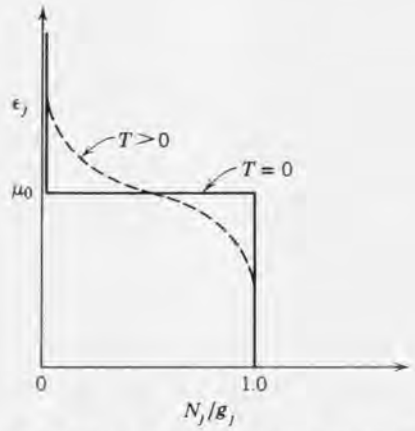


FIGURE 18.10 The Fermi–Dirac distribution.

is, an electron in any translational state can have a spin of either $+\frac{1}{2}$ or $-\frac{1}{2}$. Thus, the total number of quantum states available to the electron gas in an interval of energy ϵ to $\epsilon + d\epsilon$ is

$$\mathbf{g}_\epsilon = \frac{8\pi mV}{h^3}(2m\epsilon)^{1/2}\,d\epsilon \tag{18.114}$$

At absolute-zero temperature, Eq. 18.114 also represents the number of particles, dN_ϵ, in the energy range ϵ to $\epsilon + d\epsilon$ for all energies less than the Fermi level μ_0, because all quantum states below μ_0 are filled at this condition. Therefore, the total number of electrons, N, in the system is found to be

$$N = \int_{N_{\epsilon=0}}^{N_{\epsilon=\mu_0}} dN_\epsilon = \frac{8\pi mV}{h^3}(2m)^{1/2}\int_0^{\mu_0} \epsilon^{1/2}\,d\epsilon = \frac{8\pi V}{3h^3}(2m\mu_0)^{3/2} \tag{18.115}$$

The Fermi energy μ_0 is found from Eq. 18.115 to be

$$\mu_0 = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \tag{18.116}$$

The total energy U_0 of the system at absolute-zero temperature is

$$\begin{aligned} U_0 &= \int_{N_{\epsilon=0}}^{N_{\epsilon=\mu_0}} \epsilon\,dN_\epsilon = \frac{8\pi mV}{h^3}(2m)^{1/2}\int_0^{\mu_0} \epsilon^{3/2}\,d\epsilon \\ &= \tfrac{3}{5}N\mu_0 \end{aligned} \tag{18.117}$$

We note that the average energy per electron, U_0/N, at absolute zero is equal to three-fifths of the maximum energy μ_0.

At zero temperature, each quantum state below the Fermi level of energy contains one particle and each state above that level is empty. Thus, the system entropy is zero, or

$$S_0 = 0 \tag{18.118}$$

The zero-point Helmholtz function A_0 is seen to be

$$A_0 = U_0 - T_0S_0 = U_0 \tag{18.119}$$

and the Gibbs function is

$$G_0 = A_0 + P_0V = U_0 + P_0V \tag{18.120}$$

However, from Eq. 18.117,

$$G_0 = N\mu_0 = \tfrac{5}{3}U_0 \tag{18.121}$$

so that, for the electron gas,

$$P_0V = \tfrac{2}{3}U_0 \tag{18.122}$$

A representative calculation of the Fermi energy for the electron gas in a metal, by using Eq. 18.116, indicates that μ_0 is an extremely large number, of the order of magnitude of $10^5 \times k$. Consequently, it is reasonable to treat the behavior of the electron gas at ordinary temperatures, room temperature, for example, as merely small perturbations from the zero-temperature behavior. This procedure involves

a number of series expansions and approximations and is quite complex mathematically. It is found that the chemical potential for the electron gas in a metal is, in terms of the zero-point value,

$$\mu = \mu_0\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\mu_0}\right)^2 + \cdots\right] \tag{18.123}$$

Similarly, the energy is

$$U = U_0\left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\mu_0}\right)^2 - \cdots\right] \tag{18.124}$$

The specific-heat contribution is therefore

$$\overline{C}_v = \left[\frac{\partial(U/n)}{\partial T}\right]_V = \frac{N_0\pi^2k^2T}{2\mu_0} - \cdots \tag{18.125}$$

The entropy of the electron gas is readily found from the classical expression, as the integral of $(\overline{C}_v/T)\,dT$ from 0 to T.

Because of the large value of μ_0 just mentioned, the specific-heat contribution of the electron gas is quite small at ordinary temperature, of the order of magnitude of $10^{-2} \times \overline{R}$. This agrees with experimental observations for metals, in which the principal contribution to the specific heat at ordinary temperature is due to the lattice vibrations, which, in the classical limit, have a specific-heat contribution of $3 \times \overline{R}$.

18.10 MIXTURES OF GASES

This section is related to the discussion of mixtures of ideal gases from the classical view in Section 11.1, and it is intended to provide another means for analyzing the behavior of such a system. We consider a mixture of two components A and B, and assume a system of independent particles obeying Boltzmann statistics.

The first problem in analyzing the behavior and properties of a mixture is determining the equilibrium state; the procedure is analogous to that given in Section 17.1 for determining the equilibrium state of a pure gas. We consider a system of volume V containing a fixed number of particles N_A of species A and a fixed number N_B of species B, with the system having a given internal energy U. Since the particles are independent, we assume that specification of the system boundary parameter V fixes independent sets of quantum states available to species A and to species B. Thus, each species has its own set of energy levels, which for component A are

$$\epsilon_{A_1}, \epsilon_{A_2}, \ldots, \epsilon_{A_j}$$

with degeneracies

$$g_{A_1}, g_{A_2}, \ldots, g_{A_j}$$

and for component B the levels are

$$\epsilon_{B_1}, \epsilon_{B_2}, \ldots, \epsilon_{B_j}$$

with degeneracies

$$\mathbf{g}_{B_1}, \mathbf{g}_{B_2}, \ldots, \mathbf{g}_{B_j}$$

At any instant, the N_A particles of A are distributed in some manner among the energy levels for A, and the N_B particles of B are distributed in some manner among the energy levels for B. Any given system macrostate is then specified in terms of the number of particles of each species that are found in each of its levels, that is, by the sets

$$N_{A_1}, N_{A_2}, \ldots, N_{A_j}$$
$$N_{B_1}, N_{B_2}, \ldots, N_{B_j}$$

The possible macrostates are, of course, subject to the restrictions

$$N_A = \sum_{A_j} N_{A_j} \tag{18.126}$$

$$N_B = \sum_{B_j} N_{B_j} \tag{18.127}$$

and because the system energy U is given,

$$U = U_A + U_B = \sum_{A_j} N_{A_j}\epsilon_{A_j} + \sum_{B_j} N_{B_j}\epsilon_{B_j} \tag{18.128}$$

The thermodynamic probabilities w_A, w_B for the components are multiplicative, since any of the microstates of component A can exist in combination with any of those for component B. Thus, the thermodynamic probability w for the mixture is, using the Boltzmann expression Eq. 16.32 for A and B,

$$\mathrm{w} = \mathrm{w}_A\mathrm{w}_B = \left(\prod_{A_j} \frac{\mathbf{g}_{A_j}^{N_{A_j}}}{N_{A_j}!}\right)\left(\prod_{B_j} \frac{\mathbf{g}_{B_j}^{N_{B_j}}}{N_{B_j}!}\right) \tag{18.129}$$

If we rewrite Eq. 18.129 in logarithmic form and expand each term by Stirling's formula, the expression for w becomes

$$\ln \mathrm{w} = N_A + \sum_{A_j} N_{A_j} \ln \frac{\mathbf{g}_{A_j}}{N_{A_j}} + N_B + \sum_{B_j} N_{B_j} \ln \frac{\mathbf{g}_{B_j}}{N_{B_j}} \tag{18.130}$$

We seek the most probable distribution of the sets of particles N_A, N_B, among their respective sets of energy levels, that is, the macrostate having the maximum value of w. If we differentiate Eq. 18.130 and set $d \ln \mathrm{w} = 0$ as in the previous developments, we find that

$$\sum_{A_j} \ln \frac{\mathbf{g}_{A_j}}{N_{A_j}}\, dN_{A_j} + \sum_{B_j} \ln \frac{\mathbf{g}_{B_j}}{N_{B_j}}\, dN_{B_j} = 0 \tag{18.131}$$

This relation specifies the most probable macrostate, subject to the constraints

$$dN_A = \sum_{A_j} dN_{A_j} = 0 \tag{18.132}$$

$$dN_B = \sum_{B_j} dN_{B_j} = 0 \tag{18.133}$$

and

$$dU = \sum_{A_j} \epsilon_{A_j}\, dN_{A_j} + \sum_{B_j} \epsilon_{B_j}\, dN_{B_j} = 0 \tag{18.134}$$

Using the method of undetermined multipliers, we multiply Eq. 18.132 by α_A, Eq. 18.133 by α_B, and Eq. 18.134 by β. Adding the three resulting expressions to the negative of Eq. 18.131, we have

$$\sum_{A_j}\left(\ln\frac{N_{A_j}}{\mathbf{g}_{A_j}}+\alpha_A+\beta\epsilon_{A_j}\right)dN_{A_j}+\sum_{B_j}\left(\ln\frac{N_{B_j}}{\mathbf{g}_{B_j}}+\alpha_B+\beta\epsilon_{B_j}\right)dN_{B_j}=0 \quad (18.135)$$

Because components A and B are independent, we conclude from Eq. 18.135 that, for the most probable macrostate,

$$N_{A_j}=\mathbf{g}_{A_j}e^{-\alpha_A}e^{-\epsilon_{A_j}/kT} \quad (18.136)$$

for all values of A_j, and

$$N_{B_j}=\mathbf{g}_{B_j}e^{-\alpha_B}e^{-\epsilon_{B_j}/kT} \quad (18.137)$$

for all values of B_j. In both expressions the relation $\beta = 1/kT$ has been assumed, as was previously found to be the case for Boltzmann statistics.

If we now sum Eq. 18.136 over all A_j's,

$$N_A=e^{-\alpha_A}\sum_{A_j}\mathbf{g}_{A_j}e^{-\epsilon_{A_j}/kT}=e^{-\alpha_A}Z_A \quad (18.138)$$

where, according to Eq. 17.54, Z_A is the partition function for A:

$$Z_A=\sum_{A_j}\mathbf{g}_{A_j}e^{-\epsilon_{A_j}/kT} \quad (18.139)$$

Similarly, for component B, from Eq. 18.137, we have

$$N_B=e^{-\alpha_B}\sum_{B_j}\mathbf{g}_{B_j}e^{-\epsilon_{B_j}/kT}=e^{-\alpha_B}Z_B \quad (18.140)$$

where

$$Z_B=\sum_{B_j}\mathbf{g}_{B_j}e^{-\epsilon_{B_j}/kT} \quad (18.141)$$

Thus, with the multipliers α_A, α_B eliminated, the equilibrium distribution for the binary mixture whose components obey Boltzmann statistics can be expressed as

$$N_{A_j}=\frac{N_A\mathbf{g}_{A_j}e^{-\epsilon_{A_j}/kT}}{Z_A} \qquad \text{for all } A_j \quad (18.142)$$

$$N_{B_j}=\frac{N_B\mathbf{g}_{B_j}e^{-\epsilon_{B_j}/kT}}{Z_B} \qquad \text{for all } B_j \quad (18.143)$$

It is important to note that the component partition functions Z_A, Z_B, are to be evaluated for A and B, respectively, each at the temperature and volume of the system. Thus, we conclude that each of the components of the mixture behaves as though it existed alone in the total volume V at the temperature of the mixture. We find, then, that the assumption of the existence of independent sets of energy levels at the microscopic level, as specified by the boundary parameter, leads logically to a means for expressing the equilibrium state that is identical to a mixture model assumed in the classical development in Chapter 11.

Let us now examine the thermodynamic properties for this mixture of gases. Substituting Eqs. 18.142 and 18.143 for N_{A_j} and N_{B_j}, and by the same procedure as in Section 17.5, we have for U_A

$$U_A = \sum_{A_j} N_{A_j}\epsilon_{A_j} = \frac{N_A}{Z_A}\sum_{A_j} \mathbf{g}_{A_j}\epsilon_{A_j} e^{-\epsilon_{A_j}/kT}$$
$$= \frac{N_A kT^2}{Z_A}\left(\frac{\partial Z_A}{\partial T}\right)_V = n_A \bar{R}T^2\left(\frac{\partial \ln Z_A}{\partial T}\right)_V \tag{18.144}$$

and similarly for U_B,

$$U_B = \sum_{B_j} N_{B_j}\epsilon_{B_j} = n_B \bar{R}T^2\left(\frac{\partial \ln Z_B}{\partial T}\right)_V \tag{18.145}$$

Substituting these relations into Eq. 18.128, we find that the integral energy of the system is

$$U = n_A \bar{R}T^2\left(\frac{\partial \ln Z_A}{\partial T}\right)_V + n_B \bar{R}T^2\left(\frac{\partial \ln Z_B}{\partial T}\right)_V = n_A \bar{u}_A + n_B \bar{u}_B \tag{18.146}$$

where $\bar{u}_A$ is the molal internal energy for substance A as though it existed alone in volume V at temperature T, and $\bar{u}_B$ is the corresponding value for substance B. This conclusion is in accord with the corresponding analysis of an ideal-gas mixture from the view of classical thermodynamics in Chapter 11.

The entropy of a system at equilibrium is defined by Eq. 17.28:

$$S = k \ln \mathrm{w}_{\mathrm{mp}}$$

Therefore, substituting Eqs. 18.142 and 18.143 for the ratios $\mathbf{g}_{A_j}/N_{A_j}$ and $\mathbf{g}_{B_j}/N_{B_j}$, which correspond to the most probable distributions, into Eq. 18.130, we obtain

$$\ln \mathrm{w}_{\mathrm{mp}} = N_A + \sum_{A_j} N_{A_j} \ln\left(\frac{Z_A}{N_A} e^{+\epsilon_{A_j}/kT}\right) + N_B + \sum_{B_j} N_{B_j} \ln\left(\frac{Z_B}{N_B} e^{+\epsilon_{B_j}/kT}\right)$$
$$= N_A + \ln\frac{Z_A}{N_A}\sum_{A_j} N_{A_j} + \frac{1}{kT}\sum_{A_j} N_{A_j}\epsilon_{A_j}$$
$$+ N_B + \ln\frac{Z_B}{N_B}\sum_{B_j} N_{B_j} + \frac{1}{kT}\sum_{B_j} N_{B_j}\epsilon_{B_j}$$
$$= N_A + N_A \ln\frac{Z_A}{N_A} + \frac{U_A}{kT} + N_B + N_B \ln\frac{Z_B}{N_B} + \frac{U_B}{kT}$$
$$= N_A\left(\ln\frac{Z_A}{N_A} + 1\right) + \frac{U_A}{kT} + N_B\left(\ln\frac{Z_B}{N_B} + 1\right) + \frac{U_B}{kT}$$

If we now substitute this result into Eq. 17.28, we obtain for the entropy of the mixture

$$S = N_A k\left(\ln\frac{Z_A}{N_A} + 1\right) + \frac{U_A}{T} + N_B k\left(\ln\frac{Z_B}{N_B} + 1\right) + \frac{U_B}{T}$$
$$= n_A\left[\bar{R}\left(\ln\frac{Z_A}{N_A} + 1\right) + \frac{\bar{u}_A}{T}\right] + n_B\left[\bar{R}\left(\ln\frac{Z_B}{N_B} + 1\right) + \frac{\bar{u}_B}{T}\right] \tag{18.147}$$

or

$$\bar{s} = n_A \bar{s}_A + n_B \bar{s}_B \tag{18.148}$$

In Eq. 18.148, $\bar{s}_A$ is the entropy of substance A evaluated as though it exists alone in the system volume V at temperature T, and $\bar{s}_B$ is the corresponding value for substance B. We find again that the analysis is in accord with that of an ideal-gas mixture made from the classical view.

Expressions for the other thermodynamic properties of interest for ideal-gas mixtures, $\overline{C}_{p0}$, $\overline{C}_{v0}$, H, A, and G, follow readily from their definitions and the relations for internal energy, entropy, and the ideal-gas equation of state.

18.11 CHEMICAL REACTION AND EQUILIBRIUM

This final section is concerned with the special topics of chemical reaction and equilibrium, and is intended as supplementary material to Chapters 13 and 14. It is not intended to cover these subjects in detail, but rather to examine two particular topics: the enthalpy of formation and the concept of chemical equilibrium from the molecular view.

To summarize briefly the classical presentation of enthalpy of formation in Chapter 13, we used the calorimetric approach, that is, we measured the heat transfer associated with a chemical reaction. These reactions were specified to occur at a constant temperature of 25°C. It was then noted that since one element cannot be converted into another in a chemical reaction, we are free to choose reference values for enthalpy of the various elements independently of one another. For convenience, we choose these reference values for the stable forms of the elements (for example, C, N_2, H_2) as zero at the specified temperature of 25°C. Then, measurement of the heat transfer for the various chemical reactions establishes the enthalpy of formation of other forms of these elements and also of compounds relative to this arbitrarily selected reference.

Although this argument presents a logical picture for the establishment of the concept of enthalpy of formation, the numerical values as presented in Table A.15 are not determined by calorimetric procedures, as implied. Instead, it is more precise to determine the fundamental reference value D_0, as shown in Fig. 18.8, from spectroscopic measurements on the molecular species. The enthalpy of formation (25°C reference) can then be calculated from this value and the properties of the gases. The procedure for such a calculation is most easily demonstrated by an example.

EXAMPLE 18.8

Calculate the enthalpy of formation of monatomic nitrogen relative to the 25°C chemical reference base.

Solution

First, for the monatomic species, N, at 298.15 K,

$$(\bar{h})_N = \bar{h}_t + \bar{h}_e + \bar{h}_{\text{chem}}$$

From Eq. 18.25,

$$\bar{h}_t = \tfrac{5}{2}\bar{R}T = \tfrac{5}{2}(8.3144)(298.15) = 6197 \text{ kJ/kmol}$$

From the electronic level data in Table 15.2 and Eqs. 18.37, 18.38, and 18.40,

$$\bar{h}_e = \bar{R}T\frac{Z_e'}{Z_e} \approx 0$$

The spectroscopic reference base is taken as zero at 0 K for the monatomic species, as indicated in Fig. 18.8. Therefore,

$$\bar{h}_{\text{chem}} = 0$$

and

$$(\bar{h})_{\text{N}} = 6197 + 0 + 0 = 6197 \text{ kJ/kmol}$$

Now, for the diatomic species, N_2, at 298.15 K,

$$(\bar{h})_{\text{N}_2} = \bar{h}_t + \bar{h}_r + (\bar{h}_v - \bar{u}_{v0}) + \bar{h}_e + \bar{h}_{\text{chem}}$$

As for the monatomic form,

$$\bar{h}_t = \tfrac{5}{2}\bar{R}T = 6197 \text{ kJ/kmol}$$

For the simple internal model, from Eq. 18.81,

$$\bar{h}_r = \bar{R}T = 8.3144(298.15) = 2479 \text{ kJ/kmol}$$

From the data in Table A.19 and Eq. 18.88,

$$\theta_v = \frac{hc\omega_e}{k} = 14.3879(235.76) = 3392 \text{ K}$$

so that at 298.15 K

$$x = \frac{\theta_v}{T} = \frac{3392}{298.15} = 11.377$$

and from Eq. 18.92,

$$\bar{h}_v - \bar{u}_{v0} = \bar{R}T\left(\frac{x}{e^x - 1}\right) \approx 0$$

For the simple internal model, from Eq. 18.97,

$$\bar{h}_e = 0$$

and from Table A.19 and Eq. 18.101,

$$\begin{aligned}\bar{h}_{\text{chem}} &= -N_0 D_0 \\ &= -6.022\,045 \times 10^{23}(7871.50)(6.626\,176 \times 10^{-34})(2.997\,925 \times 10^{11}) \\ &= -941\,641 \text{ kJ/kmol}\end{aligned}$$

Thus,

$$\begin{aligned}(\bar{h})_{\text{N}_2} &= 6197 + 2479 + 0 + 0 - 941\,641 \\ &= -932\,965 \text{ kJ/kmol}\end{aligned}$$

We now have the enthalpies of both species at 298.15 K relative to the spectroscopic reference base. Consequently, for the chemical reaction,

$$\begin{aligned} &\tfrac{1}{2}N_2 \rightarrow N \\ \Delta H^\circ_{298} &= (\bar{h})_N - \tfrac{1}{2}(\bar{h})_{N_2} \\ &= 6197 - \tfrac{1}{2}(-932\,965) \\ &= +472\,680 \text{ kJ} \end{aligned}$$

which is equivalent to the calorimetric heat transfer for the constant-temperature reaction at 25°C. Therefore, relative to the 25°C chemical reference value,

$$(\bar{h}^\circ_f)_{N_2} = 0$$

We find that

$$\begin{aligned} (\bar{h}^\circ_f)_N &= \Delta H^\circ_{298} + \tfrac{1}{2}(\bar{h}^\circ_f)_{N_2} \\ &= +472\,680 \text{ kJ/kmol of N} \end{aligned}$$

which agrees with the value listed for N in Table A.12.

The second topic that we wish to examine in this section from the molecular view is that of the concept of chemical equilibrium. Let us consider the dissociation of a diatomic species AB to the two monatomic species A and B. The reaction equation is written as

$$AB \rightleftharpoons A + B \tag{18.149}$$

We assume that the equilibrium mixture behaves as an ideal-gas mixture of the three components, AB, A, and B. The analysis of this mixture from the molecular view is analogous to that in Section 18.10 for a binary mixture, except that now we have three distinguishable components in volume V and therefore three independent sets of energy levels, one for each species.

Let us consider a mixture comprising a given total number of particles of each species N_{AB}, N_A, N_B (not necessarily the number of each at a condition of chemical equilibrium) contained in volume V at some temperature T. These particles are distributed in some manner among the various energy levels. The macrostate is specified by the number of particles of each species in each of its energy levels,

$$\begin{gathered} N_{AB_1}, N_{AB_2}, \ldots, N_{AB_j} \\ N_{A_1}, N_{A_2}, \ldots, N_{A_j} \\ N_{B_1}, N_{B_2}, \ldots, N_{B_j} \end{gathered} \tag{18.150}$$

with the restrictions

$$\begin{aligned} N_{AB} &= \sum_{AB_j} N_{AB_j} \\ N_A &= \sum_{A_j} N_{A_j} \\ N_B &= \sum_{B_j} N_{B_j} \end{aligned} \tag{18.151}$$

For any given macrostate, the thermodynamic probability w for the mixture is

$$\begin{aligned} \mathrm{w} &= (\mathrm{w}_{AB})(\mathrm{w}_{A})(\mathrm{w}_{B}) \\ &= \left(\prod_{AB_j} \frac{\mathbf{g}_{AB_j}^{N_{AB_j}}}{N_{AB_j}!}\right)\left(\prod_{A_j} \frac{\mathbf{g}_{A_j}^{N_{A_j}}}{N_{A_j}!}\right)\left(\prod_{B_j} \frac{\mathbf{g}_{B_j}^{N_{B_j}}}{N_{B_j}!}\right) \end{aligned} \tag{18.152}$$

As discussed in Section 18.10, each state for component A can be associated with any state of B or of AB, and so on. Therefore, the value of w for the mixture is the product of those for the individual constituents, as indicated in Eq. 18.152. The energy corresponding to this given macrostate is expressed by

$$U = \sum_{AB_j} N_{AB_j}\epsilon_{AB_j} + \sum_{A_j} N_{A_j}\epsilon_{A_j} + \sum_{B_j} N_{B_j}\epsilon_{B_j} \tag{18.153}$$

We seek the most probable macrostate for this system, subject to the given constraints, Eqs. 18.151 and 18.153, a fixed number of particles of each type, and the fixed energy of the system. This most probable macrostate is found by maximizing Eq. 18.152 subject to these constraints. From the summarizing equations of Section 18.10, Eqs. 18.142 and 18.143, it is easily seen that the summarizing equations here are

$$N_{AB_j} = \frac{N_{AB}}{Z_{AB}}\mathbf{g}_{AB_j}e^{-\epsilon_{AB_j}/kT}, \qquad \text{for all } AB_j \tag{18.154}$$

$$N_{A_j} = \frac{N_{A}}{Z_{A}}\mathbf{g}_{A_j}e^{-\epsilon_{A_j}/kT}, \qquad \text{for all } A_j \tag{18.155}$$

$$N_{B_j} = \frac{N_{B}}{Z_{B}}\mathbf{g}_{B_j}e^{-\epsilon_{B_j}/kT}, \qquad \text{for all } B_j \tag{18.156}$$

This is the most probable macrostate for the given values N_{AB}, N_A, N_B, and U. The thermodynamic probability corresponding to this most probable macrostate is, using Eq. 18.146 for three components,

$$\begin{aligned} \ln \mathrm{w}_{\mathrm{mp}} = {} & N_{AB}\left(\ln \frac{Z_{AB}}{N_{AB}} + 1\right) + N_{A}\left(\ln \frac{Z_{A}}{N_{A}} + 1\right) \\ & + N_{B}\left(\ln \frac{Z_{B}}{N_{B}} + 1\right) + \frac{U}{kT} \end{aligned} \tag{18.157}$$

To review briefly, we began our analysis by considering a mixture made up of given N_{AB}, N_A, and N_B, but not necessarily in the proportions for chemical equilibrium, and we found that the thermodynamic probability for the most probable macrostate in the mixture of these proportions is given by Eq. 18.157. There will be an equation of the same form for each mixture of different proportions (different values of N_{AB}, N_A, N_B), but of course the value of w_{mp} will be different for each different mixture. The particular mixture with the largest value of w_{mp} is the chemical equilibrium mixture and can be found by determining the maximum of Eq. 18.157 while varying N_{AB}, N_A, N_B. The possible values of N_{AB}, N_A, N_B are, however, restricted according to the initial composition in the system. The total number of atoms of A must remain the same, whether in the diatomic form AB or in the monatomic form, and the total number of atoms of B must similarly remain

constant. Since there is one atom of A and one of B in AB,

$$\text{Total atoms of type } A = N_{AB} + N_A = \text{constant} \tag{18.158}$$

$$\text{Total atoms of type } B = N_{AB} + N_B = \text{constant} \tag{18.159}$$

To find the maximum in Eq. 18.157 subject to these interrelations, we differentiate Eq. 18.157 with respect to N_{AB}, N_A, N_B, at fixed U, V and set the result equal to zero. Upon performing this differentiation, we find that, for the chemical equilibrium composition,

$$d \ln \mathrm{w}_{\mathrm{mp}} = \ln \frac{Z_{AB}}{N_{AB}}\, dN_{AB} + \ln \frac{Z_A}{N_A}\, dN_A + \ln \frac{Z_B}{N_B}\, dN_B = 0 \tag{18.160}$$

subject to the constraints

$$dN_{AB} + dN_A = 0 \tag{18.161}$$

$$dN_{AB} + dN_B = 0 \tag{18.162}$$

We now multiply Eq. 18.161 by γ and Eq. 18.162 by δ and add the result to Eq. 18.160. By the method of undetermined multipliers, we conclude that, for the equilibrium composition N_{AB_e}, N_{A_e}, N_{B_e},

$$\gamma + \delta + \ln \frac{Z_{AB}}{N_{AB_e}} = 0 \tag{18.163}$$

$$\gamma + \ln \frac{Z_A}{N_{A_e}} = 0 \tag{18.164}$$

$$\delta + \ln \frac{Z_B}{N_{B_e}} = 0 \tag{18.165}$$

Eliminating the multipliers γ and δ from these equations, we have

$$\frac{N_{A_e} N_{B_e}}{N_{AB_e}} = \frac{Z_A Z_B}{Z_{AB}} \tag{18.166}$$

which is the equilibrium equation and is analogous to the expression, Eq. 14.35, developed from the classical view. To demonstrate this analogy, recall that the mole fraction of component i is

$$y_i = \frac{n_i}{n} = \frac{N_i}{N} \tag{18.167}$$

and that the partition function, including all contributions, can be written for component i as

$$Z_i = V \times f_i(T) \tag{18.168}$$

Therefore, substituting these relations into Eq. 18.166 for the three species, we have

$$\frac{y_A y_B}{y_{AB}} = \frac{V}{N} f(T) = \frac{kT}{P} f(T) = K\left(\frac{P^\circ}{P}\right) \tag{18.169}$$

which is the classical expression (Eq. 14.35 applied to the reaction Eq. 18.151) in terms of the equilibrium constant K.

PROBLEMS

18.1 In Section 18.2, the translational partition function was determined for a system of dimensions $X = Y = Z$. Repeat this development for a system in which X, Y, and Z are not equal.

18.2 Consider the evaluation of the translational partition function, Eq. 18.22, from the quantum mechanical energy expression, Eq. 18.21. For argon at -100°C, 100-kPa pressure, estimate the error introduced by neglecting the $\frac{1}{2}$ term in this analysis.

18.3 A two-dimensional ideal gas is a useful model for certain applications (for example, in analyzing the behavior of atoms adsorbed on a surface but still free to move in two directions. Consider such a gas confined to a surface of dimensions $X = Y$ and possessing only translational energy.

(a) Show that the energy of a quantum state is given by

$$\epsilon_{k_x,k_y} = \frac{h^2}{8m\mathscr{A}}(\mathbf{k}_x^2 + \mathbf{k}_y^2)$$

where $\mathscr{A}$ is the surface area.

(b) Find expressions for the internal energy and entropy of this gas.

(c) Using the thermodynamic relation,

$$P = -\left(\frac{\partial A}{\partial \mathscr{A}}\right)_T$$

determine the "pressure," force per unit length, for such a two-dimensional gas in terms of the energy and area.

18.4 The correct quantum statistical model for helium is the Bose–Einstein model. As an indication of the validity of the Boltzmann approximation, evaluate the quantity e^{α} for helium at 100-kPa pressure and temperatures of 5, 50, and 500 K, assuming the Boltzmann model to be valid. What conclusions can be drawn from the results?

18.5 Consider a monatomic gas made up of electrons (which is correctly represented by Fermi–Dirac statistics). In certain cases, the behavior of the electron gas can be accurately represented by the approximate Boltzmann model. Is this true for a temperature of 1000 K and an electron number density $N/V = 10^{16}$ l/m^3?

18.6 Evaluate the translational partition function using the approach of Section 18.3, beginning with Eq. 18.35 for the number of translational states in an energy interval ϵ to $\epsilon + d\epsilon$.

18.7 Consider a 1000-mm^3 sample of oxygen at 20°C, 100-kPa pressure. Using Eq. 18.35, calculate the number of translational quantum states in the interval of energy kT to $1.001\ kT$.

18.8 Calculate the entropy per kilomole of argon gas at 300 K, 200-kPa pressure.

18.9 Calculate the entropy per kilomole of monatomic hydrogen gas at 400 K, 100-kPa pressure, and compare the result with the value given in Table A.12.

18.10 Calculate the entropy of singly ionized nitrogen (N atoms minus one electron) at 2000 K, 10-Pa pressure. Observed electronic terms for N^+ are

Term	(ϵ/hc), mm^{-1}
$^3P_0$	0
$^3P_1$	4.91
$^3P_2$	13.13
$^1D_2$	1531.57

18.11 Calculate the values of $\bar{h}$, $\overline{C}_{p0}$, and $\bar{s}$ for monatomic oxygen at 100 K and 1000 K, 100-kPa pressure. Compare the enthalpy and entropy values with those listed in Table A.12.

18.12 Calculate the enthalpy and entropy for (hypothetical) ideal-gas carbon at 25°C, 100 kPa. The energies and degeneracies of the first several electronic terms are as follows.

$(\epsilon/hc)_j$, mm^{-1}	g_j
0	1
1.64	3
4.34	5
1019.263	5
2164.801	1
3373.52	5

18.13 Plot the electronic contribution to specific heat versus temperature for monatomic oxygen.

18.14 The following are the first several electronic terms observed for monatomic chlorine gas.

Term	(ϵ/hc), mm^{-1}
$^2P_{3/2}$	0
$^2P_{1/2}$	88.1
$^4P_{5/2}$	7195.4
$^4P_{3/2}$	7248.4
$^4P_{1/2}$	7282.3

Sketch the specific heat $\overline{C}_{p0}$ as a function of temperature. Include estimates of any temperatures at which unusual behavior occurs.

18.15 Consider a monatomic gas having two nondegenerate electronic states $\epsilon_{e0} = 0$ and ϵ_{e1}.

(a) Plot the electronic contribution to specific heat versus "reduced" temperature, kT/ϵ_{e1}.

(b) Determine analytically the value of reduced temperature at which the specific-heat contribution is a maximum.

18.16 Assuming a Maxwell–Boltzmann velocity distribution, compare the average speeds of helium and xenon at 300 and 3000 K.

18.17 Consider a monatomic gas having a Maxwell–Boltzmann velocity distribution.

(a) Show that the corresponding energy distribution is given by

$$\frac{dN_\epsilon}{N} = \frac{2}{\sqrt{\pi}(kT)^{3/2}} \epsilon^{1/2} e^{-\epsilon/kT}\, d\epsilon$$

where dN_ϵ is the number of particles having energy in the interval ϵ to $\epsilon + d\epsilon$.

(b) For a system having the energy distribution of part a, calculate the most probable energy and the average energy.

18.18 (a) For a gas with a Maxwell–Boltzmann velocity distribution, show that the fraction of atoms in the system having a speed between 0 and $\mathbf{V}$ can be expressed as

$$\frac{N_{0 \text{ to } \mathbf{V}}}{N} = \text{erf}(x) - \frac{2}{\sqrt{\pi}} x e^{-x^2}$$

where $x = \mathbf{V}/\mathbf{V}_{mp}$.

(b) Calculate the fraction of atoms in argon gas at 300 K with speeds less than 500 m/s at any instant of time.

18.19 At what temperature will 70 percent of the atoms in a helium-filled tank have speeds greater than 1500 m/s?

18.20 Consider a wall of a tank containing a monatomic gas. Taking x, y coordinates in the plane of the wall and z as the inward-directed normal, show that the distribution of particles striking the surface can be expressed in spherical coordinates as

$$\frac{\text{Number } (\mathbf{V}, \theta, \phi)}{\text{m}^2\text{s}} = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} \mathbf{V}^3 e^{-(m/2kT)\mathbf{V}^2} \cos\theta \sin\theta \, d\theta \, d\phi \, d\mathbf{V}$$

18.21 (a) Consider a gas contained in volume V and having an arbitrary speed distribution $dN_{\mathbf{V}}$ (the number of particles in an interval $\mathbf{V}$ to $\mathbf{V} + d\mathbf{V}$, and any θ, ϕ). Using the result of Problem 18.20, show that the rate at which particles of speed $\mathbf{V}$ strike a unit area of wall surface is given by

$$\frac{1}{4}\frac{\mathbf{V}}{V} dN_{\mathbf{V}}$$

(b) Derive Eq. 18.64 using the result of part a.

18.22 Neon gas is contained in a cubic 1-L tank at 25°C, 100-kPa pressure.

(a) Calculate the rate at which neon atoms strike a 1-mm^2 area of the wall surface.

(b) How many times per second, on the average, does an atom strike a wall of the tank?

18.23 A very small pinhole develops in the wall of a vessel, and every atom of the gas inside that strikes the hole escapes from the tank. Show that the average energy per particle escaping is $2kT$. Why is this different from the average energy of the gas inside the tank?

18.24 The equilibrium of a liquid with its vapor is of a dynamic character. At equilibrium, molecules of liquid evaporate at the same rate at which molecules of vapor condense, so that there is no net change in the amount of each phase present. Consider mercury at 0°C, at which temperature the vapor pressure is 0.0247 Pa. If every vapor molecule striking the liquid surface condenses, what are the rates at which condensation and evaporation occur at equilibrium?

18.25 A tank of volume V contains a gas (molecular weight M) at conditions P_0, T, as shown in Fig. 18.11. The tank is located in a large environment of the same gas at conditions P_A, T, where $P_A > P_0$. A very small hole of area A develops in a wall of the tank. Its size is such that every particle striking the hole from either side passes through freely. Assuming that T is constant, derive an expression for the pressure inside the tank as a function of time.

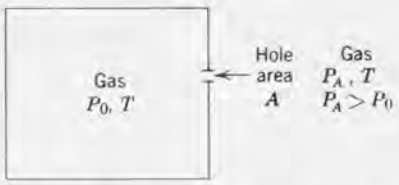


FIGURE 18.11 Sketch for Problem 18.25.

18.26 A 1-L vacuum container is maintained at 0.1-Pa pressure. Air at 100 kPa, 20°C, surrounds the container. A pinhole of 10^{-5}-mm diameter then develops in the wall.

(a) Find the initial rate at which molecules pass through the hole in each direction, by treating air as a pure substance with $M = 28.97$.

(b) What is the pressure inside the vacuum container after two hours?

18.27 A "getter" is a substance used to remove gas molecules from a closed volume, by adsorption or chemical combination; it finds considerable application in high-vacuum technology. As an example, consider a 1-L volume containing air that is initially pumped to 100-Pa pressure and then sealed. Inside this volume is a "getter" of 100-mm^2 surface, which is assumed to remove 0.1 percent of the molecules striking the surface. Determine the pressure inside the volume as a function of time, assuming that the temperature remains constant at 25°C.

18.28 A "potential barrier" model is useful for many applications, especially in the field of electronics. Consider a monatomic ideal gas having Maxwell–Boltzmann velocity distribution and confined in an enclosure, one "wall" of which consists of a potential barrier φ (perhaps owing to an electric field). Thus, all particles that reach this wall with a normal component of kinetic energy greater than φ escape, and all those with an energy component less than φ are reflected. Develop an expression for the flux of particles through this barrier in terms of the significant parameters.

18.29 A monatomic gas is contained in a vessel of volume V at initial conditions P_0, T_0. The gas slowly escapes through a small hole of area A under conditions of free molecule flow. There is no flow into the vessel from outside. The vessel is well insulated, so that there is no heat transfer with the surroundings, and the specific heat of the walls can be neglected.

(a) Find the relation between P and T inside the vessel at any point during the process.

(b) Compare the result of part a with the case in which the hole area is much larger than the mean free path of the gas.

18.30 Determine the expression for temperature inside the vessel as a function of time for Problem 18.29.

18.31 Plot the distribution of molecules among the various rotational levels for carbon monoxide at 100 and 300 K.

18.32 For HCl, find the temperature at which exactly 50 percent of the molecules have a rotational quantum number greater than 3.

18.33 When T/θ_r is not much greater than unity, the rotational partition function for a heteronuclear molecule can be evaluated by direct expansion of Eq. 18.75.

(a) For such a region, develop an expression for the rotational internal energy.

(b) Plot the rotational internal energy versus T for HF at temperatures below 300 K, using the appropriate method for determining u_r.

(c) Repeat parts a and b for the rotational specific heat of HF.

18.34 Hydrogen deuteride (HD), the diatomic molecule made up of a hydrogen atom and a deuteron (one proton and one neutron in the nucleus), has a characteristic rotational temperature $\theta_r = 63$ K. Calculate the rotational entropy of HD at 20, 100, and 500 K, using whatever method is appropriate at each temperature.

18.35 Prove that the vibrational entropy is independent of the selection for the ground level reference of energy, u_{v0}.

18.36 For diatomic nitrogen at 2000 K, calculate the probability that a molecule will have a vibrational quantum number less than 3.

18.37 Plot the distribution of molecules among the various vibrational levels for diatomic bromine at 300 and 3000 K.

18.38 For diatomic fluorine at 200-kPa pressure, compare the relative magnitudes of the various contributions to $\overline{C}_{p0}$ and $\overline{s}$ at 300 and 3000 K.

18.39 Calculate the entropy of diatomic bromine at 800 K, 500-kPa pressure. Clearly specify any assumptions made in the calculation.

18.40 Calculate the entropy of nitric oxide (NO) at 300 K, 100 kPa. The electronic term is $^2\Pi$, a total of four states—two of which lie 12.11 mm^{-1} above the other two. Is the simple integrated result valid for the rotational partition function at this temperature?

18.41 Diatomic chlorine at 1000 K, 100 kPa, is cooled in a constant-pressure, steady-flow process to 300 K. Calculate the heat transfer and entropy change per mole during this process.

18.42 Atoms from a monatomic gas are adsorbed onto a surface of area $\mathscr{A}$ until an equilibrium condition is established (Gibbs function per kilomole of the adsorbed atoms equal to that of the free gas). Assume the ground electronic state for each. For the adsorbed atoms, assume a two-dimensional translation on the adsorbing surface plus a vibrational degree of freedom normal to the surface. (The vibration is represented by θ_v and a ground point energy ϵ_0). Derive an expression for the concentration of adsorbed atoms on the surface (atoms/m^2) in terms of the free gas number density (atoms/m^3) and other relevant parameters.

18.43 The first three electronic levels of diatomic oxygen are

Term	(ϵ/hc), mm^{-1}
$^3\Sigma_g^-$	0
$^1\Delta_g$	788.2
$^1\Sigma_g^+$	1312.1

Assume a rigid rotator–harmonic oscillator for which the constants r_e and ω_e are the same for each of the electronic levels, and no higher electronic levels are populated.

(a) Calculate the fraction of molecules in each of the three electronic levels at 5000 K.

(b) Determine the constant-pressure specific heat of oxygen at 5000 K.

18.44 Calculate the enthalpy and the entropy of diatomic oxygen at 5000 K, 100-kPa pressure, and compare the results with the values given by Table A.12.

18.45 Calculate the Gibbs function with respect to ground state energy for nitrous oxide (N_2O) at 800 K, 100-kPa pressure.

18.46 Carbon dioxide at 300 K, 100-kPa pressure, is heated in a constant-pressure, steady-flow process to 1200 K.

(a) Calculate the heat transfer for the process and the entropy change of the carbon dioxide.

(b) Repeat part a using the gas tables, Table A.12.

18.47 Calculate the enthalpy and entropy for the linear polyatomic molecule HCN at 25°C and the ideal-gas standard-state pressure, 100 kPa.

18.48 Calculate the Fermi energy μ_0 and the pressure exerted by the electron gas in a metal at 0 K. Assume one conduction electron per atom of metal and a metal density of 100 kmol/m^3.

18.49 Consider the electron gas in a metal.

(a) Using the thermodynamic relation

$$P = -\left(\frac{\partial A}{\partial V}\right)_T$$

show that, at room temperature,

$$PV = \tfrac{2}{3}U$$

(b) Using the data of Problem 18.48, calculate μ and the electron gas pressure at 300 K.

18.50 (a) Using Eqs. 18.111 and 18.114 for an electron gas, show that the number of electrons, dN_ϵ, in an interval of energy ϵ to $\epsilon + d\epsilon$ is

$$dN_\epsilon = \frac{4\pi V}{h^3}\frac{(2m)^{3/2}\epsilon^{1/2}}{e^{(\epsilon-\mu)/kT}+1}\,d\epsilon$$

(b) Plot the function $dN_\epsilon/d\epsilon$ versus ϵ for the electron gas of a 1000-mm^3 sample of copper at 0 and 300 K. Use a density of 8960 kg/m^3 and one conduction electron per atom for copper.

18.51 (a) Use the result of Problem 18.50a to find the speed distribution in an electron gas. Show that the number of electrons, $dN_{\mathbf{V}}$, in an interval $\mathbf{V}$ to $\mathbf{V} + d\mathbf{V}$ is

$$dN_{\mathbf{V}} = \frac{8\pi m^3 V}{h^3}\frac{\mathbf{V}^2}{\exp\left[\left(\frac{m\mathbf{V}^2}{2}-\mu\right)\Big/kT\right]+1}\,d\mathbf{V}$$

(b) Find an expression for the average speed of an electron gas at 0 K. What is the order of magnitude of this value for a typical metal?

18.52 Substitute the relation $d\mathbf{V}_x\,d\mathbf{V}_y\,d\mathbf{V}_z = 4\pi\mathbf{V}^2\,d\mathbf{V}$ into the result of Problem 18.51a to obtain a relation for the distribution of component velocities in an electron gas. Using this result, show that the number of electrons having an x-component in the

interval $\mathbf{V}_x$ to $\mathbf{V}_x + d\mathbf{V}_x$ and any $\mathbf{V}_y$, $\mathbf{V}_z$ is

$$dN_{\mathbf{V}_x} = \frac{4\pi V m^2 kT}{h^3} \ln\left[e^{(\mu - \epsilon_{x'})/kT} + 1\right] d\mathbf{V}_x$$

(Transform $\mathbf{V}_y$, $\mathbf{V}_z$ to polar coordinates to perform the necessary integration.)

18.53 The problem of particles meeting a potential barrier at a surface was analyzed for Boltzmann statistics in Problem 18.28. For analyzing the phenomenon of thermionic emission, the emission of electrons from an incandescent cathode metal, however, it is necessary to utilize Fermi–Dirac statistics.

(a) Show that the rate at which electrons of a given $\mathbf{V}_x$ strike a unit surface (from the interior) is

$$\frac{\text{Number of } \mathbf{V}_x}{\text{m}^2\text{s}} = \frac{\mathbf{V}_x}{V} dN_{\mathbf{V}_x}$$

where $dN_{\mathbf{V}_x}$ is the number of electrons in the metal in the interval $\mathbf{V}_x$ to $\mathbf{V}_x + d\mathbf{V}_x$, and x is taken normal to the surface.

(b) If ϵ_m is the minimum kinetic energy normal to the surface with which an electron can escape the surface, show that the total rate of electron flow per unit area of cathode is given by

$$\frac{\text{Number of electrons}}{\text{m}^2\text{s}} = CT^2 e^{-\varphi/kT}$$

where $\varphi = \epsilon_m - \mu$ is called the work function of the cathode. Compare this result with that of Problem 18.28.

(c) Each electron escaping from the cathode surface carries the charge e. Therefore, the electrical current density J_{sat}/A is given by

$$\frac{J_{\text{sat}}}{A} = CeT^2 e^{-\varphi/kT}$$

which is termed the Richardson–Dushman equation for thermionic emission. Using the value $\varphi = 3630\ \text{mm}^{-1}$ and the theoretical value for C, calculate J_{sat}/A for tungsten at 3000 K. What assumption is implied in using the theoretical value of C in such a calculation?

18.54 A large tank contains a mixture of two gases A and B at temperature T and pressure P. The mole fractions are y_A and y_B, respectively. A very small hole is then opened in the wall of the container; thus, every particle striking the hole may be assumed to escape. Does the escaping stream of particles have the same composition as the mixture in the tank? How do the relative proportions depend on molecular weights?

18.55 A 10-L tank contains a mixture of 50 percent helium, 50 percent nitrogen at 30°C, 10 kPa. At one end of the tank is a porous plug containing many very fine holes, through which the gas is to be withdrawn. The total hole area is estimated to be $10^{-6}\ \text{mm}^2$. Determine the pressure and composition inside the tank as a function of time.

18.56 Two dissimilar ideal gases A and B are contained in an insulated tank separated by a wall. There are N_A molecules of A in volume V_A and N_B molecules of B in volume V_B. Both are at the same pressure and temperature. The wall is then broken, and the gases are allowed to mix.

(a) Use the partition functions to show that the entropy change which is due to mixing is given by

$$-\overline{R}\sum_i n_i \ln y_i$$

(b) If gases A and B are identical, show that there is no change in entropy when the wall is broken.

18.57 A 1-L tank containing helium initially at 50-kPa pressure is located in a large environment of argon at 100-kPa pressure. The temperature is uniform and constant at 20°C. In the tank wall is a covered porous plug that contains very small holes. The total hole area is 10^{-5} mm^2. The cover is removed from the porous plug for 20 minutes. Assume that any helium atoms leaving the tank do not reenter, but argon atoms entering from outside may flow out again. Calculate the pressure and composition inside the tank at the end of the 20-minute period, and explain why the values come out as they do.

18.58 To demonstrate the necessity of including the constant ground electronic level contribution to entropy, consider the following process: 1 kmol of HF is dissociated to form 1 kmol of H and 1 kmol of F. Assuming each substance to be in its ground electronic level, calculate the electronic contribution to the change in entropy for the process.

18.59 Using a value $D_0 = 13\,350$ mm^{-1} for carbon dioxide, calculate the equilibrium constant at 3000 K for the reaction

$$2CO_2 \rightleftharpoons 2CO + O_2$$

and compare the result with the value given in Table A.16.

18.60 Calculate the equilibrium constant for the reaction $N_2 \rightleftharpoons 2N$ at 2000 K and at 6000 K, and compare the results with the values listed in Table A.16.

18.61 At temperatures above 10 000 K, nitrogen is essentially completely dissociated to the monatomic species and ionization begins to be significant.

(a) Determine the ionization equilibrium constant at 15 000 K for the reaction

$$N \rightleftharpoons N^+ + e^-$$

For monatomic N, use Table 15.2 for the electronic levels, and use an ionization energy (ground level of N^+ above N) of 11 730 mm^{-1}. For the positive ion N^+, use the electronic term data given in Problem 18.10.

(b) For an initial composition of pure N_2 at room temperature, what is the equilibrium composition at 15 000 K, 10 kPa?

18.62 Show that, if Eq. 18.157 is maximized at constant U, V, the result is Eq. 18.160.

18.63 Carry out a maximization at constant T, V, analogous to that of Eqs. 18.157 to 18.160. (In terms of the independent variables T, V, it is necessary to use the Helmholtz function instead of entropy.)

18.64 Consider the molecular dissociation $A_2 \rightleftharpoons 2A$, where A is an arbitrary substance. Develop an expression for the chemical equilibrium constant in terms of the significant fundamental parameters. Assume ground electronic levels only, with degeneracies $\mathbf{g}_{e_{A1}}$, $\mathbf{g}_{e_{A2}}$, and use the simple internal model for A_2.

COMPUTER PROBLEMS

18.1C Write a program to solve the general case of Problem 18.11. The properties of monatomic oxygen as a function of temperature are to be calculated. Include a plot of specific heat versus temperature.

18.2C Write a program to solve the general case of Problem 18.26, assuming free molecular flow. The volume, temperature, and both initial pressures are to be the input variables.

18.3C Write a program to solve the general case of Problems 18.33 and 18.34. The rotational partition function and thermodynamic properties for any heteronuclear diatomic molecule, at any given temperature, are to be determined.

18.4C Write a program to calculate the ideal-gas properties for any substance listed in Appendix Table A.19, for any given temperature and pressure.

18.5C Write a program to solve the general case of Problems 18.43 and 18.44 for diatomic oxygen.

18.6C Write a program to solve the general case of Problem 18.45 for carbon dioxide, including a change of entropy calculation.

18.7C Write a program to solve the general case of Problem 18.57. The temperature and both initial pressures are to be input variables.

18.8C Write a program to solve the general case of Problem 18.60. The equilibrium constant as a function of temperature is to be calculated.

18.9C Extend the program of Problem 18.8C to include ionization of the monatomic nitrogen, as in the solution of Problem 18.61.

APPENDIX A

TABLES, FIGURES, AND CHARTS

TABLE A.1SI Thermodynamic Properties of Steam (SI Units)

TABLE A.1.1SI Saturated Steam: Temperature Table (SI Units)

		Specific Volume m^3/kg		Internal Energy kJ/kg			Enthalpy kJ/kg			Entropy kJ/kg K		
Temp. °C T	Press. kPa P	Sat. Liquid v_f	Sat. Liquid v_g	Sat. Vapor u_f	Evap. u_{fg}	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
0.01	0.6113	0.001 000	206.14	.00	2375.3	2375.3	.01	2501.3	2501.4	.0000	9.1562	9.1562
5	0.8721	0.001 000	147.12	20.97	2361.3	2382.3	20.98	2489.6	2510.6	.0761	8.9496	9.0257
10	1.2276	0.001 000	106.38	42.00	2347.2	2389.2	42.01	2477.7	2519.8	.1510	8.7498	8.9008
15	1.7051	0.001 001	77.93	62.99	2333.1	2396.1	62.99	2465.9	2528.9	.2245	8.5569	8.7814
20	2.339	0.001 002	57.79	83.95	2319.0	2402.9	83.96	2454.1	2538.1	.2966	8.3706	8.6672
25	3.169	0.001 003	43.36	104.88	2304.9	2409.8	104.89	2442.3	2547.2	.3674	8.1905	8.5580
30	4.246	0.001 004	32.89	125.78	2290.8	2416.6	125.79	2430.5	2556.3	.4369	8.0164	8.4533
35	5.628	0.001 006	25.22	146.67	2276.7	2423.4	146.68	2418.6	2565.3	.5053	7.8478	8.3531
40	7.384	0.001 008	19.52	167.56	2262.6	2430.1	167.57	2406.7	2574.3	.5725	7.6845	8.2570
45	9.593	0.001 010	15.26	188.44	2248.4	2436.8	188.45	2394.8	2583.2	.6387	7.5261	8.1648
50	12.349	0.001 012	12.03	209.32	2234.2	2443.5	209.33	2382.7	2592.1	.7038	7.3725	8.0763
55	15.758	0.001 015	9.568	230.21	2219.9	2450.1	230.23	2370.7	2600.9	.7679	7.2234	7.9913
60	19.940	0.001 017	7.671	251.11	2205.5	2456.6	251.13	2358.5	2609.6	.8312	7.0784	7.9096
65	25.03	0.001 020	6.197	272.02	2191.1	2463.1	272.06	2346.2	2618.3	.8935	6.9375	7.8310
70	31.19	0.001 023	5.042	292.95	2176.6	2469.6	292.98	2333.8	2626.8	.9549	6.8004	7.7553
75	38.58	0.001 026	4.131	313.90	2162.0	2475.9	313.93	2321.4	2635.3	1.0155	6.6669	7.6824
80	47.39	0.001 029	3.407	334.86	2147.4	2482.2	334.91	2308.8	2643.7	1.0753	6.5369	7.6122
85	57.83	0.001 033	2.828	355.84	2132.6	2488.4	355.90	2296.0	2651.9	1.1343	6.4102	7.5445
90	70.14	0.001 036	2.361	376.85	2117.7	2494.5	376.92	2283.2	2660.1	1.1925	6.2866	7.4791
95	84.55	0.001 040	1.982	397.88	2102.7	2500.6	397.96	2270.2	2668.1	1.2500	6.1659	7.4159

Source: Adapted from Joseph H. Keenan, Frederick G. Keyes, Philip G. Hill, and Joan G. Moore, *Steam Tables*, John Wiley and Sons, New York, 1978.

TABLE A.1.1SI *(Continued)* Saturated Steam: Temperature Table (SI Units)

		Specific Volume m^3/kg		Internal Energy kJ/kg			Enthalpy kJ/kg			Entropy kJ/kg K		
Temp. °C T	Press. MPa P	Sat. Liquid v_f	Sat. Vapor v_g	Sat. Liquid u_f	Evap. u_{fg}	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
100	0.101 35	0.001 044	1.6729	418.94	2087.6	2506.5	419.04	2257.0	2676.1	1.3069	6.0480	7.3549
105	0.120 82	0.001 048	1.4194	440.02	2072.3	2512.4	440.15	2243.7	2683.8	1.3630	5.9328	7.2958
110	0.143 27	0.001 052	1.2102	461.14	2057.0	2518.1	461.30	2230.2	2691.5	1.4185	5.8202	7.2387
115	0.169 06	0.001 056	1.0366	482.30	2041.4	2523.7	482.48	2216.5	2699.0	1.4734	5.7100	7.1833
120	0.198 53	0.001 060	0.8919	503.50	2025.8	2529.3	503.71	2202.6	2706.3	1.5276	5.6020	7.1296
125	0.2321	0.001 065	0.7706	524.74	2009.9	2534.6	524.99	2188.5	2713.5	1.5813	5.4962	7.0775
130	0.2701	0.001 070	0.6685	546.02	1993.9	2539.9	546.31	2174.2	2720.5	1.6344	5.3925	7.0269
135	0.3130	0.001 075	0.5822	567.35	1977.7	2545.0	567.69	2159.6	2727.3	1.6870	5.2907	6.9777
140	0.3613	0.001 080	0.5089	588.74	1961.3	2550.0	589.13	2144.7	2733.9	1.7391	5.1908	6.9299
145	0.4154	0.001 085	0.4463	610.18	1944.7	2554.9	610.63	2129.6	2740.3	1.7907	5.0926	6.8833
150	0.4758	0.001 091	0.3928	631.68	1927.9	2559.5	632.20	2114.3	2746.5	1.8418	4.9960	6.8379
155	0.5431	0.001 096	0.3468	653.24	1910.8	2564.1	653.84	2098.6	2752.4	1.8925	4.9010	6.7935
160	0.6178	0.001 102	0.3071	674.87	1893.5	2568.4	675.55	2082.6	2758.1	1.9427	4.8075	6.7502
165	0.7005	0.001 108	0.2727	696.56	1876.0	2572.5	697.34	2066.2	2763.5	1.9925	4.7153	6.7078
170	0.7917	0.001 114	0.2428	718.33	1858.1	2576.5	719.21	2049.5	2768.7	2.0419	4.6244	6.6663
175	0.8920	0.001 121	0.2168	740.17	1840.0	2580.2	741.17	2032.4	2773.6	2.0909	4.5347	6.6256
180	1.0021	0.001 127	0.194 05	762.09	1821.6	2583.7	763.22	2015.0	2778.2	2.1396	4.4461	6.5857
185	1.1227	0.001 134	0.174 09	784.10	1802.9	2587.0	785.37	1997.1	2782.4	2.1879	4.3586	6.5465
190	1.2544	0.001 141	0.156 54	806.19	1783.8	2590.0	807.62	1978.8	2786.4	2.2359	4.2720	6.5079
195	1.3978	0.001 149	0.141 05	828.37	1764.4	2592.8	829.98	1960.0	2790.0	2.2835	4.1863	6.4698
200	1.5538	0.001 157	0.127 36	850.65	1744.7	2595.3	852.45	1940.7	2793.2	2.3309	4.1014	6.4323
205	1.7230	0.001 164	0.115 21	873.04	1724.5	2597.5	875.04	1921.0	2796.0	2.3780	4.0172	6.3952
210	1.9062	0.001 173	0.104 41	895.53	1703.9	2599.5	897.76	1900.7	2798.5	2.4248	3.9337	6.3585

215	2.104	0.001 181	0.094 79	918.14	1682.9	2601.1	920.62	1879.9	2800.5	2.4714	3.8507	6.3221
220	2.318	0.001 190	0.086 19	940.87	1661.5	2602.4	943.62	1858.5	2802.1	2.5178	3.7683	6.2861
225	2.548	0.001 199	0.078 49	963.73	1639.6	2603.3	966.78	1836.5	2803.3	2.5639	3.6863	6.2503
230	2.795	0.001 209	0.071 58	986.74	1617.2	2603.9	990.12	1813.8	2804.0	2.6099	3.6047	6.2146
235	3.060	0.001 219	0.065 37	1009.89	1594.2	2604.1	1013.62	1790.5	2804.2	2.6558	3.5233	6.1791
240	3.344	0.001 229	0.059 76	1033.21	1570.8	2604.0	1037.32	1766.5	2803.8	2.7015	3.4422	6.1437
245	3.648	0.001 240	0.054 71	1056.71	1546.7	2603.4	1061.23	1741.7	2803.0	2.7472	3.3612	6.1083
250	3.973	0.001 251	0.050 13	1080.39	1522.0	2602.4	1085.36	1716.2	2801.5	2.7927	3.2802	6.0730
255	4.319	0.001 263	0.045 98	1104.28	1496.7	2600.9	1109.73	1689.8	2799.5	2.8383	3.1992	6.0375
260	4.688	0.001 276	0.042 21	1128.39	1470.6	2599.0	1134.37	1662.5	2796.9	2.8838	3.1181	6.0019
265	5.081	0.001 289	0.038 77	1152.74	1443.9	2596.6	1159.28	1634.4	2793.6	2.9294	3.0368	5.9662
270	5.499	0.001 302	0.035 64	1177.36	1416.3	2593.7	1184.51	1605.2	2789.7	2.9751	2.9551	5.9301
275	5.942	0.001 317	0.032 79	1202.25	1387.9	2590.2	1210.07	1574.9	2785.0	3.0208	2.8730	5.8938
280	6.412	0.001 332	0.030 17	1227.46	1358.7	2586.1	1235.99	1543.6	2779.6	3.0668	2.7903	5.8571
285	6.909	0.001 348	0.027 77	1253.00	1328.4	2581.4	1262.31	1511.0	2773.3	3.1130	2.7070	5.8199
290	7.436	0.001 366	0.025 57	1278.92	1297.1	2576.0	1289.07	1477.1	2766.2	3.1594	2.6227	5.7821
295	7.993	0.001 384	0.023 54	1305.2	1264.7	2569.9	1316.3	1441.8	2758.1	3.2062	2.5375	5.7437
300	8.581	0.001 404	0.021 67	1332.0	1231.0	2563.0	1344.0	1404.9	2749.0	3.2534	2.4511	5.7045
305	9.202	0.001 425	0.019 948	1359.3	1195.9	2555.2	1372.4	1366.4	2738.7	3.3010	2.3633	5.6643
310	9.856	0.001 447	0.018 350	1387.1	1159.4	2546.4	1401.3	1326.0	2727.3	3.3493	2.2737	5.6230
315	10.547	0.001 472	0.016 867	1415.5	1121.1	2536.6	1431.0	1283.5	2714.5	3.3982	2.1821	5.5804
320	11.274	0.001 499	0.015 488	1444.6	1080.9	2525.5	1461.5	1238.6	2700.1	3.4480	2.0882	5.5362
330	12.845	0.001 561	0.012 996	1505.3	993.7	2498.9	1525.3	1140.6	2665.9	3.5507	1.8909	5.4417
340	14.586	0.001 638	0.010 797	1570.3	894.3	2464.6	1594.2	1027.9	2622.0	3.6594	1.6763	5.3357
350	16.513	0.001 740	0.008 813	1641.9	776.6	2418.4	1670.6	893.4	2563.9	3.7777	1.4335	5.2112
360	18.651	0.001 893	0.006 945	1725.2	626.3	2351.5	1760.5	720.5	2481.0	3.9147	1.1379	5.0526
370	21.03	0.002 213	0.004 925	1844.0	384.5	2228.5	1890.5	441.6	2332.1	4.1106	.6865	4.7971
374.14	22.09	0.003 155	0.003 155	2029.6	0	2029.6	2099.3	0	2099.3	4.4298	0	4.4298

TABLE A.1.2SI Saturated Steam: Pressure Table (SI Units)

		Specific Volume		Internal Energy			Enthalpy			Entropy		
Press. kPa P	Temp. °C T	Sat. Liquid v_f	Sat. Vapor v_g	Sat. Liquid u_f	Evap. u_{fg}	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
0.6113	0.01	0.001 000	206.14	.00	2375.3	2375.3	.01	2501.3	2501.4	.0000	9.1562	9.1562
1.0	6.98	0.001 000	129.21	29.30	2355.7	2385.0	29.30	2484.9	2514.2	.1059	8.8697	8.9756
1.5	13.03	0.001 001	87.98	54.71	2338.6	2393.3	54.71	2470.6	2525.3	.1957	8.6322	8.8279
2.0	17.50	0.001 001	67.00	73.48	2326.0	2399.5	73.48	2460.0	2533.5	.2607	8.4629	8.7237
2.5	21.08	0.001 002	54.25	88.48	2315.9	2404.4	88.49	2451.6	2540.0	.3120	8.3311	8.6432
3.0	24.08	0.001 003	45.67	101.04	2307.5	2408.5	101.05	2444.5	2545.5	.3545	8.2231	8.5776
4.0	28.96	0.001 004	34.80	121.45	2293.7	2415.2	121.46	2432.9	2554.4	.4226	8.0520	8.4746
5.0	32.88	0.001 005	28.19	137.81	2282.7	2420.5	137.82	2423.7	2561.5	.4764	7.9187	8.3951
7.5	40.29	0.001 008	19.24	168.78	2261.7	2430.5	168.79	2406.0	2574.8	.5764	7.6750	8.2515
10	45.81	0.001 010	14.67	191.82	2246.1	2437.9	191.83	2392.8	2584.7	.6493	7.5009	8.1502
15	53.97	0.001 014	10.02	225.92	2222.8	2448.7	225.94	2373.1	2599.1	.7549	7.2536	8.0085
20	60.06	0.001 017	7.649	251.38	2205.4	2456.7	251.40	2358.3	2609.7	.8320	7.0766	7.9085
25	64.97	0.001 020	6.204	271.90	2191.2	2463.1	271.93	2346.3	2618.2	.8931	6.9383	7.8314
30	69.10	0.001 022	5.229	289.20	2179.2	2468.4	289.23	2336.1	2625.3	.9439	6.8247	7.7686
40	75.87	0.001 027	3.993	317.53	2159.5	2477.0	317.58	2319.2	2636.8	1.0259	6.6441	7.6700
50	81.33	0.001 030	3.240	340.44	2143.4	2483.9	340.49	2305.4	2645.9	1.0910	6.5029	7.5939
75	91.78	0.001 037	2.217	384.31	2112.4	2496.7	384.39	2278.6	2663.0	1.2130	6.2434	7.4564
MPa												
0.100	99.63	0.001 043	1.6940	417.36	2088.7	2506.1	417.46	2258.0	2675.5	1.3026	6.0568	7.3594
0.125	105.99	0.001 048	1.3749	444.19	2069.3	2513.5	444.32	2241.0	2685.4	1.3740	5.9104	7.2844
0.150	111.37	0.001 053	1.1593	466.94	2052.7	2519.7	467.11	2226.5	2693.6	1.4336	5.7897	7.2233
0.175	116.06	0.001 057	1.0036	486.80	2038.1	2524.9	486.99	2213.6	2700.6	1.4849	5.6868	7.1717
0.200	120.23	0.001 061	0.8857	504.49	2025.0	2529.5	504.70	2201.9	2706.7	1.5301	5.5970	7.1271

0.225	124.00	0.001 064	0.7933	520.47	2013.1	2533.6	520.72	2191.3	2712.1	1.5706	5.5173	7.0878
0.250	127.44	0.001 067	0.7187	535.10	2002.1	2537.2	535.37	2181.5	2716.9	1.6072	5.4455	7.0527
0.275	130.60	0.001 070	0.6573	548.59	1991.9	2540.5	548.89	2172.4	2721.3	1.6408	5.3801	7.0209
0.300	133.55	0.001 073	0.6058	561.15	1982.4	2543.6	561.47	2163.8	2725.3	1.6718	5.3201	6.9919
0.325	136.30	0.001 076	0.5620	572.90	1973.5	2546.4	573.25	2155.8	2729.0	1.7006	5.2646	6.9652
0.350	138.88	0.001 079	0.5243	583.95	1965.0	2548.9	584.33	2148.1	2732.4	1.7275	5.2130	6.9405
0.375	141.32	0.001 081	0.4914	594.40	1956.9	2551.3	594.81	2140.8	2735.6	1.7528	5.1647	6.9175
0.40	143.63	0.001 084	0.4625	604.31	1949.3	2553.6	604.74	2133.8	2738.6	1.7766	5.1193	6.8959
0.45	147.93	0.001 088	0.4140	622.77	1934.9	2557.6	623.25	2120.7	2743.9	1.8207	5.0359	6.8565
0.50	151.86	0.001 093	0.3749	639.68	1921.6	2561.2	640.23	2108.5	2748.7	1.8607	4.9606	6.8213
0.55	155.48	0.001 097	0.3427	655.32	1909.2	2564.5	655.93	2097.0	2753.0	1.8973	4.8920	6.7893
0.60	158.85	0.001 101	0.3157	669.90	1897.5	2567.4	670.56	2086.3	2756.8	1.9312	4.8288	6.7600
0.65	162.01	0.001 104	0.2927	683.56	1886.5	2570.1	684.28	2076.0	2760.3	1.9627	4.7703	6.7331
0.70	164.97	0.001 108	0.2729	696.44	1876.1	2572.5	697.22	2066.3	2763.5	1.9922	4.7158	6.7080
0.75	167.78	0.001 112	0.2556	708.64	1866.1	2574.7	709.47	2057.0	2766.4	2.0200	4.6647	6.6847
0.80	170.43	0.001 115	0.2404	720.22	1856.6	2576.8	721.11	2048.0	2769.1	2.0462	4.6166	6.6628
0.85	172.96	0.001 118	0.2270	731.27	1847.4	2578.7	732.22	2039.4	2771.6	2.0710	4.5711	6.6421
0.90	175.38	0.001 121	0.2150	741.83	1838.6	2580.5	742.83	2031.1	2773.9	2.0946	4.5280	6.6226
0.95	177.69	0.001 124	0.2042	751.95	1830.2	2582.1	753.02	2023.1	2776.1	2.1172	4.4869	6.6041
1.00	179.91	0.001 127	0.194 44	761.68	1822.0	2583.6	762.81	2015.3	2778.1	2.1387	4.4478	6.5865
1.10	184.09	0.001 133	0.177 53	780.09	1806.3	2586.4	781.34	2000.4	2781.7	2.1792	4.3744	6.5536
1.20	187.99	0.001 139	0.163 33	797.29	1791.5	2588.8	798.65	1986.2	2784.8	2.2166	4.3067	6.5233
1.30	191.64	0.001 144	0.151 25	813.44	1777.5	2591.0	814.93	1972.7	2787.6	2.2515	4.2438	6.4953
1.40	195.07	0.001 149	0.140 84	828.70	1764.1	2592.8	830.30	1959.7	2790.0	2.2842	4.1850	6.4693
1.50	198.32	0.001 154	0.131 77	843.16	1751.3	2594.5	844.89	1947.3	2792.2	2.3150	4.1298	6.4448
1.75	205.76	0.001 166	0.113 49	876.46	1721.4	2597.8	878.50	1917.9	2796.4	2.3851	4.0044	6.3896
2.00	212.42	0.001 177	0.099 63	906.44	1693.8	2600.3	908.79	1890.7	2799.5	2.4474	3.8935	6.3409
2.25	218.45	0.001 187	0.088 75	933.83	1668.2	2602.0	936.49	1865.2	2801.7	2.5035	3.7937	6.2972
2.5	223.99	0.001 197	0.079 98	959.11	1644.0	2603.1	962.11	1841.0	2803.1	2.5547	3.7028	6.2575
3.0	233.90	0.001 217	0.066 68	1004.78	1599.3	2604.1	1008.42	1795.7	2804.2	2.6457	3.5412	6.1869

(Continued)

TABLE A.1.2SI *(Continued)* Saturated Steam: Pressure Table (SI Units)

		Specific Volume		Internal Energy			Enthalpy			Entropy		
Press. MPa P	Temp. °C T	Sat. Liquid v_f	Sat. Vapor v_g	Sat. Liquid u_f	Evap. u_{fg}	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
3.5	242.60	0.001 235	0.057 07	1045.43	1558.3	2603.7	1049.75	1753.7	2803.4	2.7253	3.4000	6.1253
4	250.40	0.001 252	0.049 78	1082.31	1520.0	2602.3	1087.31	1714.1	2801.4	2.7964	3.2737	6.0701
5	263.99	0.001 286	0.039 44	1147.81	1449.3	2597.1	1154.23	1640.1	2794.3	2.9202	3.0532	5.9734
6	275.64	0.001 319	0.032 44	1205.44	1384.3	2589.7	1213.35	1571.0	2784.3	3.0267	2.8625	5.8892
7	285.88	0.001 351	0.027 37	1257.55	1323.0	2580.5	1267.00	1505.1	2772.1	3.1211	2.6922	5.8133
8	295.06	0.001 384	0.023 52	1305.57	1264.2	2569.8	1316.64	1441.3	2758.0	3.2068	2.5364	5.7432
9	303.40	0.001 418	0.020 48	1350.51	1207.3	2557.8	1363.26	1378.9	2742.1	3.2858	2.3915	5.6772
10	311.06	0.001 452	0.018 026	1393.04	1151.4	2544.4	1407.56	1317.1	2724.7	3.3596	2.2544	5.6141
11	318.15	0.001 489	0.015 987	1433.7	1096.0	2529.8	1450.1	1255.5	2705.6	3.4295	2.1233	5.5527
12	324.75	0.001 527	0.014 263	1473.0	1040.7	2513.7	1491.3	1193.6	2684.9	3.4962	1.9962	5.4924
13	330.93	0.001 567	0.012 780	1511.1	985.0	2496.1	1531.5	1130.7	2662.2	3.5606	1.8718	5.4323
14	336.75	0.001 611	0.011 485	1548.6	928.2	2476.8	1571.1	1066.5	2637.6	3.6232	1.7485	5.3717
15	342.24	0.001 658	0.010 337	1585.6	869.8	2455.5	1610.5	1000.0	2610.5	3.6848	1.6249	5.3098
16	347.44	0.001 711	0.009 306	1622.7	809.0	2431.7	1650.1	930.6	2580.6	3.7461	1.4994	5.2455
17	352.37	0.001 770	0.008 364	1660.2	744.8	2405.0	1690.3	856.9	2547.2	3.8079	1.3698	5.1777
18	357.06	0.001 840	0.007 489	1698.9	675.4	2374.3	1732.0	777.1	2509.1	3.8715	1.2329	5.1044
19	361.54	0.001 924	0.006 657	1739.9	598.1	2338.1	1776.5	688.0	2464.5	3.9388	1.0839	5.0228
20	365.81	0.002 036	0.005 834	1785.6	507.5	2293.0	1826.3	583.4	2409.7	4.0139	.9130	4.9269
21	369.89	0.002 207	0.004 952	1842.1	388.5	2230.6	1888.4	446.2	2334.6	4.1075	.6938	4.8013
22	373.80	0.002 742	0.003 568	1961.9	125.2	2087.1	2022.2	143.4	2165.6	4.3110	.2216	4.5327
22.09	374.14	0.003 155	0.003 155	2029.6	0	2029.6	2099.3	0	2099.3	4.4298	0	4.4298

TABLE A.1.3SI Superheated Vapor (SI Units)

	P = .010 MPa (45.81)				P = .050 MPa (81.33)				P = .10 MPa (99.63)			
T	v	u	h	s	v	u	h	s	v	u	h	s
Sat.	14.674	2437.9	2584.7	8.1502	3.240	2483.9	2645.9	7.5939	1.6940	2506.1	2675.5	7.3594
50	14.869	2443.9	2592.6	8.1749								
100	17.196	2515.5	2687.5	8.4479	3.418	2511.6	2682.5	7.6947	1.6958	2506.7	2676.2	7.3614
150	19.512	2587.9	2783.0	8.6882	3.889	2585.6	2780.1	7.9401	1.9364	2582.8	2776.4	7.6134
200	21.825	2661.3	2879.5	8.9038	4.356	2659.9	2877.7	8.1580	2.172	2658.1	2875.3	7.8343
250	24.136	2736.0	2977.3	9.1002	4.820	2735.0	2976.0	8.3556	2.406	2733.7	2974.3	8.0333
300	26.445	2812.1	3076.5	9.2813	5.284	2811.3	3075.5	8.5373	2.639	2810.4	3074.3	8.2158
400	31.063	2968.9	3279.6	9.6077	6.209	2968.5	3278.9	8.8642	3.103	2967.9	3278.2	8.5435
500	35.679	3132.3	3489.1	9.8978	7.134	3132.0	3488.7	9.1546	3.565	3131.6	3488.1	8.8342
600	40.295	3302.5	3705.4	10.1608	8.057	3302.2	3705.1	9.4178	4.028	3301.9	3704.7	9.0976
700	44.911	3479.6	3928.7	10.4028	8.981	3479.4	3928.5	9.6599	4.490	3479.2	3928.2	9.3398
800	49.526	3663.8	4159.0	10.6281	9.904	3663.6	4158.9	9.8852	4.952	3663.5	4158.6	9.5652
900	54.141	3855.0	4396.4	10.8396	10.828	3854.9	4396.3	10.0967	5.414	3854.8	4396.1	9.7767
1000	58.757	4053.0	4640.6	11.0393	11.751	4052.9	4640.5	10.2964	5.875	4052.8	4640.3	9.9764
1100	63.372	4257.5	4891.2	11.2287	12.674	4257.4	4891.1	10.4859	6.337	4257.3	4891.0	10.1659
1200	67.987	4467.9	5147.8	11.4091	13.597	4467.8	5147.7	10.6662	6.799	4467.7	5147.6	10.3463
1300	72.602	4683.7	5409.7	11.5811	14.521	4683.6	5409.6	10.8382	7.260	4683.5	5409.5	10.5183
	P = .20 MPa (120.23)				P = .30 MPa (133.55)				P = .40 MPa (143.63)			
Sat.	.8857	2529.5	2706.7	7.1272	.6058	2543.6	2725.3	6.9919	.4625	2553.6	2738.6	6.8959
150	.9596	2576.9	2768.8	7.2795	.6339	2570.8	2761.0	7.0778	.4708	2564.5	2752.8	6.9299
200	1.0803	2654.4	2870.5	7.5066	.7163	2650.7	2865.6	7.3115	.5342	2646.8	2860.5	7.1706
250	1.1988	2731.2	2971.0	7.7086	.7964	2728.7	2967.6	7.5166	.5951	2726.1	2964.2	7.3789
300	1.3162	2808.6	3071.8	7.8926	.8753	2806.7	3069.3	7.7022	.6548	2804.8	3066.8	7.5662
400	1.5493	2966.7	3276.6	8.2218	1.0315	2965.6	3275.0	8.0330	.7726	2964.4	3273.4	7.8985

(Continued)

TABLE A.1.3SI *(Continued)* Superheated Vapor (SI Units)

T	v	u	h	s	v	u	h	s	v	u	h	s
	P = .20 MPa (120.23)				**P = .30 MPa (133.55)**				**P = .40 MPa (143.63)**			
500	1.7814	3130.8	3487.1	8.5133	1.1867	3130.0	3486.0	8.3251	.8893	3129.2	3484.9	8.1913
600	2.013	3301.4	3704.0	8.7770	1.3414	3300.8	3703.2	8.5892	1.0055	3300.2	3702.4	8.4558
700	2.244	3478.8	3927.6	9.0194	1.4957	3478.4	3927.1	8.8319	1.1215	3477.9	3926.5	8.6987
800	2.475	3663.1	4158.2	9.2449	1.6499	3662.9	4157.8	9.0576	1.2372	3662.4	4157.3	8.9244
900	2.706	3854.5	4395.8	9.4566	1.8041	3854.2	4395.4	9.2692	1.3529	3853.9	4395.1	9.1362
1000	2.937	4052.5	4640.0	9.6563	1.9581	4052.3	4639.7	9.4690	1.4685	4052.0	4639.4	9.3360
1100	3.168	4257.0	4890.7	9.8458	2.1121	4256.8	4890.4	9.6585	1.5840	4256.5	4890.2	9.5256
1200	3.399	4467.5	5147.3	10.0262	2.2661	4467.2	5147.1	9.8389	1.6996	4467.0	5146.8	9.7060
1300	3.630	4683.2	5409.3	10.1982	2.4201	4683.0	5409.0	10.0110	1.8151	4682.8	5408.8	9.8780
	P = .50 MPa (151.86)				**P = .60 MPa (158.85)**				**P = .80 MPa (170.43)**			
Sat.	.3749	2561.2	2748.7	6.8213	.3157	2567.4	2756.8	6.7600	.2404	2576.8	2769.1	6.6628
200	.4249	2642.9	2855.4	7.0592	.3520	2638.9	2850.1	6.9665	.2608	2630.6	2839.3	6.8158
250	.4744	2723.5	2960.7	7.2709	.3938	2720.9	2957.2	7.1816	.2931	2715.5	2950.0	7.0384
300	.5226	2802.9	3064.2	7.4599	.4344	2801.0	3061.6	7.3724	.3241	2797.2	3056.5	7.2328
350	.5701	2882.6	3167.7	7.6329	.4742	2881.2	3165.7	7.5464	.3544	2878.2	3161.7	7.4089
400	.6173	2963.2	3271.9	7.7938	.5137	2962.1	3270.3	7.7079	.3843	2959.7	3267.1	7.5716
500	.7109	3128.4	3483.9	8.0873	.5920	3127.6	3482.8	8.0021	.4433	3126.0	3480.6	7.8673
600	.8041	3299.6	3701.7	7.3522	.6697	3299.1	3700.9	8.2674	.5018	3297.9	3699.4	8.1333
700	.8969	3477.5	3925.9	8.5952	.7472	3477.0	3925.3	8.5107	.5601	3476.2	3924.2	8.3770
800	.9896	3662.1	4156.9	8.8211	.8245	3661.8	4156.5	8.7367	.6181	3661.1	4155.6	8.6033
900	1.0822	3853.6	4394.7	9.0329	.9017	3853.4	4394.4	8.9486	.6761	3852.8	4393.7	8.8153
1000	1.1747	4051.8	4639.1	9.2328	.9788	4051.5	4638.8	9.1485	.7340	4051.0	4638.2	9.0153

1100	1.2672	4256.3	4889.9	9.4224	1.0559	4256.1	4889.6	9.3381	.7919	4255.6	4889.1	9.2050
1200	1.3596	4466.8	5146.6	9.6029	1.1330	4466.5	5146.3	9.5185	.8497	4466.1	5145.9	9.3855
1300	1.4521	4682.5	5408.6	9.7749	1.2101	4682.3	5408.3	9.6906	.9076	4681.8	5407.9	9.5575
	P = 1.00 MPa (179.91)				**P = 1.20 MPa (187.99)**				**P = 1.40 MPa (195.07)**			
Sat.	.194 44	2583.6	2778.1	6.5865	.163 33	2588.8	2784.8	6.5233	.140 84	2592.8	2790.0	6.4693
200	.2060	2621.9	2827.9	6.6940	.169 30	2612.8	2815.9	6.5898	.143 02	2603.1	2803.3	6.4975
250	.2327	2709.9	2942.6	6.9247	.192 34	2704.2	2935.0	6.8294	.163 50	2698.3	2927.2	6.7467
300	.2579	2793.2	3051.2	7.1229	.2138	2789.2	3045.8	7.0317	.182 28	2785.2	3040.4	6.9534
350	.2825	2875.2	3157.7	7.3011	.2345	2872.2	3153.6	7.2121	.2003	2869.2	3149.5	7.1360
400	.3066	2957.3	3263.9	7.4651	.2548	2954.9	3260.7	7.3774	.2178	2952.5	3257.5	7.3026
500	.3541	3124.4	3478.5	7.7622	.2946	3122.8	3476.3	7.6759	.2521	3121.1	3474.1	7.6027
600	.4011	3296.8	3697.9	8.0290	.3339	3295.6	3696.3	7.9435	.2860	3294.4	3694.8	7.8710
700	.4478	3475.3	3923.1	8.2731	.3729	3474.4	3922.0	8.1881	.3195	3473.6	3920.8	8.1160
800	.4943	3660.4	4154.7	8.4996	.4118	3659.7	4153.8	8.4148	.3528	3659.0	4153.0	8.3431
900	.5407	3852.2	4392.9	8.7118	.4505	3851.6	4392.2	8.6272	.3861	3851.1	4391.5	8.5556
1000	.5871	4050.5	4637.6	8.9119	.4892	4050.0	4637.0	8.8274	.4192	4049.5	4636.4	8.7559
1100	.6335	4255.1	4888.6	9.1017	.5278	4254.6	4888.0	9.0172	.4524	4254.1	4887.5	8.9457
1200	.6798	4465.6	5145.4	9.2822	.5665	4465.1	5144.9	9.1977	.4855	4464.7	5144.4	9.1262
1300	.7261	4681.3	5407.4	9.4543	.6051	4680.9	5407.0	9.3698	.5186	4680.4	5406.5	9.2984
	P = 1.60 MPa (201.41)				**P = 1.80 MPa (207.15)**				**P = 2.00 MPa (212.42)**			
Sat.	.123 80	2596.0	2794.0	6.4218	.110 42	2598.4	2797.1	6.3794	.099 63	2600.3	2799.5	6.3409
225	.132 87	2644.7	2857.3	6.5518	.116 73	2636.6	2846.7	6.4808	.103 77	2628.3	2835.8	6.4147
250	.141 84	2692.3	2919.2	6.6732	.124 97	2686.0	2911.0	6.6066	.111 44	2679.6	2902.5	6.5453
300	.158 62	2781.1	3034.8	6.8844	.140 21	2776.9	3029.2	6.8226	.125 47	2772.6	3023.5	6.7664
350	.174 56	2866.1	3145.4	7.0694	.154 57	2863.0	3141.2	7.0100	.138 57	2859.8	3137.0	6.9563
400	.190 05	2950.1	3254.2	7.2374	.168 47	2947.7	3250.9	7.1794	.151 20	2945.2	3247.6	7.1271
500	.2203	3119.5	3472.0	7.5390	.195 50	3117.9	3469.8	7.4825	.175 68	3116.2	3467.6	7.4317
600	.2500	3293.3	3693.2	7.8080	.2220	3292.1	3691.7	7.7523	.199 60	3290.9	3690.1	7.7024
700	.2794	3472.7	3919.7	8.0535	.2482	3471.8	3918.5	7.9983	.2232	3470.9	3917.4	7.9487

(*Continued*)

TABLE A.1.3SI *(Continued)* Superheated Vapor (SI Units)

T	v	u	h	s	v	u	h	s	v	u	h	s
	$P = 1.60$ MPa (201.41)				$P = 1.80$ MPa (207.15)				$P = 2.00$ MPa (212.42)			
800	.3086	3658.3	4152.1	8.2808	.2742	3657.6	4151.2	8.2258	.2467	3657.0	4150.3	8.1765
900	.3377	3850.5	4390.8	8.4935	.3001	3849.9	4390.1	8.4386	.2700	3849.3	4389.4	8.3895
1000	.3668	4049.0	4635.8	8.6938	.3260	4048.5	4635.2	8.6391	.2933	4048.0	4634.6	8.5901
1100	.3958	4253.7	4887.0	8.8837	.3518	4253.2	4886.4	8.8290	.3166	4252.7	4885.9	8.7800
1200	.4248	4464.2	5143.9	9.0643	.3776	4463.7	5143.4	9.0096	.3398	4463.3	5142.9	8.9607
1300	.4538	4679.9	5406.0	9.2364	.4034	4679.5	5405.6	9.1818	.3631	4679.0	5405.1	9.1329
	$P = 2.50$ MPa (223.99)				$P = 3.00$ MPa (233.90)				$P = 3.50$ MPa (242.60)			
Sat.	.079 98	2603.1	2803.1	6.2575	.066 68	2604.1	2804.2	6.1869	.057 07	2603.7	2803.4	6.1253
225	.080 27	2605.6	2806.3	6.2639								
250	.087 00	2662.6	2880.1	6.4085	.070 58	2644.0	2855.8	6.2872	.058 72	2623.7	2829.2	6.1749
300	.098 90	2761.6	3008.8	6.6438	.081 14	2750.1	2993.5	6.5390	.068 42	2738.0	2977.5	6.4461
350	.109 76	2851.9	3126.3	6.8403	.090 53	2843.7	3115.3	6.7428	.076 78	2835.3	3104.0	6.6579
400	.120 10	2939.1	3239.3	7.0148	.099 36	2932.8	3230.9	6.9212	.084 53	2926.4	3222.3	6.8405
450	.130 14	3025.5	3350.8	7.1746	.107 87	3020.4	3344.0	7.0834	.091 96	3015.3	3337.2	7.0052
500	.139 98	3112.1	3462.1	7.3234	.116 19	3108.0	3456.5	7.2338	.099 18	3103.0	3450.9	7.1572
600	.159 30	3288.0	3686.3	7.5960	.132 43	3285.0	3682.3	7.5085	.113 24	3282.1	3678.4	7.4339
700	.178 32	3468.7	3914.5	7.8435	.148 38	3466.5	3911.7	7.7571	.126 99	3464.3	3908.8	7.6837
800	.197 16	3655.3	4148.2	8.0720	.164 14	3653.5	4145.9	7.9862	.140 56	3651.8	4143.7	7.9134
900	.215 90	3847.9	4387.6	8.2853	.179 80	3846.5	4385.9	8.1999	.154 02	3845.0	4384.1	8.1276
1000	.2346	4046.7	4633.1	8.4861	.195 41	4045.4	4631.6	8.4009	.167 43	4044.1	4630.1	8.3288
1100	.2532	4251.5	4884.6	8.6762	.210 98	4250.3	4883.3	8.5912	.180 80	4249.2	4881.9	8.5192
1200	.2718	4462.1	5141.7	8.8569	.226 52	4460.9	5140.5	8.7720	.194 15	4459.8	5139.3	8.7000
1300	.2905	4677.8	5404.0	9.0291	.242 06	4676.6	5402.8	8.9442	.207 49	4675.5	5401.7	8.8723

	P = 4.0 MPa (250.40)				P = 4.5 MPa (257.49)				P = 5.0 MPa (263.99)			
Sat.	.049 78	2602.3	2801.4	6.0701	.044 06	2600.1	2798.3	6.0198	.039 44	2597.1	2794.3	5.9734
275	.054 57	2667.9	2886.2	6.2285	.047 30	2650.3	2863.2	6.1401	.041 41	2631.3	2838.3	6.0544
300	.058 84	2725.3	2960.7	6.3615	.051 35	2712.0	2943.1	6.2828	.045 32	2698.0	2924.5	6.2084
350	.066 45	2826.7	3092.5	6.5821	.058 40	2817.8	3080.6	6.5131	.051 94	2808.7	3068.4	6.4493
400	.073 41	2919.9	3213.6	6.7690	.064 75	2913.3	3204.7	6.7047	.057 81	2906.6	3195.7	6.6459
450	.080 02	3010.2	3330.3	6.9363	.070 74	3005.0	3323.3	6.8746	.063 30	2999.7	3316.2	6.8186
500	.086 43	3099.5	3445.3	7.0901	.076 51	3095.3	3439.6	7.0301	.068 57	3091.0	3433.8	6.9759
600	.098 85	3279.1	3674.4	7.3688	.087 65	3276.0	3670.5	7.3110	.078 69	3273.0	3666.5	7.2589
700	.110 95	3462.1	3905.9	7.6198	.098 47	3459.9	3903.0	7.5631	.088 49	3457.6	3900.1	7.5122
800	.122 87	3650.0	4141.5	7.8502	.109 11	3648.3	4139.3	7.7942	.098 11	3646.6	4137.1	7.7440
900	.134 69	3843.6	4382.3	8.0647	.119 65	3842.2	4380.6	8.0091	.107 62	3840.7	4378.8	7.9593
1000	.146 45	4042.9	4628.7	8.2662	.130 13	4041.6	4627.2	8.2108	.117 07	4040.4	4625.7	8.1612
1100	.158 17	4248.0	4880.6	8.4567	.140 56	4246.8	4879.3	8.4015	.126 48	4245.6	4878.0	8.3520
1200	.169 87	4458.6	5138.1	8.6376	.150 98	4457.5	5136.9	8.5825	.135 87	4456.3	5135.7	8.5331
1300	.181 56	4674.3	5400.5	8.8100	.161 39	4673.1	5399.4	8.7549	.145 26	4672.0	5398.2	8.7055
	P = 6.0 MPa (275.64)				P = 7.0 MPa (285.88)				P = 8.0 MPa (295.06)			
Sat.	.032 44	2589.7	2784.3	5.8892	.027 37	2580.5	2772.1	5.8133	.023 52	2569.8	2758.0	5.7432
300	.036 16	2667.2	2884.2	6.0674	.029 47	2632.2	2838.4	5.9305	.024 26	2590.9	2785.0	5.7906
350	.042 23	2789.6	3043.0	6.3335	.035 24	2769.4	3016.0	6.2283	.029 95	2747.7	2987.3	6.1301
400	.047 39	2892.9	3177.2	6.5408	.039 93	2878.6	3158.1	6.4478	.034 32	2863.8	3138.3	6.3634
450	.052 14	2988.9	3301.8	6.7193	.044 16	2978.0	3287.1	6.6327	.038 17	2966.7	3272.0	6.5551
500	.056 65	3082.2	3422.2	6.8803	.048 14	3073.4	3410.3	6.7975	.041 75	3064.3	3398.3	6.7240
550	.061 01	3174.6	3540.6	7.0288	.051 95	3167.2	3530.9	6.9486	.045 16	3159.8	3521.0	6.8778
600	.065 25	3266.9	3658.4	7.1677	.055 65	3260.7	3650.3	7.0894	.048 45	3254.4	3642.0	7.0206
700	.073 52	3453.1	3894.2	7.4234	.062 83	3448.5	3888.3	7.3476	.054 81	3443.9	3882.4	7.2812
800	.081 60	3643.1	4132.7	7.6566	.069 81	3639.5	4128.2	7.5822	.060 97	3636.0	4123.8	7.5173
900	.089 58	3837.8	4375.3	7.8727	.076 69	3835.0	4371.8	7.7991	.067 02	3832.1	4368.3	7.7351
1000	.097 49	4037.8	4622.7	8.0751	.083 50	4035.3	4619.8	8.0020	.073 01	4032.8	4616.9	7.9384
1100	.105 36	4243.3	4875.4	8.2661	.090 27	4240.9	4872.8	8.1933	.078 96	4238.6	4870.3	8.1300

(Continued)

TABLE A.1.3SI *(Continued)* Superheated Vapor (SI Units)

T	v	u	h	s	v	u	h	s	v	u	h	s
	P = 6.0 MPa (275.64)				**P = 7.0 MPa (285.88)**				**P = 8.0 MPa (295.06)**			
1200	.113 21	4454.0	5133.3	8.4474	.097 03	4451.7	5130.9	8.3747	.084 89	4449.5	5128.5	8.3115
1300	.121 06	4669.6	5396.0	8.6199	.103 77	4667.3	5393.7	8.5473	.090 80	4665.0	5391.5	8.4842
	P = 9.0 MPa (303.40)				**P = 10.0 MPa (311.06)**				**P = 12.5 MPa (327.89)**			
Sat.	.020 48	2557.8	2742.1	5.6772	.018 026	2544.4	2724.7	5.6141	.013 495	2505.1	2673.8	5.4624
325	.023 27	2646.6	2856.0	5.8712	.019 861	2610.4	2809.1	5.7568				
350	.025 80	2724.4	2956.6	6.0361	.022 42	2699.2	2923.4	5.9443	.016 126	2624.6	2826.2	5.7118
400	.029 93	2848.4	3117.8	6.2854	.026 41	2832.4	3096.5	6.2120	.020 00	2789.3	3039.3	6.0417
450	.033 50	2955.2	3256.6	6.4844	.029 75	2943.4	3240.9	6.4190	.022 99	2912.5	3199.8	6.2719
500	.036 77	3055.2	3386.1	6.6576	.032 79	3045.8	3373.7	6.5966	.025 60	3021.7	3341.8	6.4618
550	.039 87	3152.2	3511.0	6.8142	.035 64	3144.6	3500.9	6.7561	.028 01	3125.0	3475.2	6.6290
600	.042 85	3248.1	3633.7	6.9589	.038 37	3241.7	3625.3	6.9029	.030 29	3225.4	3604.0	6.7810
650	.045 74	3343.6	3755.3	7.0943	.041 01	3338.2	3748.2	7.0398	.032 48	3324.4	3730.4	6.9218
700	.048 57	3439.3	3876.5	7.2221	.043 58	3434.7	3870.5	7.1687	.034 60	3422.9	3855.3	7.0536
800	.054 09	3632.5	4119.3	7.4596	.048 59	3628.9	4114.8	7.4077	.038 69	3620.0	4103.6	7.2965
900	.059 50	3829.2	4364.8	7.6783	.053 49	3826.3	4361.2	7.6272	.042 67	3819.1	4352.5	7.5182
1000	.064 85	4030.3	4614.0	7.8821	.058 32	4027.8	4611.0	7.8315	.046 58	4021.6	4603.8	7.7237
1100	.070 16	4236.3	4867.7	8.0740	.063 12	4234.0	4865.1	8.0237	.050 45	4228.2	4858.8	7.9165
1200	.075 44	4447.2	5126.2	8.2556	.067 89	4444.9	5123.8	8.2055	.054 30	4439.3	5118.0	8.0987
1300	.080 72	4662.7	5389.2	8.4284	.072 65	4460.5	5387.0	8.3783	.058 13	4654.8	5381.4	8.2717
	P = 15.0 MPa (342.24)				**P = 17.5 MPa (354.75)**				**P = 20.0 MPa (365.81)**			
Sat.	.010 337	2455.5	2610.5	5.3098	.007 920	2390.2	2528.8	5.1419	.005 834	2293.0	2409.7	4.9269
350	.011 470	2520.4	2692.4	5.4421								

400	.015 649	2740.7	2975.5	5.8811	.012 447	2685.0	2902.9	5.7213	.009 942	2619.3	2818.1	5.5540
450	.018 445	2879.5	3156.2	6.1404	.015 174	2844.2	3109.7	6.0184	.012 695	2806.2	3060.1	5.9017
500	.020 80	2996.6	3308.6	6.3443	.017 358	2970.3	3274.1	6.2383	.014 768	2942.9	3238.2	6.1401
550	.022 93	3104.7	3448.6	6.5199	.019 288	3083.9	3421.4	6.4230	.016 555	3062.4	3393.5	6.3348
600	.024 91	3208.6	3582.3	6.6776	.021 06	3191.5	3560.1	6.5866	.018 178	3174.0	3537.6	6.5048
650	.026 80	3310.3	3712.3	6.8224	.022 74	3296.0	3693.9	6.7357	.019 693	3281.4	3675.3	6.6582
700	.028 61	3410.9	3840.1	6.9572	.024 34	3398.7	3824.6	6.8736	.021 13	3386.4	3809.0	6.7993
800	.032 10	3610.9	4092.4	7.2040	.027 38	3601.8	4081.1	7.1244	.023 85	3592.7	4069.7	7.0544
900	.035 46	3811.9	4343.8	7.4279	.030 31	3804.7	4335.1	7.3507	.026 45	3797.5	4326.4	7.2830
1000	.038 75	4015.4	4596.6	7.6348	.033 16	4009.3	4589.5	7.5589	.028 97	4003.1	4582.5	7.4925
1100	.042 00	4222.6	4852.6	7.8283	.035 97	4216.9	4846.4	7.7531	.031 45	4211.3	4840.2	7.6874
1200	.045 23	4433.8	5112.3	8.0108	.038 76	4428.3	5106.6	7.9360	.033 91	4422.8	5101.0	7.8707
1300	.048 45	4649.1	5376.0	8.1840	.041 54	4643.5	5370.5	8.1093	.036 36	4638.0	5365.1	8.0442
	$P = 25.0$ MPa				**$P = 30.0$ MPa**				**$P = 35.0$ MPa**			
375	.001 973 1	1798.7	1848.0	4.0320	.001 789 2	1737.8	1791.5	3.9305	.001 700 3	1702.9	1762.4	3.8722
400	.006 004	2430.1	2580.2	5.1418	.002 790	2067.4	2151.1	4.4728	.002 100	1914.1	1987.6	4.2126
425	.007 881	2609.2	2806.3	5.4723	.005 303	2455.1	2614.2	5.1504	.003 428	2253.4	2373.4	4.7747
450	.009 162	2720.7	2949.7	5.6744	.006 735	2619.3	2821.4	5.4424	.004 961	2498.7	2672.4	5.1962
500	.011 123	2884.3	3162.4	5.9592	.008 678	2820.7	3081.1	5.7905	.006 927	2751.9	2994.4	5.6282
550	.012 724	3017.5	3335.6	6.1765	.010 168	2970.3	3275.4	6.0342	.008 345	2921.0	3213.0	5.9026
600	.014 137	3137.9	3491.4	6.3602	.011 446	3100.5	3443.9	6.2331	.009 527	3062.0	3395.5	6.1179
650	.015 433	3251.6	3637.4	6.5229	.012 596	3221.0	3598.9	6.4058	.010 575	3189.8	3559.9	6.3010
700	.016 646	3361.3	3777.5	6.6707	.013 661	3335.8	3745.6	6.5606	.011 533	3309.8	3713.5	6.4631
800	.018 912	3574.3	4047.1	6.9345	.015 623	3555.5	4024.2	6.8332	.013 278	3536.7	4001.5	6.7450
900	.021 045	3783.0	4309.1	7.1680	.017 448	3768.5	4291.9	7.0718	.014 883	3754.0	4274.9	6.9886
1000	.023 10	3990.9	4568.5	7.3802	.019 196	3978.8	4554.7	7.2867	.016 410	3966.7	4541.1	7.2064
1100	.025 12	4200.2	4828.2	7.5765	.020 903	4189.2	4816.3	7.4845	.017 895	4178.3	4804.6	7.4057

(*Continued*)

TABLE A.1.3SI *(Continued)* Superheated Vapor (SI Units)

T	v	u	h	s	v	u	h	s	v	u	h	s
	P = 25.0 MPa				**P = 30.0 MPa**				**P = 35.0 MPa**			
1200	.027 11	4412.0	5089.9	7.7605	.022 589	4401.3	5079.0	7.6692	.019 360	4390.7	5068.3	7.5910
1300	.029 10	4626.9	5354.4	7.9342	.024 266	4616.0	5344.0	7.8432	.020 815	4605.1	5333.6	7.7653
	P = 40.0 MPa				**P = 50.0 MPa**				**P = 60.0 MPa**			
375	.001 640 7	1677.1	1742.8	3.8290	.001 559 4	1638.6	1716.6	3.7639	.001 502 8	1609.4	1699.5	3.7141
400	.001 907 7	1854.6	1930.9	4.1135	.001 730 9	1788.1	1874.6	4.0031	.001 633 5	1745.4	1843.4	3.9318
425	.002 532	2096.9	2198.1	4.5029	.002 007	1959.7	2060.0	4.2734	.001 816 5	1892.7	2001.7	4.1626
450	.003 693	2365.1	2512.8	4.9459	.002 486	2159.6	2284.0	4.5884	.002 085	2053.9	2179.0	4.4121
500	.005 622	2678.4	2903.3	5.4700	.003 892	2525.5	2720.1	5.1726	.002 956	2390.6	2567.9	4.9321
550	.006 984	2869.7	3149.1	5.7785	.005 118	2763.6	3019.5	5.5485	.003 956	2658.8	2896.2	5.3441
600	.008 094	3022.6	3346.4	6.0114	.006 112	2942.0	3247.6	5.8178	.004 834	2861.1	3151.2	5.6452
650	.009 063	3158.0	3520.6	6.2054	.006 966	3093.5	3441.8	6.0342	.005 595	3028.8	3364.5	5.8829
700	.009 941	3283.6	3681.2	6.3750	.007 727	3230.5	3616.8	6.2189	.006 272	3177.2	3553.5	6.0824
800	.011 523	3517.8	3978.7	6.6662	.009 076	3479.8	3933.6	6.5290	.007 459	3441.5	3889.1	6.4109
900	.012 962	3739.4	4257.9	6.9150	.010 283	3710.3	4224.4	6.7882	.008 508	3681.0	4191.5	6.6805
1000	.014 324	3954.6	4527.6	7.1356	.011 411	3930.5	4501.1	7.0146	.009 480	3906.4	4475.2	6.9127
1100	.015 642	4167.4	4793.1	7.3364	.012 496	4145.7	4770.5	7.2184	.010 409	4124.1	4748.6	7.1195
1200	.016 940	4380.1	5057.7	7.5224	.013 561	4359.1	5037.2	7.4058	.011 317	4338.2	5017.2	7.3083
1300	.018 229	4594.3	5323.5	7.6969	.014 616	4572.8	5303.6	7.5808	.012 215	4551.4	5284.3	7.4837

TABLE A.1.4SI Compressed Liquid (SI Units)

	$P = 5$ MPa (263.99)				$P = 10$ MPa (311.06)				$P = 15$ MPa (342.24)			
T	v	u	h	s	v	u	h	s	v	u	h	s
Sat.	.001 285 9	1147.8	1154.2	2.9202	.001 452 4	1393.0	1407.6	3.3596	.001 658 1	1585.6	1610.5	3.6848
0	.000 997 7	.04	5.04	.0001	.000 995 2	.09	10.04	.0002	.000 992 8	.15	15.05	.0004
20	.000 999 5	83.65	88.65	.2956	.000 997 2	83.36	93.33	.2945	.000 995 0	83.06	97.99	.2934
40	.001 005 6	166.95	171.97	.5705	.001 003 4	166.35	176.38	.5686	.001 001 3	165.76	180.78	.5666
60	.001 014 9	250.23	255.30	.8285	.001 012 7	249.36	259.49	.8258	.001 010 5	248.51	263.67	.8232
80	.001 026 8	333.72	338.85	1.0720	.001 024 5	332.59	342.83	1.0688	.001 022 2	331.48	346.81	1.0656
100	.001 041 0	417.52	422.72	1.3030	.001 038 5	416.12	426.50	1.2992	.001 036 1	414.74	430.28	1.2955
120	.001 057 6	501.80	507.09	1.5233	.001 054 9	500.08	510.64	1.5189	.001 052 2	498.40	514.19	1.5145
140	.001 076 8	586.76	592.15	1.7343	.001 073 7	584.68	595.42	1.7292	.001 070 7	582.66	598.72	1.7242
160	.001 098 8	672.62	678.12	1.9375	.001 095 3	670.13	681.08	1.9317	.001 091 8	667.71	684.09	1.9260
180	.001 124 0	759.63	765.25	2.1341	.001 119 9	756.65	767.84	2.1275	.001 115 9	753.76	770.50	2.1210
200	.001 153 0	848.1	853.9	2.3255	.001 148 0	844.5	856.0	2.3178	.001 143 3	841.0	858.2	2.3104
220	.001 186 6	938.4	944.4	2.5128	.001 180 5	934.1	945.9	2.5039	.001 174 8	929.9	947.5	2.4953
240	.001 226 4	1031.4	1037.5	2.6979	.001 218 7	1026.0	1038.1	2.6872	.001 211 4	1020.8	1039.0	2.6771
260	.001 274 9	1127.9	1134.3	2.8830	.001 264 5	1121.1	1133.7	2.8699	.001 255 0	1114.6	1133.4	2.8576
280					.001 321 6	1220.9	1234.1	3.0548	.001 308 4	1212.5	1232.1	3.0393
300					.001 397 2	1328.4	1342.3	3.2469	.001 377 0	1316.6	1337.3	3.2260
320									.001 472 4	1431.1	1453.2	3.4247
340									.001 631 1	1567.5	1591.9	3.6546

TABLE A.1.4SI *(Continued)* Compressed Liquid (SI Units)

	$P = 20$ MPa (365.81)				$P = 30$ MPa				$P = 50$ MPa			
T	v	u	h	s	v	u	h	s	v	u	h	s
Sat.	.002 036	1785.6	1826.3	4.0139								
0	.000 990 4	.19	20.01	.0004	.000 985 6	.25	29.82	.0001	.000 976 6	.20	49.03	−.0014
20	.000 992 8	82.77	102.62	.2923	.000 988 6	82.17	111.84	.2899	.000 980 4	81.00	130.02	.2848
40	.000 999 2	165.17	185.16	.5646	.000 995 1	164.04	193.89	.5607	.000 987 2	161.86	211.21	.5527
60	.001 008 4	247.68	267.85	.8206	.001 004 2	246.06	276.19	.8154	.000 996 2	242.98	292.79	.8052
80	.001 019 9	330.40	350.80	1.0624	.001 015 6	328.30	358.77	1.0561	.001 007 3	324.34	374.70	1.0440
100	.001 033 7	413.39	434.06	1.2917	.001 029 0	410.78	441.66	1.2844	.001 020 1	405.88	456.89	1.2703
120	.001 049 6	496.76	517.76	1.5102	.001 044 5	493.59	524.93	1.5018	.001 034 8	487.65	539.39	1.4857
140	.001 067 8	580.69	602.04	1.7193	.001 062 1	576.88	608.75	1.7098	.001 051 5	569.77	622.35	1.6915
160	.001 088 5	665.35	687.12	1.9204	.001 082 1	660.82	693.28	1.9096	.001 070 3	652.41	705.92	1.8891
180	.001 112 0	750.95	773.20	2.1147	.001 104 7	745.59	778.73	2.1024	.001 091 2	735.69	790.25	2.0794
200	.001 138 8	837.7	860.5	2.3031	.001 130 2	831.4	865.3	2.2893	.001 114 6	819.7	875.5	2.2634
220	.001 169 3	925.9	949.3	2.4870	.001 159 0	918.3	953.1	2.4711	.001 140 8	904.7	961.7	2.4419
240	.001 204 6	1016.0	1040.0	2.6674	.001 192 0	1006.9	1042.6	2.6490	.001 170 2	990.7	1049.2	2.6158
260	.001 246 2	1108.6	1133.5	2.8459	.001 230 3	1097.4	1134.3	2.8243	.001 203 4	1078.1	1138.2	2.7860
280	.001 296 5	1204.7	1230.6	3.0248	.001 275 5	1190.7	1229.0	2.9986	.001 241 5	1167.2	1229.3	2.9537
300	.001 359 6	1306.1	1333.3	3.2071	.001 330 4	1287.9	1327.8	3.1741	.001 286 0	1258.7	1323.0	3.1200
320	.001 443 7	1415.7	1444.6	3.3979	.001 399 7	1390.7	1432.7	3.3539	.001 338 8	1353.3	1420.2	3.2868
340	.001 568 4	1539.7	1571.0	3.6075	.001 492 0	1501.7	1546.5	3.5426	.001 403 2	1452.0	1522.1	3.4557
360	.001 822 6	1702.8	1739.3	3.8772	.001 626 5	1626.6	1675.4	3.7494	.001 483 8	1556.0	1630.2	3.6291
380					.001 869 1	1781.4	1837.5	4.0012	.001 588 4	1667.2	1746.6	3.8101

TABLE A.1.5SI Saturated Solid—Saturated Vapor (SI Units)

		Specific Volume		Internal Energy			Enthalpy			Entropy		
Temp. °C T	Press. kPa P	Sat. Solid $v_i \times 10^3$	Sat. Vapor v	Sat. Solid u_i	Subl. u_{ig}	Sat. Vapor u_g	Sat. Solid h_i	Subl. h_{ig}	Sat. Vapor h_g	Sat. Solid s_i	Subl. s_{ig}	Sat. Vapor s_g
.01	.6113	1.0908	206.1	−333.40	2708.7	2375.3	−333.40	2834.8	2501.4	−1.221	10.378	9.156
0	.6108	1.0908	206.3	−333.43	2708.8	2375.3	−333.43	2834.8	2501.3	−1.221	10.378	9.157
−2	.5176	1.0904	241.7	−337.62	2710.2	2372.6	−337.62	2835.3	2497.7	−1.237	10.456	9.219
−4	.4375	1.0901	283.8	−341.78	2711.6	2369.8	−341.78	2835.7	2494.0	−1.253	10.536	9.283
−6	.3689	1.0898	334.2	−345.91	2712.9	2367.0	−345.91	2836.2	2490.3	−1.268	10.616	9.348
−8	.3102	1.0894	394.4	−350.02	2714.2	2364.2	−350.02	2836.6	2486.6	−1.284	10.698	9.414
−10	.2602	1.0891	466.7	−354.09	2715.5	2361.4	−354.09	2837.0	2482.9	−1.299	10.781	9.481
−12	.2176	1.0888	553.7	−358.14	2716.8	2358.7	−358.14	2837.3	2479.2	−1.315	10.865	9.550
−14	.1815	1.0884	658.8	−362.15	2718.0	2355.9	−362.15	2837.6	2475.5	−1.331	10.950	9.619
−16	.1510	1.0881	786.0	−366.14	2719.2	2353.1	−366.14	2837.9	2471.8	−1.346	11.036	9.690
−18	.1252	1.0878	940.5	−370.10	2720.4	2350.3	−370.10	2838.2	2468.1	−1.362	11.123	9.762
−20	.1035	1.0874	1128.6	−374.03	2721.6	2347.5	−374.03	2838.4	2464.3	−1.377	11.212	9.835
−22	.0853	1.0871	1358.4	−377.93	2722.7	2344.7	−377.93	2838.6	2460.6	−1.393	11.302	9.909
−24	.0701	1.0868	1640.1	−381.80	2723.7	2342.0	−381.80	2838.7	2456.9	−1.408	11.394	9.985
−26	.0574	1.0864	1986.4	−385.64	2724.8	2339.2	−385.64	2838.9	2453.2	−1.424	11.486	10.062
−28	.0469	1.0861	2413.7	−389.45	2725.8	2336.4	−389.45	2839.0	2449.5	−1.439	11.580	10.141
−30	.0381	1.0858	2943	−393.23	2726.8	2333.6	−393.23	2839.0	2445.8	−1.455	11.676	10.221
−32	.0309	1.0854	3600	−396.98	2727.8	2330.8	−396.98	2839.1	2442.1	−1.471	11.773	10.303
−34	.0250	1.0851	4419	−400.71	2728.7	2328.0	−400.71	2839.1	2438.4	−1.486	11.872	10.386
−36	.0201	1.0848	5444	−404.40	2729.6	2325.2	−404.40	2839.1	2434.7	−1.501	11.972	10.470
−38	.0161	1.0844	6731	−408.06	2730.5	2322.4	−408.06	2839.0	2430.9	−1.517	12.073	10.556
−40	.0129	1.0841	8354	−411.70	2731.3	2319.6	−411.70	2838.9	2427.2	−1.532	12.176	10.644

TABLE A.1E Thermodynamic Properties of Steam (English Units)

TABLE A.1.1E Saturated Steam: Temperature Table (English Units)

		Specific Volume ft³/lbm		Internal Energy Btu/lbm			Enthalpy Btu/lbm			Entropy Btu/lbm R		
Temp. F. T	Press. lbf/ sq. in. P	Sat. Liquid v_f	Sat. Vapor v_g	Sat. Liquid u_f	Evap. u_{fg}	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
32.018	0.088 66	0.016 022	3302	0.00	1021.2	1021.2	0.01	1075.4	1075.4	0.000 00	2.1869	2.1869
35	0.099 92	0.016 021	2948	2.99	1019.2	1022.2	3.00	1073.7	1076.7	0.006 07	2.1704	2.1764
40	0.121 66	0.016 020	2445	8.02	1015.8	1023.9	8.02	1070.9	1078.9	0.016 17	2.1430	2.1592
45	0.147 48	0.016 021	2037	13.04	1012.5	1025.5	13.04	1068.1	1081.1	0.026 18	2.1162	2.1423
50	0.178 03	0.016 024	1704.2	18.06	1009.1	1027.2	18.06	1065.2	1083.3	0.036 07	2.0899	2.1259
60	0.2563	0.016 035	1206.9	28.08	1002.4	1030.4	28.08	1059.6	1087.7	0.055 55	2.0388	2.0943
70	0.3632	0.016 051	867.7	38.09	995.6	1033.7	38.09	1054.0	1092.0	0.074 63	1.9896	2.0642
80	0.5073	0.016 073	632.8	48.08	988.9	1037.0	48.09	1048.3	1096.4	0.093 32	1.9423	2.0356
90	0.6988	0.016 099	467.7	58.07	982.2	1040.2	58.07	1042.7	1100.7	0.111 65	1.8966	2.0083
100	0.9503	0.016 130	350.0	68.04	975.4	1043.5	68.05	1037.0	1105.0	0.129 63	1.8526	1.9822
110	1.2763	0.016 166	265.1	78.02	968.7	1046.7	78.02	1031.3	1109.3	0.147 30	1.8101	1.9574
120	1.6945	0.016 205	203.0	87.99	961.9	1049.9	88.00	1025.5	1113.5	0.164 65	1.7690	1.9336
130	2.225	0.016 247	157.17	97.97	955.1	1053.0	97.98	1019.8	1117.8	0.181 72	1.7292	1.9109
140	2.892	0.016 293	122.88	107.95	948.2	1056.2	107.96	1014.0	1121.9	0.198 51	1.6907	1.8892
150	3.722	0.016 343	96.99	117.95	941.3	1059.3	117.96	1008.1	1126.1	0.215 03	1.6533	1.8684
160	4.745	0.016 395	77.23	127.94	934.4	1062.3	127.96	1002.2	1130.1	0.231 30	1.6171	1.8484
170	5.996	0.016 450	62.02	137.95	927.4	1065.4	137.97	996.2	1134.2	0.247 32	1.5819	1.8293
180	7.515	0.016 509	50.20	147.97	920.4	1068.3	147.99	990.2	1138.2	0.263 11	1.5478	1.8109

Source: Abridged from Joseph H. Keenan, Frederick G. Keyes, Philip G. Hill, and Joan G. Moore, *Steam Tables*, John Wiley and Sons, New York, 1969.

TABLE A.1.1E *(Continued)* Saturated Steam: Temperature Table (English Units)

Temp. F. T	Press. lbf/ sq. in. P	Specific Volume ft³/lbm		Internal Energy Btu/lbm			Enthalpy Btu/lbm			Entropy Btu/lbm R		
		Sat. Liquid v_f	Sat. Vapor v_g	Sat. Liquid u_f	Evap. u_{fg}	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
190	9.343	0.016 570	40.95	158.00	913.3	1071.3	158.03	984.1	1142.1	0.278 66	1.5146	1.7932
200	11.529	0.016 634	33.63	168.04	906.2	1074.2	168.07	977.9	1145.9	0.294 00	1.4822	1.7762
210	14.125	0.016 702	27.82	178.10	898.9	1077.0	178.14	971.6	1149.7	0.309 13	1.4508	1.7599
212	14.698	0.016 716	26.80	180.11	897.5	1077.6	180.16	970.3	1150.5	0.312 13	1.4446	1.7567
220	17.188	0.016 772	23.15	188.17	891.7	1079.8	188.22	965.3	1153.5	0.324 06	1.4201	1.7441
230	20.78	0.016 845	19.386	198.26	884.3	1082.6	198.32	958.8	1157.1	0.338 80	1.3901	1.7289
240	24.97	0.016 922	16.327	208.36	876.9	1085.3	208.44	952.3	1160.7	0.353 35	1.3609	1.7143
250	29.82	0.017 001	13.826	218.49	869.4	1087.9	218.59	945.6	1164.2	0.367 72	1.3324	1.7001
260	35.42	0.017 084	11.768	228.64	861.8	1090.5	228.76	938.8	1167.6	0.381 93	1.3044	1.6864
270	41.85	0.017 170	10.066	238.82	854.1	1093.0	238.95	932.0	1170.9	0.395 97	1.2771	1.6731
280	49.18	0.017 259	8.650	249.02	846.3	1095.4	249.18	924.9	1174.1	0.409 86	1.2504	1.6602
290	57.53	0.017 352	7.467	259.25	838.5	1097.7	259.44	917.8	1177.2	0.423 60	1.2241	1.6477
300	66.98	0.017 448	6.472	269.52	830.5	1100.0	269.73	910.4	1180.2	0.437 20	1.1984	1.6356
310	77.64	0.017 548	5.632	279.81	822.3	1102.1	280.06	903.0	1183.0	0.450 67	1.1731	1.6238
320	89.60	0.017 652	4.919	290.14	814.1	1104.2	290.43	895.3	1185.8	0.464 00	1.1483	1.6123
330	103.00	0.017 760	4.312	300.51	805.7	1106.2	300.84	887.5	1188.4	0.477 22	1.1238	1.6010
340	117.93	0.017 872	3.792	310.91	797.1	1108.0	311.30	879.5	1190.8	0.490 31	1.0997	1.5901
350	134.53	0.017 988	3.346	321.35	788.4	1109.8	321.80	871.3	1193.1	0.503 29	1.0760	1.5793
360	152.92	0.018 108	2.961	331.84	779.6	1111.4	332.35	862.9	1195.2	0.516 17	1.0526	1.5688
370	173.23	0.018 233	2.628	342.37	770.6	1112.9	342.96	854.2	1197.2	0.528 94	1.0295	1.5585
380	195.60	0.018 363	2.339	352.95	761.4	1114.3	353.62	845.4	1199.0	0.541 63	1.0067	1.5483
390	220.2	0.018 498	2.087	363.58	752.0	1115.6	364.34	836.2	1200.6	0.554 22	0.9841	1.5383
400	247.1	0.018 638	1.8661	374.27	742.4	1116.6	375.12	826.8	1202.0	0.566 72	0.9617	1.5284
410	276.5	0.018 784	1.6726	385.01	732.6	1117.6	385.97	817.2	1203.1	0.579 16	0.9395	1.5187

420	308.5	0.018 936	1.5024	395.81	722.5	1118.3	396.89	807.2	1204.1	0.591 52	0.9175	1.5091
430	343.3	0.019 094	1.3521	406.68	712.2	1118.9	407.89	796.9	1204.8	0.603 81	0.8957	1.4995
440	381.2	0.019 260	1.2192	417.62	701.7	1119.3	418.98	786.3	1205.3	0.616 05	0.8740	1.4900
450	422.1	0.019 433	1.1011	428.6	690.9	1119.5	430.2	775.4	1205.6	0.6282	0.8523	1.4806
460	466.3	0.019 614	0.9961	439.7	679.8	1119.6	441.4	764.1	1205.5	0.6404	0.8308	1.4712
470	514.1	0.019 803	0.9025	450.9	668.4	1119.4	452.8	752.4	1205.2	0.6525	0.8093	1.4618
480	565.5	0.020 002	0.8187	462.2	656.7	1118.9	464.3	740.3	1204.6	0.6646	0.7878	1.4524
490	620.7	0.020 211	0.7436	473.6	644.7	1118.3	475.9	727.8	1203.7	0.6767	0.7663	1.4430
500	680.0	0.020 43	0.6761	485.1	632.3	1117.4	487.7	714.8	1202.5	0.6888	0.7448	1.4335
520	811.4	0.020 91	0.5605	508.5	606.2	1114.8	511.7	687.3	1198.9	0.7130	0.7015	1.4145
540	961.5	0.021 45	0.4658	532.6	578.4	1111.0	536.4	657.5	1193.8	0.7374	0.6576	1.3950
560	1131.8	0.022 07	0.3877	557.4	548.4	1105.8	562.0	625.0	1187.0	0.7620	0.6129	1.3749
580	1324.3	0.022 78	0.3225	583.1	515.9	1098.9	588.6	589.3	1178.0	0.7872	0.5668	1.3540
600	1541.0	0.023 63	0.2677	609.9	480.1	1090.0	616.7	549.7	1166.4	0.8130	0.5187	1.3317
620	1784.4	0.024 65	0.2209	638.3	440.2	1078.5	646.4	505.0	1151.4	0.8398	0.4677	1.3075
640	2057.1	0.025 93	0.1805	668.7	394.5	1063.2	678.6	453.4	1131.9	0.8681	0.4122	1.2803
660	2362	0.027 67	0.144 59	702.3	340.0	1042.3	714.4	391.1	1105.5	0.8990	0.3493	1.2483
680	2705	0.030 32	0.111 27	741.7	269.3	1011.0	756.9	309.8	1066.7	0.9350	0.2718	1.2068
700	3090	0.036 66	0.074 38	801.7	145.9	947.7	822.7	167.5	990.2	0.9902	0.1444	1.1346
705.44	3204	0.050 53	0.050 53	872.6	0	872.6	902.5	0	902.5	1.0580	0	1.0580

TABLE A.1.2E Saturated Steam: Pressure Table (English Units)

Press. Lbf/ Sq. In. P	Temp. Fahr. T	Specific Volume ft^3/lbm Sat Liquid v_f	Specific Volume ft^3/lbm Sat. Vapor v_g	Internal Energy Btu/lbm Sat. Liquid u_f	Internal Energy Btu/lbm Evap. u_{fg}	Internal Energy Btu/lbm Sat. Vapor u_g	Enthalpy Btu/lbm Sat. Liquid h_f	Enthalpy Btu/lbm Evap. h_{fg}	Enthalpy Btu/lbm Sat. Vapor h_g	Entropy Btu/lbm R Sat. Liquid s_f	Entropy Btu/lbm R Evap. s_{fg}	Entropy Btu/lbm R Sat. Vapor s_g
1.0	101.70	0.016 136	333.6	69.74	974.3	1044.0	69.74	1036.0	1105.8	0.132 66	1.8453	1.9779
2.0	126.04	0.016 230	173.75	94.02	957.8	1051.8	94.02	1022.1	1116.1	0.174 99	1.7448	1.9198
3.0	141.43	0.016 300	118.72	109.38	947.2	1056.6	109.39	1013.1	1122.5	0.200 89	1.6852	1.8861
4.0	152.93	0.016 358	90.64	120.88	939.3	1060.2	120.89	1006.4	1127.3	0.219 83	1.6426	1.8624
5.0	162.21	0.016 407	73.53	130.15	932.9	1063.0	130.17	1000.9	1131.0	0.234 86	1.6093	1.8441
6.0	170.03	0.016 451	61.98	137.98	927.4	1065.4	138.00	996.2	1134.2	0.247 36	1.5819	1.8292
8.0	182.84	0.016 526	47.35	150.81	918.4	1069.2	150.84	988.4	1139.3	0.267 54	1.5383	1.8058
10	193.19	0.016 590	38.42	161.20	911.0	1072.2	161.23	982.1	1143.3	0.283 58	1.5041	1.7877
14.696	211.99	0.016 715	26.80	180.10	897.5	1077.6	180.15	970.4	1150.5	0.312 12	1.4446	1.7567
15	213.03	0.016 723	26.29	181.14	896.8	1077.9	181.19	969.7	1150.9	0.313 67	1.4414	1.7551
20	227.96	0.016 830	20.09	196.19	885.8	1082.0	196.26	960.1	1156.4	0.335 80	1.3962	1.7320
25	240.08	0.016 922	16.306	208.44	876.9	1085.3	208.52	952.2	1160.7	0.353 45	1.3607	1.7142
30	250.34	0.017 004	13.748	218.84	869.2	1088.0	218.93	945.4	1164.3	0.368 21	1.3314	1.6996
35	259.30	0.017 073	11.900	227.93	862.4	1090.3	228.04	939.3	1167.4	0.380 93	1.3064	1.6873
40	267.26	0.017 146	10.501	236.03	856.2	1092.3	236.16	933.8	1170.0	0.392 14	1.2845	1.6767
45	274.46	0.017 209	9.403	243.37	850.7	1094.0	243.51	928.8	1172.3	0.402 18	1.2651	1.6673
50	281.03	0.017 269	8.518	250.08	845.5	1095.6	250.24	924.2	1174.4	0.411 29	1.2476	1.6589
55	287.10	0.017 325	7.789	256.28	840.8	1097.0	256.46	919.9	1176.3	0.419 63	1.2317	1.6513
60	292.73	0.017 378	7.177	262.06	836.3	1098.3	262.25	915.8	1178.0	0.427 33	1.2170	1.6444
65	298.00	0.017 429	6.657	267.46	832.1	1099.5	267.67	911.9	1179.6	0.434 50	1.2035	1.6380
70	302.96	0.017 478	6.209	272.56	828.1	1100.6	272.79	908.3	1181.0	0.441 20	1.1909	1.6321
75	307.63	0.017 524	5.818	277.37	824.3	1101.6	277.61	904.8	1182.4	0.447 49	1.1790	1.6265
80	312.07	0.017 570	5.474	281.95	820.6	1102.6	282.21	901.4	1183.6	0.453 44	1.1679	1.6214
85	316.29	0.017 613	5.170	286.30	817.1	1103.5	286.58	898.2	1184.8	0.459 07	1.1574	1.6165

90	320.31	0.017 655	4.898	290.46	813.8	1104.3	290.76	895.1	1185.9	0.464 42	1.1475	1.6119
95	324.16	0.017 696	4.654	294.45	810.6	1105.0	294.76	892.1	1186.9	0.469 52	1.1380	1.6076
100	327.86	0.017 736	4.434	298.28	807.5	1105.8	298.61	889.2	1187.8	0.474 39	1.1290	1.6034
110	334.82	0.017 813	4.051	305.52	801.6	1107.1	305.88	883.7	1189.6	0.483 55	1.1122	1.5957
120	341.30	0.017 886	3.730	312.27	796.0	1108.3	312.67	878.5	1191.1	0.492 01	1.0966	1.5886
130	347.37	0.017 957	3.457	318.61	790.7	1109.4	319.04	873.5	1192.5	0.499 89	1.0822	1.5821
140	353.08	0.018 024	3.221	324.58	785.7	1110.3	325.05	868.7	1193.8	0.507 27	1.0688	1.5761
150	358.48	0.018 089	3.016	330.24	781.0	1111.2	330.75	864.2	1194.9	0.514 22	1.0562	1.5704
160	363.60	0.018 152	2.836	335.63	776.4	1112.0	336.16	859.8	1196.0	0.520 78	1.0443	1.5651
170	368.47	0.018 214	2.676	340.76	772.0	1112.7	341.33	855.6	1196.9	0.527 00	1.0330	1.5600
180	373.13	0.018 273	2.533	345.68	767.7	1113.4	346.29	851.5	1197.8	0.532 92	1.0223	1.5553
190	377.59	0.018 331	2.405	350.39	763.6	1114.0	351.04	847.5	1198.6	0.538 57	1.0122	1.5507
200	381.86	0.018 387	2.289	354.9	759.6	1114.6	355.6	843.7	1199.3	0.5440	1.0025	1.5464
250	401.04	0.018 653	1.8448	375.4	741.4	1116.7	376.2	825.8	1202.1	0.5680	0.9594	1.5274
300	417.43	0.018 896	1.5442	393.0	725.1	1118.2	394.1	809.8	1203.9	0.5883	0.9232	1.5115
350	431.82	0.019 124	1.3267	408.7	710.3	1119.0	409.9	795.0	1204.9	0.6060	0.8917	1.4978
400	444.70	0.019 340	1.1620	422.8	696.7	1119.5	424.2	781.2	1205.5	0.6218	0.8638	1.4856
450	456.39	0.019 547	1.0326	435.7	683.9	1119.6	437.4	768.2	1205.6	0.6360	0.8385	1.4746
500	467.13	0.019 748	0.9283	447.7	671.7	1119.4	449.5	755.8	1205.3	0.6490	0.8154	1.4645
550	477.07	0.019 943	0.8423	458.9	660.2	1119.1	460.9	743.9	1204.8	0.6611	0.7941	1.4551
600	486.33	0.020 13	0.7702	469.4	649.1	1118.6	471.7	732.4	1204.1	0.6723	0.7742	1.4464
700	503.23	0.020 51	0.6558	488.9	628.2	1117.0	491.5	710.5	1202.0	0.6927	0.7378	1.4305
800	518.36	0.020 87	0.5691	506.6	608.4	1115.0	509.7	689.6	1199.3	0.7110	0.7050	1.4160
900	532.12	0.021 23	0.5009	523.0	589.6	1112.6	526.6	669.5	1196.0	0.7277	0.6750	1.4027
1000	544.75	0.021 59	0.4459	538.4	571.5	1109.9	542.4	650.0	1192.4	0.7432	0.6471	1.3903
1200	567.37	0.022 32	0.3623	566.7	536.8	1103.5	571.7	612.3	1183.9	0.7712	0.5961	1.3673
1400	587.25	0.023 07	0.3016	592.7	503.3	1096.0	598.6	575.5	1174.1	0.7964	0.5497	1.3461
1600	605.06	0.023 86	0.2552	616.9	470.5	1087.4	624.0	538.9	1162.9	0.8196	0.5062	1.3258
1800	621.21	0.024 72	0.2183	640.0	437.6	1077.7	648.3	502.1	1150.4	0.8414	0.4645	1.3060
2000	636.00	0.025 65	0.18813	662.4	404.2	1066.6	671.9	464.4	1136.3	0.8623	0.4238	1.2861
2500	668.31	0.028 60	0.13059	717.7	313.4	1031.0	730.9	360.5	1091.4	0.9131	0.3196	1.2327
3000	695.52	0.034 31	0.08404	783.4	185.4	968.8	802.5	213.0	1015.5	0.9732	0.1843	1.1575
3203.6	705.44	0.050 53	0.05053	872.6	0	872.6	902.5	0	902.5	1.0580	0	1.0580

TABLE A.1.3E Superheated Vapor (English Units)

F	*v*	*u*	*h*	*s*	*v*	*u*	*h*	*s*	*v*	*u*	*h*	*s*
		$P = 1.0(101.70)$				**$P = 5.0(162.21)$**				**$P = 10.0(193.19)$**		
Sat	333.6	1044.0	1105.8	1.9779	73.53	1063.0	1131.0	1.8441	38.42	1072.2	1143.3	1.7877
200	392.5	1077.5	1150.1	2.0508	78.15	1076.3	1148.6	1.8715	38.85	1074.7	1146.6	1.7927
240	416.4	1091.2	1168.3	2.0775	83.00	1090.3	1167.1	1.8987	41.32	1089.0	1165.5	1.8205
280	440.3	1105.0	1186.5	2.1028	87.83	1104.3	1185.5	1.9244	43.77	1103.3	1184.3	1.8467
320	464.2	1118.9	1204.8	2.1269	92.64	1118.3	1204.0	1.9487	46.20	1117.6	1203.1	1.8714
360	488.1	1132.9	1223.2	2.1500	97.45	1132.4	1222.6	1.9719	48.62	1131.8	1221.8	1.8948
400	511.9	1147.0	1241.8	2.1720	102.24	1146.6	1241.2	1.9941	51.03	1146.1	1240.5	1.9171
440	535.8	1161.2	1260.4	2.1932	107.03	1160.9	1259.9	2.0154	53.44	1160.5	1259.3	1.9385
500	571.5	1182.8	1288.5	2.2235	114.20	1182.5	1288.2	2.0458	57.04	1182.2	1287.7	1.9690
600	631.1	1219.3	1336.1	2.2706	126.15	1219.1	1335.8	2.0930	63.03	1218.9	1335.5	2.0164
700	690.7	1256.7	1384.5	2.3142	138.08	1256.5	1384.3	2.1367	69.01	1256.3	1384.0	2.0601
800	750.3	1294.9	1433.7	2.3550	150.01	1294.7	1433.5	2.1775	74.98	1294.6	1433.3	2.1009
1000	869.5	1373.9	1534.8	2.4294	173.86	1373.9	1534.7	2.2520	86.91	1373.8	1534.6	2.1755
1200	988.6	1456.7	1639.6	2.4967	197.70	1456.6	1639.5	2.3192	98.84	1456.5	1639.4	2.2428
1400	1107.7	1543.1	1748.1	2.5584	221.54	1543.1	1748.1	2.3810	110.76	1543.0	1748.0	2.3045
		$P = 14.696(211.99)$				**$P = 20(227.96)$**				**$P = 40(267.26)$**		
Sat	26.80	1077.6	1150.5	1.7567	20.09	1082.0	1156.4	1.7320	10.501	1092.3	1170.0	1.6767
240	28.00	1087.9	1164.0	1.7764	20.47	1086.5	1162.3	1.7405				
280	29.69	1102.4	1183.1	1.8030	21.73	1101.4	1181.8	1.7676	10.711	1097.3	1176.6	1.6857
320	31.36	1116.8	1202.1	1.8280	22.98	1116.0	1201.0	1.7930	11.360	1112.8	1196.9	1.7124
360	33.02	1131.2	1221.0	1.8516	24.21	1130.6	1220.1	1.8168	11.996	1128.0	1216.8	1.7373
400	34.67	1145.6	1239.9	1.8741	25.43	1145.1	1239.2	1.8395	12.623	1143.0	1236.4	1.7606
440	36.31	1160.1	1258.8	1.8956	26.64	1159.6	1258.2	1.8611	13.243	1157.8	1255.8	1.7828
500	38.77	1181.8	1287.3	1.9263	28.46	1181.5	1286.8	1.8919	14.164	1180.1	1284.9	1.8140

600	42.86	1218.6	1335.2	1.9737	31.47	1218.4	1334.8	1.9395	15.685	1217.3	1333.4	1.8621
700	46.93	1256.1	1383.8	2.0175	34.47	1255.9	1383.5	1.9834	17.196	1255.1	1382.4	1.9063
800	51.00	1294.4	1433.1	2.0584	37.46	1294.3	1432.9	2.0243	18.701	1293.7	1432.1	1.9474
1000	59.13	1373.7	1534.5	2.1330	43.44	1373.5	1534.3	2.0989	21.70	1373.1	1533.8	2.0223
1200	67.25	1456.5	1639.3	2.2003	49.41	1456.4	1639.2	2.1663	24.69	1456.1	1638.9	2.0897
1400	75.36	1543.0	1747.9	2.2621	55.37	1542.9	1747.9	2.2281	27.68	1542.7	1747.6	2.1515
1600	83.47	1633.2	1860.2	2.3194	61.33	1633.2	1860.1	2.2854	30.66	1633.0	1859.9	2.2089
		P = 60(292.73)				**P = 80(312.07)**				**P = 100(327.86)**		
Sat	7.177	1098.3	1178.0	1.6444	5.474	1102.6	1183.6	1.6214	4.434	1105.8	1187.8	1.6034
320	7.485	1109.5	1192.6	1.6634	5.544	1106.0	1188.0	1.6271				
360	7.924	1125.3	1213.3	1.6893	5.886	1122.5	1209.7	1.6541	4.662	1119.7	1205.9	1.6259
400	8.353	1140.8	1233.5	1.7134	6.217	1138.5	1230.6	1.6790	4.934	1136.2	1227.5	1.6517
440	8.775	1156.0	1253.4	1.7360	6.541	1154.2	1251.0	1.7022	5.199	1152.3	1248.5	1.6755
500	9.399	1178.6	1283.0	1.7678	7.017	1177.2	1281.1	1.7346	5.587	1175.7	1279.1	1.7085
600	10.425	1216.3	1332.1	1.8165	7.794	1215.3	1330.7	1.7838	6.216	1214.2	1329.3	1.7582
700	11.440	1254.4	1381.4	1.8609	8.561	1253.6	1380.3	1.8285	6.834	1252.8	1379.2	1.8033
800	12.448	1293.0	1431.2	1.9022	9.321	1292.4	1430.4	1.8700	7.445	1291.8	1429.6	1.8449
1000	14.454	1372.7	1533.2	1.9773	10.831	1372.3	1532.6	1.9453	8.657	1371.9	1532.1	1.9204
1200	16.452	1455.8	1638.5	2.0448	12.333	1455.5	1638.1	2.0130	9.861	1455.2	1637.7	1.9882
1400	18.445	1542.5	1747.3	2.1067	13.830	1542.3	1747.0	2.0749	11.060	1542.0	1746.7	2.0502
1600	20.44	1632.8	1859.7	2.1641	15.324	1632.6	1859.5	2.1323	12.257	1632.4	1859.3	2.1076
1800	22.43	1726.7	1975.7	2.2179	16.818	1726.5	1975.5	2.1861	13.452	1726.4	1975.3	2.1614
2000	24.41	1824.0	2095.1	2.2685	18.310	1823.9	2094.9	2.2367	14.647	1823.7	2094.8	2.2121
		P = 120(341.30)				**P = 140(353.08)**				**P = 160(363.60)**		
Sat	3.730	1108.3	1191.1	1.5886	3.221	1110.3	1193.8	1.5761	2.836	1112.0	1196.0	1.5651
360	3.844	1116.7	1202.0	1.6021	3.259	1113.5	1198.0	1.5812				
400	4.079	1133.8	1224.4	1.6288	3.466	1131.4	1221.2	1.6088	3.007	1128.8	1217.8	1.5911
450	4.360	1154.3	1251.2	1.6590	3.713	1152.4	1248.6	1.6399	3.228	1150.5	1246.1	1.6230

(Continued)

TABLE A.1.3E *(Continued)* Superheated Vapor (English Units)

F	v	u	h	s	v	u	h	s	v	u	h	s
	$P = 120(341.30)$				$P = 140(353.08)$				$P = 160(363.60)$			
500	4.633	1174.2	1277.1	1.6868	3.952	1172.7	1275.1	1.6682	3.440	1171.2	1273.0	1.6518
550	4.900	1193.8	1302.6	1.7127	4.184	1192.6	1300.9	1.6944	3.646	1191.3	1299.2	1.6784
600	5.164	1213.2	1327.8	1.7371	4.412	1212.1	1326.4	1.7191	3.848	1211.1	1325.0	1.7034
700	5.682	1252.0	1378.2	1.7825	4.860	1251.2	1377.1	1.7648	4.243	1250.4	1376.0	1.7494
800	6.195	1291.2	1428.7	1.8243	5.301	1290.5	1427.9	1.8068	4.631	1289.9	1427.0	1.7916
1000	7.208	1371.5	1531.5	1.9000	6.173	1371.0	1531.0	1.8827	5.397	1370.6	1530.4	1.8677
1200	8.213	1454.9	1637.3	1.9679	7.036	1454.6	1636.9	1.9507	6.154	1454.3	1636.5	1.9358
1400	9.214	1541.8	1746.4	2.0300	7.895	1541.6	1746.1	2.0129	6.906	1541.4	1745.9	1.9980
1600	10.212	1632.3	1859.0	2.0875	8.752	1632.1	1858.8	2.0704	7.656	1631.9	1858.6	2.0556
1800	11.209	1726.2	1975.1	2.1413	9.607	1726.1	1975.0	2.1242	8.405	1725.9	1974.8	2.1094
2000	12.205	1823.6	2094.6	2.1919	10.461	1823.5	2094.5	2.1749	9.153	1823.3	2094.3	2.1601
	$P = 180(373.13)$				$P = 200(381.86)$				$P = 225(391.87)$			
Sat	2.533	1113.4	1197.8	1.5553	2.289	1114.6	1199.3	1.5464	2.043	1115.8	1200.8	1.5365
400	2.648	1126.2	1214.4	1.5749	2.361	1123.5	1210.8	1.5600	2.073	1119.9	1206.2	1.5427
450	2.850	1148.5	1243.4	1.6078	2.548	1146.4	1240.7	1.5938	2.245	1143.8	1237.3	1.5779
500	3.042	1169.6	1270.9	1.6372	2.724	1168.0	1268.8	1.6239	2.405	1165.9	1266.1	1.6087
550	3.228	1190.0	1297.5	1.6642	2.893	1188.7	1295.7	1.6512	2.558	1187.0	1293.5	1.6366
600	3.409	1210.0	1323.5	1.6893	3.058	1208.9	1322.1	1.6767	2.707	1207.5	1320.2	1.6624
700	3.763	1249.6	1374.9	1.7357	3.379	1248.8	1373.8	1.7234	2.995	1247.7	1372.4	1.7095
800	4.110	1289.3	1426.2	1.7781	3.693	1288.6	1425.3	1.7660	3.276	1287.8	1424.2	1.7523
900	4.453	1329.4	1477.7	1.8175	4.003	1328.9	1477.1	1.8055	3.553	1328.3	1476.2	1.7920
1000	4.793	1370.2	1529.8	1.8545	4.310	1369.8	1529.3	1.8425	3.827	1369.3	1528.6	1.8292
1200	5.467	1454.0	1636.1	1.9227	4.918	1453.7	1635.7	1.9109	4.369	1453.4	1635.3	1.8977
1400	6.137	1541.2	1745.6	1.9849	5.521	1540.9	1745.3	1.9732	4.906	1540.7	1744.9	1.9600

1600	6.804	1631.7	1858.4	2.0425	6.123	1631.6	1858.2	2.0308	5.441	1631.3	1857.9	2.0177
1800	7.470	1725.8	1974.6	2.0964	6.722	1725.6	1974.4	2.0847	5.975	1725.4	1974.2	2.0716
2000	8.135	1823.2	2094.2	2.1470	7.321	1823.0	2094.0	2.1354	6.507	1822.9	2093.8	2.1223
		P = 250(401.04)				**P = 275(409.52)**				**P = 300(417.43)**		
Sat	1.8448	1116.7	1202.1	1.5274	1.6813	1117.5	1203.1	1.5192	1.5442	1118.2	1203.9	1.5115
450	2.002	1141.1	1233.7	1.5632	1.8026	1138.3	1230.0	1.5495	1.6361	1135.4	1226.2	1.5365
500	2.150	1163.8	1263.3	1.5948	1.9407	1161.7	1260.4	1.5820	1.7662	1159.5	1257.5	1.5701
550	2.290	1185.3	1291.3	1.6233	2.071	1183.6	1289.0	1.6110	1.8878	1181.9	1286.7	1.5997
600	2.426	1206.1	1318.3	1.6494	2.196	1204.7	1316.4	1.6376	2.004	1203.2	1314.5	1.6266
650	2.558	1226.5	1344.9	1.6739	2.317	1225.3	1343.2	1.6623	2.117	1224.1	1341.6	1.6516
700	2.688	1246.7	1371.1	1.6970	2.436	1245.7	1369.7	1.6856	2.227	1244.6	1368.3	1.6751
800	2.943	1287.0	1423.2	1.7401	2.670	1286.2	1422.1	1.7289	2.442	1285.4	1421.0	1.7187
900	3.193	1327.6	1475.3	1.7799	2.898	1327.0	1474.5	1.7689	2.653	1326.3	1473.6	1.7589
1000	3.440	1368.7	1527.9	1.8172	3.124	1368.2	1527.2	1.8064	2.860	1367.7	1526.5	1.7964
1200	3.929	1453.0	1634.8	1.8858	3.570	1452.6	1634.3	1.8751	3.270	1452.2	1633.8	1.8653
1400	4.414	1540.4	1744.6	1.9483	4.011	1540.1	1744.2	1.9376	3.675	1539.8	1743.8	1.9279
1600	4.896	1631.1	1857.6	2.0060	4.450	1630.9	1857.3	1.9954	4.078	1630.7	1857.0	1.9857
1800	5.376	1725.2	1974.0	2.0599	4.887	1725.0	1973.7	2.0493	4.479	1724.9	1973.5	2.0396
2000	5.856	1822.7	2093.6	2.1106	5.323	1822.5	2093.4	2.1000	4.879	1822.3	2093.2	2.0904
		P = 350(431.82)				**P = 400(444.70)**				**P = 450(456.39)**		
Sat	1.3267	1119.0	1204.9	1.4978	1.1620	1119.5	1205.5	1.4856	1.0326	1119.6	1205.6	1.4746
450	1.3733	1129.2	1218.2	1.5125	1.1745	1122.6	1209.6	1.4901				
500	1.4913	1154.9	1251.5	1.5482	1.2843	1150.1	1245.2	1.5282	1.1226	1145.1	1238.5	1.5097
550	1.5998	1178.3	1281.9	1.5790	1.3833	1174.6	1277.0	1.5605	1.2146	1170.7	1271.9	1.5436
600	1.7025	1200.3	1310.6	1.6068	1.4760	1197.3	1306.6	1.5892	1.2996	1194.3	1302.5	1.5732
650	1.8013	1221.6	1338.3	1.6323	1.5645	1219.1	1334.9	1.6153	1.3803	1216.6	1331.5	1.6000
700	1.8975	1242.5	1365.4	1.6562	1.6503	1240.4	1362.5	1.6397	1.4580	1238.2	1359.6	1.6248
800	2.085	1283.8	1418.8	1.7004	1.8163	1282.1	1416.6	1.6844	1.6077	1280.5	1414.4	1.6701

TABLE A.1.3E (*Continued*) Superheated Vapor (English Units)

F	*v*	*u*	*h*	*s*	*v*	*u*	*h*	*s*	*v*	*u*	*h*	*s*
	P = 350(431.82)				**P = 400(444.70)**				**P = 450(456.39)**			
900	2.267	1325.0	1471.8	1.7409	1.9776	1323.7	1470.1	1.7252	1.7524	1322.4	1468.3	1.7113
1000	2.446	1366.6	1525.0	1.7787	2.136	1365.5	1523.6	1.7632	1.8941	1364.4	1522.2	1.7495
1200	2.799	1451.5	1632.8	1.8478	2.446	1450.7	1631.8	1.8327	2.172	1450.0	1630.8	1.8192
1400	3.148	1539.3	1743.1	1.9106	2.752	1538.7	1742.4	1.8956	2.444	1538.1	1741.7	1.8823
1600	3.494	1630.2	1856.5	1.9685	3.055	1629.8	1855.9	1.9535	2.715	1629.3	1855.4	1.9403
1800	3.838	1724.5	1973.1	2.0225	3.357	1724.1	1972.6	2.0076	2.983	1723.7	1972.1	1.9944
2000	4.182	1822.0	2092.8	2.0733	3.658	1821.6	2092.4	2.0584	3.251	1821.3	2092.0	2.0453
	P = 500(467.13)				**P = 600(486.33)**				**P = 700(503.23)**			
Sat	0.9283	1119.4	1205.3	1.4645	0.7702	1118.6	1204.1	1.4464	0.6558	1117.0	1202.0	1.4305
500	0.9924	1139.7	1231.5	1.4923	0.7947	1128.0	1216.2	1.4592				
550	1.0792	1166.7	1266.6	1.5279	0.8749	1158.2	1255.4	1.4990	0.7275	1149.0	1243.2	1.4723
600	1.1583	1191.1	1298.3	1.5585	0.9456	1184.5	1289.5	1.5320	0.7929	1177.5	1280.2	1.5081
650	1.2327	1214.0	1328.0	1.5860	1.0109	1208.6	1320.9	1.5609	0.8520	1203.1	1313.4	1.5387
700	1.3040	1236.0	1356.7	1.6112	1.0727	1231.5	1350.6	1.5872	0.9073	1226.9	1344.4	1.5661
800	1.4407	1278.8	1412.1	1.6571	1.1900	1275.4	1407.6	1.6343	1.0109	1272.0	1402.9	1.6145
900	1.5723	1321.0	1466.5	1.6987	1.3021	1318.4	1462.9	1.6766	1.1089	1315.6	1459.3	1.6576
1000	1.7008	1363.3	1520.7	1.7371	1.4108	1361.2	1517.8	1.7155	1.2036	1358.9	1514.9	1.6970
1100	1.8271	1406.0	1575.1	1.7731	1.5173	1404.2	1572.7	1.7519	1.2960	1402.4	1570.2	1.7337
1200	1.9518	1449.2	1629.8	1.8072	1.6222	1447.7	1627.8	1.7861	1.3868	1446.2	1625.8	1.7682
1400	2.198	1537.6	1741.0	1.8704	1.8289	1536.5	1739.5	1.8497	1.5652	1535.3	1738.1	1.8321
1600	2.442	1628.9	1854.8	1.9285	2.033	1628.0	1853.7	1.9080	1.7409	1627.1	1852.6	1.8906
1800	2.684	1723.3	1971.7	1.9827	2.236	1722.6	1970.8	1.9622	1.9152	1721.8	1969.9	1.9449
2000	2.926	1820.9	2091.6	2.0335	2.438	1820.2	2090.8	2.0131	2.0887	1819.5	2090.1	1.9958

	P = 800(518.36)				P = 1000(544.75)				P = 1250(572.56)			
Sat	0.5691	1115.0	1199.3	1.4160	0.4459	1109.9	1192.4	1.3903	0.3454	1101.7	1181.6	1.3619
550	0.6154	1138.8	1229.9	1.4469	0.4534	1114.8	1198.7	1.3966				
600	0.6776	1170.1	1270.4	1.4861	0.5140	1153.7	1248.8	1.4450	0.3786	1129.0	1216.6	1.3954
650	0.7324	1197.2	1305.6	1.5186	0.5637	1184.7	1289.1	1.4822	0.4267	1167.2	1266.0	1.4410
700	0.7829	1222.1	1338.0	1.5471	0.6080	1212.0	1324.6	1.5135	0.4670	1198.4	1306.4	1.4767
750	0.8306	1245.7	1368.6	1.5730	0.6490	1237.2	1357.3	1.5412	0.5030	1226.1	1342.4	1.5070
800	0.8764	1268.5	1398.2	1.5969	0.6878	1261.2	1388.5	1.5664	0.5364	1251.8	1375.8	1.5341
900	0.9640	1312.9	1455.6	1.6408	0.7610	1307.3	1448.1	1.6120	0.5984	1300.0	1438.4	1.5820
1000	1.0482	1356.7	1511.9	1.6807	0.8305	1352.2	1505.9	1.6530	0.6563	1346.4	1498.2	1.6244
1100	1.1300	1400.5	1567.8	1.7178	0.8976	1396.8	1562.9	1.6908	0.7116	1392.0	1556.6	1.6631
1200	1.2102	1444.6	1623.8	1.7526	0.9630	1441.5	1619.7	1.7261	0.7652	1437.5	1614.5	1.6991
1400	1.3674	1534.2	1736.6	1.8167	1.0905	1531.9	1733.7	1.7909	0.8689	1529.0	1730.0	1.7648
1600	1.5218	1626.2	1851.5	1.8754	1.2152	1624.4	1849.3	1.8499	0.9699	1622.2	1846.5	1.8243
1800	1.6749	1721.0	1969.0	1.9298	1.3384	1719.5	1967.2	1.9046	1.0693	1717.6	1965.0	1.8791
2000	1.8271	1818.8	2089.3	1.9808	1.4608	1817.4	2087.7	1.9557	1.1678	1815.7	2085.8	1.9304
	P = 1500(596.39)				P = 1750(617.31)				P = 2000(636.00)			
Sat	0.2769	1091.8	1168.7	1.3359	0.2268	1080.2	1153.7	1.3109	0.18813	1066.6	1136.3	1.2861
600	0.2816	1096.6	1174.8	1.3416								
650	0.3329	1147.0	1239.4	1.4012	0.2627	1122.5	1207.6	1.3603	0.2057	1091.1	1167.2	1.3141
700	0.3716	1183.4	1286.6	1.4429	0.3022	1166.7	1264.6	1.4106	0.2487	1147.7	1239.8	1.3782
750	0.4049	1214.1	1326.5	1.4767	0.3341	1201.3	1309.5	1.4485	0.2803	1187.3	1291.1	1.4216
800	0.4350	1241.8	1362.5	1.5058	0.3622	1231.3	1348.6	1.4802	0.3071	1220.1	1333.8	1.4562
850	0.4631	1267.7	1396.2	1.5320	0.3878	1258.8	1384.4	1.5081	0.3312	1249.5	1372.0	1.4860
900	0.4897	1292.5	1428.5	1.5562	0.4119	1284.8	1418.2	1.5334	0.3534	1276.8	1407.6	1.5126
1000	0.5400	1340.4	1490.3	1.6001	0.4569	1334.3	1482.3	1.5789	0.3945	1328.1	1474.1	1.5598
1100	0.5876	1387.2	1550.3	1.6399	0.4990	1382.2	1543.8	1.6197	0.4325	1377.2	1537.2	1.6017
1200	0.6334	1433.5	1609.3	1.6765	0.5392	1429.4	1604.0	1.6571	0.4685	1425.2	1598.6	1.6398
1400	0.7213	1526.1	1726.3	1.7431	0.6158	1523.1	1722.6	1.7245	0.5368	1520.2	1718.8	1.7082
1600	0.8064	1619.9	1843.7	1.8031	0.6896	1617.6	1841.0	1.7850	0.6020	1615.4	1838.2	1.7692

(Continued)

TABLE A.1.3E *(Continued)* Superheated Vapor (English Units)

F	v	u	h	s	v	u	h	s	v	u	h	s
	$P = 1500(596.39)$				$P = 1750(617.31)$				$P = 2000(636.00)$			
1800	0.8899	1715.7	1962.7	1.8582	0.7617	1713.9	1960.5	1.8404	0.6656	1712.0	1958.3	1.8249
2000	0.9725	1814.0	2083.9	1.9096	0.8330	1812.3	2082.0	1.8919	0.7284	1810.6	2080.2	1.8765
	$P = 2500(668.31)$				$P = 3000(695.52)$				$P = 3500$			
Sat	0.130 59	1031.0	1091.4	1.2327	0.084 04	968.8	1015.5	1.1575				
650									0.024 91	663.5	679.7	0.8630
700	0.168 39	1098.7	1176.6	1.3073	0.097 71	1003.9	1058.1	1.1944	0.030 58	759.5	779.3	0.9506
750	0.2030	1155.2	1249.1	1.3686	0.148 31	1114.7	1197.1	1.3122	0.104 60	1058.4	1126.1	1.2440
800	0.2291	1195.7	1301.7	1.4112	0.175 72	1167.6	1265.2	1.3675	0.136 26	1134.7	1223.0	1.3226
850	0.2513	1229.5	1345.8	1.4456	0.197 31	1207.7	1317.2	1.4080	0.158 18	1183.4	1285.9	1.3716
900	0.2712	1259.9	1385.4	1.4752	0.2160	1241.8	1361.7	1.4414	0.176 25	1222.4	1336.5	1.4096
950	0.2896	1288.2	1422.2	1.5018	0.2328	1272.7	1402.0	1.4705	0.192 14	1256.4	1380.8	1.4416
1000	0.3069	1315.2	1457.2	1.5262	0.2485	1301.7	1439.6	1.4967	0.2066	1287.6	1421.4	1.4699
1100	0.3393	1366.8	1523.8	1.5704	0.2772	1356.2	1510.1	1.5434	0.2328	1345.2	1496.0	1.5193
1200	0.3696	1416.7	1587.7	1.6101	0.3036	1408.0	1576.6	1.5848	0.2566	1399.2	1565.3	1.5624
1400	0.4261	1514.2	1711.3	1.6804	0.3524	1508.1	1703.7	1.6571	0.2997	1501.9	1696.1	1.6368
1600	0.4795	1610.2	1832.6	1.7424	0.3978	1606.3	1827.1	1.7201	0.3395	1601.7	1821.6	1.7010
1800	0.5312	1708.2	1954.0	1.7986	0.4416	1704.5	1949.6	1.7769	0.3776	1700.8	1945.4	1.7583
2000	0.5820	1807.2	2076.4	1.8506	0.4844	1803.9	2072.8	1.8291	0.4147	1800.6	2069.2	1.8108
	$P = 4000$				$P = 5000$				$P = 6000$			
650	0.024 47	657.7	675.8	0.8574	0.02377	648.0	670.0	0.8482	0.023 22	640.0	665.8	0.8405
700	0.028 67	742.1	763.4	0.9345	0.02676	721.8	746.6	0.9156	0.025 63	708.1	736.5	0.9028

750	0.063 31	960.7	1007.5	1.1395	0.033 64	821.4	852.6	1.0049	0.029 78	788.6	821.7	0.9746
800	0.105 22	1095.0	1172.9	1.2740	0.059 32	987.2	1042.1	1.1583	0.039 42	896.9	940.7	1.0708
850	0.128 33	1156.5	1251.5	1.3352	0.085 56	1092.7	1171.9	1.2596	0.058 18	1018.8	1083.4	1.1820
900	0.146 22	1201.5	1309.7	1.3789	0.103 85	1155.1	1251.1	1.3190	0.075 88	1102.9	1187.2	1.2599
950	0.161 51	1239.2	1358.8	1.4144	0.118 53	1202.2	1311.9	1.3629	0.090 08	1162.0	1262.0	1.3140
1000	0.175 20	1272.9	1402.6	1.4449	0.131 20	1242.0	1363.4	1.3988	0.102 07	1209.1	1322.4	1.3561
1100	0.199 54	1333.9	1481.6	1.4973	0.153 02	1310.6	1452.2	1.4577	0.122 18	1286.4	1422.1	1.4222
1200	0.2213	1390.1	1553.9	1.5423	0.171 99	1371.6	1530.8	1.5066	0.139 27	1352.7	1507.3	1.4752
1300	0.2414	1443.7	1622.4	1.5823	0.189 18	1428.6	1603.7	1.5493	0.154 53	1413.3	1584.9	1.5206
1400	0.2603	1495.7	1688.4	1.6188	0.205 17	1483.2	1673.0	1.5876	0.168 54	1470.5	1657.6	1.5608
1600	0.2959	1597.1	1816.1	1.6841	0.2348	1587.9	1805.2	1.6551	0.194 20	1578.7	1794.3	1.6307
1800	0.3296	1697.1	1941.1	1.7420	0.2626	1689.8	1932.7	1.7142	0.218 01	1682.4	1924.5	1.6910
2000	0.3625	1797.3	2065.6	1.7948	0.2895	1790.8	2058.6	1.7676	0.240 87	1784.3	2051.7	1.7450

TABLE A.1.4E Compressed Liquid (English Units)

T	v	u	h	s	v	u	h	s	v	u	h	s
	$P = 500$(467.13)				$P = 1000$(544.75)				$P = 1500$(596.39)			
Sat	0.019 748	447.70	449.53	0.649 04	0.021 591	538.39	542.38	0.743 20	0.023 461	604.97	611.48	0.808 24
32	0.015 994	0.00	1.49	0.000 00	0.015 967	0.03	2.99	0.000 05	0.015 939	0.05	4.47	0.000 07
50	0.015 998	18.02	19.50	0.035 99	0.015 972	17.99	20.94	0.035 92	0.015 946	17.95	22.38	0.035 84
100	0.016 106	67.87	69.36	0.129 32	0.016 082	67.70	70.68	0.129 01	0.016 058	67.53	71.99	0.128 70
150	0.016 318	117.66	119.17	0.214 57	0.016 293	117.38	120.40	0.214 10	0.016 268	117.10	121.62	0.213 64
200	0.016 608	167.65	169.19	0.293 41	0.016 580	167.26	170.32	0.292 81	0.016 554	166.87	171.46	0.292 21
250	0.016 972	217.99	219.56	0.367 02	0.016 941	217.47	220.61	0.366 28	0.016 910	216.96	221.65	0.365 54
300	0.017 416	268.92	270.53	0.436 41	0.017 379	268.24	271.46	0.435 52	0.017 343	267.58	272.39	0.434 63
350	0.017 954	320.71	322.37	0.502 49	0.017 909	319.83	323.15	0.501 40	0.017 865	318.98	323.94	0.500 34
400	0.018 608	373.68	375.40	0.566 04	0.018 550	372.55	375.98	0.564 72	0.018 493	371.45	376.59	0.563.43
450	0.019 420	428.40	430.19	0.627 98	0.019 340	426.89	430.47	0.626 32	0.019 264	425.44	430.79	0.624 70
500					0.020 36	483.8	487.5	0.6874	0.020 24	481.8	487.4	0.6853
550									0.021 58	542.1	548.1	0.7469
	$P = 2000$(636.00)				$P = 3000$(695.52)				$P = 5000$			
Sat	0.025 649	662.40	671.89	0.862 27	0.034 310	783.45	802.50	0.973 20				
32	0.015 912	0.06	5.95	0.000 08	0.015 859	0.09	8.90	0.000 09	0.015 755	0.11	14.70	−0.000 01
50	0.015 920	17.91	23.81	0.035 75	0.015 870	17.84	26.65	0.035 55	0.015 773	17.67	32.26	0.035 08
100	0.016 034	67.37	73.30	0.128 39	0.015 987	67.04	75.91	0.127 77	0.015 897	66.40	81.11	0.126 51
200	0.016 527	166.49	172.60	0.291 62	0.016 476	165.74	174.89	0.290 46	0.016 376	164.32	179.47	0.288 18
300	0.017 308	266.93	273.33	0.433 76	0.017 240	265.66	275.23	0.432 05	0.017 110	263.25	279.08	0.428 75
400	0.018 439	370.38	377.21	0.562 16	0.018 334	368.32	378.50	0.559 70	0.018 141	364.47	381.25	0.555 06
450	0.019 191	424.04	431.14	0.623 13	0.019 053	421.36	431.93	0.620 11	0.018 803	416.44	433.84	0.614 51
500	0.020 14	479.8	487.3	0.6832	0.019 944	476.2	487.3	0.679 4	0.019 603	469.8	487.9	0.6724
560	0.021 72	551.8	559.8	0.7565	0.021 382	546.2	558.0	0.750 8	0.020 835	536.7	556.0	0.7411

TABLE A.1.5E Saturated Solid–Saturated Vapor (English Units)

	Specific Volume			Internal Energy			Enthalpy			Entropy		
Temp. Fahr. T	Press. lbf/in^2 P	Sat. Solid v_i	Sat. Vapor $v_g \times 10^{-3}$	Sat. Solid u_i	Subl. u_{ig}	Sat. Vapor u_g	Sat. Solid h_i	Subl. h_{ig}	Sat. Vapor h_g	Sat. Solid s_i	Subl. s_{ig}	Sat. Vapor s_g
32.018	0.0887	0.01747	3.302	−143.34	1164.6	1021.2	−143.34	1218.7	1075.4	−0.292	2.479	2.187
32	0.0886	0.01747	3.305	−143.35	1164.6	1021.2	−143.35	1218.7	1075.4	−0.292	2.479	2.187
30	0.0808	0.01747	3.607	−144.35	1164.9	1020.5	−144.35	1218.9	1074.5	−0.294	2.489	2.195
25	0.0641	0.01746	4.506	−146.84	1165.7	1018.9	−146.84	1219.1	1072.3	−0.299	2.515	2.216
20	0.0505	0.01745	5.655	−149.31	1166.5	1017.2	−149.31	1219.4	1070.1	−0.304	2.542	2.238
15	0.0396	0.01745	7.13	−151.75	1167.3	1015.5	−151.75	1219.7	1067.9	−0.309	2.569	2.260
10	0.0309	0.01744	9.04	−154.17	1168.1	1013.9	−154.17	1219.9	1065.7	−0.314	2.597	2.283
5	0.0240	0.01743	11.52	−156.56	1168.8	1012.2	−156.56	1220.1	1063.5	−0.320	2.626	2.306
0	0.0185	0.01743	14.77	−158.93	1169.5	1010.6	−158.93	1220.2	1061.2	−0.325	2.655	2.330
−5	0.0142	0.01742	19.03	−161.27	1170.2	1008.9	−161.27	1220.3	1059.0	−0.330	2.684	2.354
−10	0.0109	0.01741	24.66	−163.59	1170.9	1007.3	−163.59	1220.4	1056.8	−0.335	2.714	2.379
−15	0.0082	0.01740	32.2	−165.89	1171.5	1005.6	−165.89	1220.5	1054.6	−0.340	2.745	2.405
−20	0.0062	0.01740	42.2	−168.16	1172.1	1003.9	−168.16	1220.6	1052.4	−0.345	2.776	2.431
−25	0.0046	0.01739	55.7	−170.40	1172.7	1002.3	−170.40	1220.6	1050.2	−0.351	2.808	2.457
−30	0.0035	0.01738	74.1	−172.63	1173.2	1000.6	−172.63	1220.6	1048.0	−0.356	2.841	2.485
−35	0.0026	0.01737	99.2	−174.82	1173.8	998.9	−174.82	1220.6	1045.8	−0.361	2.874	2.513
−40	0.0019	0.01737	133.8	−177.00	1174.3	997.3	−177.00	1220.6	1043.6	−0.366	2.908	2.542

TABLE A.2SI *Thermodynamic Properties of Ammonia (SI Units)*

TABLE A.2.1SI *Saturated Ammonia (SI Units)*

Temp. °C	Abs. Press. kPa P	Specific Volume m^3/kg			Enthalpy kJ/kg			Entropy kJ/kg K		
		Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
−50	40.86	0.001 424	2.625 24	2.626 67	−43.76	1416.34	1372.57	−0.1916	6.3470	6.1553
−48	45.94	0.001 429	2.352 97	2.354 40	−35.04	1410.95	1375.90	−0.1528	6.2666	6.1139
−46	51.52	0.001 434	2.113 59	2.115 03	−26.31	1405.50	1379.19	−0.1142	6.1875	6.0733
−44	57.66	0.001 439	1.902 62	1.904 06	−17.56	1400.00	1382.44	−0.0759	6.1095	6.0336
−42	64.38	0.001 444	1.716 25	1.717 69	−8.79	1394.44	1385.65	−0.0378	6.0326	5.9948
−40	71.72	0.001 450	1.551 24	1.552 69	0.00	1388.82	1388.82	0.0000	5.9568	5.9568
−38	79.74	0.001 455	1.404 82	1.406 27	8.81	1383.13	1391.94	0.0376	5.8820	5.9196
−36	88.48	0.001 460	1.274 61	1.276 07	17.64	1377.39	1395.03	0.0749	5.8082	5.8831
−34	97.98	0.001 465	1.158 57	1.160 04	26.49	1371.58	1398.07	0.1120	5.7353	5.8473
−32	108.29	0.001 471	1.054 96	1.056 43	35.36	1365.70	1401.06	0.1489	5.6634	5.8123
−30	119.46	0.001 476	0.962 26	0.963 74	44.26	1359.76	1404.01	0.1856	5.5924	5.7780
−28	131.54	0.001 482	0.879 16	0.880 64	53.17	1353.74	1406.92	0.2220	5.5223	5.7443
−26	144.59	0.001 487	0.804 53	0.806 02	62.11	1347.66	1409.77	0.2582	5.4530	5.7113
−24	158.65	0.001 493	0.737 38	0.738 87	71.07	1341.51	1412.58	0.2942	5.3846	5.6788
−22	173.80	0.001 498	0.676 85	0.678 35	80.05	1335.29	1415.34	0.3301	5.3170	5.6470
−20	190.08	0.001 504	0.622 20	0.623 71	89.05	1329.00	1418.05	0.3657	5.2501	5.6158
−18	207.56	0.001 510	0.572 77	0.574 28	98.08	1322.64	1420.71	0.4011	5.1840	5.5851
−16	226.29	0.001 516	0.528 00	0.529 51	107.12	1316.20	1423.32	0.4363	5.1187	5.5550
−14	246.35	0.001 522	0.487 37	0.488 89	116.19	1309.68	1425.88	0.4713	5.0541	5.5254
−12	267.79	0.001 528	0.450 45	0.451 97	125.29	1303.09	1428.38	0.5061	4.9901	5.4963

−10	290.67	0.001 534	0.416 84	0.418 37	134.41	1296.42	1430.83	0.5408	4.9269	5.4676
−8	315.08	0.001 540	0.386 21	0.387 75	143.55	1289.67	1433.22	0.5753	4.8642	5.4395
−6	341.07	0.001 546	0.358 24	0.359 79	152.72	1282.84	1435.56	0.6095	4.8023	5.4118
−4	368.72	0.001 553	0.332 68	0.334 23	161.91	1275.93	1437.84	0.6437	4.7409	5.3846
−2	398.10	0.001 559	0.309 28	0.310 84	171.12	1268.94	1440.06	0.6776	4.6801	5.3577
0	429.29	0.001 566	0.287 83	0.289 40	180.36	1261.86	1442.22	0.7114	4.6199	5.3313
2	462.34	0.001 573	0.268 15	0.269 72	189.63	1254.69	1444.32	0.7450	4.5603	5.3053
4	497.35	0.001 579	0.250 05	0.251 63	198.93	1247.43	1446.35	0.7785	4.5012	5.2796
6	534.39	0.001 586	0.233 41	0.234 99	208.25	1240.08	1448.32	0.8118	4.4426	5.2543
8	573.54	0.001 593	0.218 07	0.219 66	217.60	1232.63	1450.23	0.8449	4.3845	5.2294
10	614.87	0.001 600	0.203 92	0.205 53	226.97	1225.10	1452.07	0.8779	4.3269	5.2048
12	658.48	0.001 608	0.190 86	0.192 47	236.38	1217.46	1453.84	0.9108	4.2698	5.1805
14	704.43	0.001 615	0.178 78	0.180 40	245.81	1209.72	1455.53	0.9435	4.2131	5.1565
16	752.81	0.001 623	0.167 61	0.169 23	255.28	1201.88	1457.16	0.9760	4.1568	5.1328
18	803.71	0.001 630	0.157 25	0.158 88	264.77	1193.94	1458.71	1.0085	4.1009	5.1094
20	857.22	0.001 638	0.147 64	0.149 28	274.30	1185.89	1460.18	1.0408	4.0455	5.0863
22	913.41	0.001 646	0.138 72	0.140 37	283.85	1177.73	1461.58	1.0730	3.9904	5.0634
24	972.38	0.001 654	0.130 43	0.132 08	293.44	1169.45	1462.89	1.1050	3.9357	5.0407
26	1034.21	0.001 663	0.122 72	0.124 38	303.07	1161.06	1464.13	1.1370	3.8813	5.0182
28	1099.00	0.001 671	0.115 53	0.117 20	312.72	1152.55	1465.27	1.1688	3.8272	4.9960
30	1166.83	0.001 680	0.108 83	0.110 51	322.42	1143.92	1466.33	1.2005	3.7735	4.9740
32	1237.80	0.001 688	0.102 58	0.104 27	332.14	1135.16	1467.30	1.2321	3.7200	4.9521
34	1312.00	0.001 697	0.096 75	0.098 45	341.91	1126.27	1468.17	1.2635	3.6669	4.9304
36	1389.52	0.001 707	0.091 29	0.093 00	351.71	1117.25	1468.95	1.2949	3.6140	4.9089
38	1470.46	0.001 716	0.086 19	0.087 90	361.55	1108.09	1469.64	1.3262	3.5613	4.8875
40	1554.92	0.001 725	0.081 41	0.083 13	371.43	1098.79	1470.22	1.3574	3.5088	4.8662
42	1642.98	0.001 735	0.076 93	0.078 66	381.35	1089.34	1470.69	1.3885	3.4566	4.8451
44	1734.75	0.001 745	0.072 72	0.074 47	391.31	1079.75	1471.06	1.4195	3.4045	4.8240
46	1830.33	0.001 755	0.068 78	0.070 53	401.32	1070.00	1471.32	1.4504	3.3526	4.8030
48	1929.82	0.001 766	0.065 07	0.066 84	411.38	1060.09	1471.46	1.4813	3.3009	4.7822
50	2033.32	0.001 777	0.061 59	0.063 36	421.48	1050.01	1471.49	1.5121	3.2493	4.7613

Source: Consistent with values presented in L. Haar and J. Gallagher, "Thermodynamic Properties of Ammonia," *J. Phys. Chem. Ref. Data*, 7, 3 (1978).

TABLE A.2.2SI Superheated Ammonia (SI Units)

Abs. Press. kPa (Sat. Temp.)		Temperature, °C											
		−20	−10	0	10	20	30	40	50	60	70	80	100
	v	2.4463	2.5471	2.6474	2.7472	2.8466	2.9458	3.0447	3.1435	3.2421	3.3406	3.4390	—
50	h	1434.6	1455.7	1476.9	1498.1	1519.3	1540.6	1562.0	1583.5	1605.1	1626.9	1648.8	—
(−46.53)	s	6.3187	6.4006	6.4795	6.5556	6.6293	6.7008	6.7703	6.8379	6.9038	6.9682	7.0312	—
	v	1.6222	1.6905	1.7582	1.8255	1.8924	1.9591	2.0255	2.0917	2.1577	2.2237	2.2895	—
75	h	1431.7	1453.3	1474.8	1496.2	1517.7	1539.2	1560.7	1582.4	1604.1	1626.0	1648.0	—
(−39.16)	s	6.1120	6.1954	6.2756	6.3527	6.4272	6.4993	6.5693	6.6373	6.7036	6.7683	6.8315	—
	v	1.2101	1.2621	1.3136	1.3647	1.4153	1.4657	1.5158	1.5658	1.6156	1.6652	1.7148	1.8137
100	h	1428.8	1450.8	1472.6	1494.4	1516.1	1537.7	1559.5	1581.2	1603.1	1625.1	1647.1	1691.7
(−33.59)	s	5.9626	6.0477	6.1291	6.2073	6.2826	6.3553	6.4258	6.4943	6.5609	6.6258	6.6892	6.8120
	v	0.9627	1.0051	1.0468	1.0881	1.1290	1.1696	1.2100	1.2502	1.2903	1.3302	1.3700	1.4494
125	h	1425.9	1448.3	1470.5	1492.5	1514.4	1536.3	1558.2	1580.1	1602.1	1624.1	1646.3	1691.0
(−29.06)	s	5.8446	5.9314	6.0141	6.0933	6.1694	6.2428	6.3138	6.3827	6.4496	6.5149	6.5785	6.7017
	v	0.7977	0.8336	0.8689	0.9037	0.9381	0.9723	1.0062	1.0398	1.0734	1.1068	1.1401	1.2065
150	h	1422.9	1445.7	1468.3	1490.6	1512.8	1534.8	1556.9	1578.9	1601.0	1623.2	1645.4	1690.2
(−25.21)	s	5.7465	5.8349	5.9189	5.9992	6.0761	6.1502	6.2217	6.2910	6.3583	6.4238	6.4877	6.6112

	v	—	0.6193	0.6465	0.6732	0.6995	0.7255	0.7513	0.7769	0.8023	0.8275	0.8527	0.9028
200	h	—	1440.6	1463.8	1486.8	1509.4	1531.9	1554.3	1576.6	1598.9	1621.3	1643.7	1688.8
(−18.85)	s	—	5.6791	5.7659	5.8484	5.9270	6.0025	6.0751	6.1453	6.2133	6.2794	6.3437	6.4679
	v	—	0.4905	0.5129	0.5348	0.5563	0.5774	0.5983	0.6190	0.6396	0.6600	0.6803	0.7206
250	h	—	1435.3	1459.3	1482.9	1506.0	1529.0	1551.7	1574.3	1596.8	1619.4	1641.9	1687.3
(−13.65)	s	—	5.5544	5.6441	5.7288	5.8093	5.8861	5.9599	6.0309	6.0997	6.1663	6.2312	6.3561
	v	—	—	0.4238	0.4425	0.4608	0.4787	0.4964	0.5138	0.5311	0.5483	0.5653	0.5992
300	h	—	—	1454.7	1478.9	1502.6	1525.9	1549.0	1571.9	1594.7	1617.5	1640.2	1685.8
(−9.22)	s	—	—	5.5420	5.6290	5.7113	5.7896	5.8645	5.9365	6.0060	6.0732	6.1385	6.2642
	v	—	—	0.3601	0.3765	0.3925	0.4081	0.4235	0.4386	0.4536	0.4685	0.4832	0.5124
350	h	—	—	1449.9	1474.9	1499.1	1522.9	1546.3	1569.5	1592.6	1615.5	1638.4	1684.3
(−5.34)	s	—	—	5.4532	5.5427	5.6270	5.7068	5.7828	5.8557	5.9259	5.9938	6.0596	6.1860
	v	—	—	0.3123	0.3270	0.3413	0.3552	0.3688	0.3823	0.3955	0.4086	0.4216	0.4473
400	h	—	—	1445.1	1470.7	1495.6	1519.8	1543.6	1567.1	1590.4	1613.6	1636.7	1682.8
(−1.87)	s	—	—	5.3741	5.4663	5.5525	5.6338	5.7111	5.7850	5.8560	5.9244	5.9907	6.1179
	v	—	—	0.2750	0.2885	0.3014	0.3140	0.3263	0.3384	0.3503	0.3620	0.3737	0.3967
450	h	—	—	1440.2	1466.5	1492.0	1516.7	1540.9	1564.7	1588.2	1611.6	1634.9	1681.3
(1.27)	s	—	—	5.3023	5.3972	5.4855	5.5685	5.6470	5.7219	5.7936	5.8627	5.9295	6.0575

(*Continued*)

TABLE A.2.2SI *(Continued)* Superheated Ammonia (SI Units)

Abs. Press. kPa (Sat. Temp.)		Temperature, °C											
		20	30	40	50	60	70	80	100	120	140	160	180
	v	0.2695	0.2810	0.2923	0.3033	0.3141	0.3248	0.3353	0.3562	0.3768	0.3972	—	—
500	h	1488.3	1513.5	1538.1	1562.3	1586.1	1609.6	1633.1	1679.8	1726.6	1773.8	—	—
(4.15)	s	5.4244	5.5090	5.5889	5.6647	5.7373	5.8070	5.8744	6.0031	6.1253	6.2422	—	—
	v	0.2215	0.2315	0.2412	0.2506	0.2598	0.2689	0.2778	0.2955	0.3128	0.3300	—	—
600	h	1480.8	1507.1	1532.5	1557.3	1581.6	1605.7	1629.5	1676.8	1724.0	1771.5	—	—
(9.29)	s	5.3156	5.4037	5.4862	5.5641	5.6383	5.7094	5.7778	5.9081	6.0314	6.1491	—	—
	v	0.1872	0.1961	0.2046	0.2129	0.2210	0.2289	0.2367	0.2521	0.2671	0.2819	—	—
700	h	1473.0	1500.4	1526.7	1552.2	1577.1	1601.6	1625.8	1673.7	1721.4	1769.2	—	—
(13.81)	s	5.2196	5.3115	5.3968	5.4770	5.5529	5.6254	5.6949	5.8268	5.9512	6.0698	—	—
	v	0.1614	0.1695	0.1772	0.1846	0.1919	0.1990	0.2059	0.2195	0.2328	0.2459	0.2589	—
800	h	1464.9	1493.5	1520.8	1547.0	1572.5	1597.5	1622.1	1670.6	1718.7	1766.9	1815.3	—
(17.86)	s	5.1328	5.2287	5.3171	5.3996	5.4774	5.5513	5.6219	5.7555	5.8811	6.0006	6.1150	—
	v	—	0.1487	0.1558	0.1626	0.1692	0.1756	0.1819	0.1942	0.2061	0.2179	0.2295	—
900	h	—	1486.5	1514.7	1541.7	1567.9	1593.3	1618.4	1667.5	1716.1	1764.5	1813.2	—
(21.53)	s	—	5.1530	5.2447	5.3296	5.4093	5.4847	5.5565	5.6919	5.8187	5.9389	6.0541	—

	v	—	0.1321	0.1387	0.1450	0.1511	0.1570	0.1627	0.1739	0.1848	0.1955	0.2060	0.2164
1000	h	—	1479.1	1508.5	1536.3	1563.1	1589.1	1614.6	1664.3	1713.4	1762.2	1811.2	1860.5
(24.91)	s	—	5.0826	5.1778	5.2654	5.3471	5.4240	5.4971	5.6342	5.7622	5.8834	5.9992	6.1105
	v	—	—	0.1129	0.1185	0.1238	0.1289	0.1339	0.1435	0.1527	0.1618	0.1707	0.1795
1200	h	—	—	1495.4	1525.1	1553.3	1580.5	1606.8	1658.0	1708.0	1757.5	1807.1	1856.9
(30.95)	s	—	—	5.0564	5.1497	5.2357	5.3159	5.3916	5.5325	5.6631	5.7860	5.9031	6.0156
	v	—	—	0.0943	0.0994	0.1042	0.1088	0.1132	0.1217	0.1299	0.1378	0.1455	0.1532
1400	h	—	—	1481.6	1513.4	1543.1	1571.5	1598.8	1651.4	1702.5	1752.8	1802.9	1853.2
(36.26)	s	—	—	4.9463	5.0462	5.1370	5.2209	5.2994	5.4443	5.5775	5.7023	5.8208	5.9343
	v	—	—	—	0.0851	0.0895	0.0937	0.0977	0.1054	0.1127	0.1197	0.1266	0.1334
1600	h	—	—	—	1501.0	1532.5	1562.3	1590.7	1644.8	1696.9	1748.0	1798.7	1849.5
(41.03)	s	—	—	—	4.9510	5.0472	5.1351	5.2167	5.3659	5.5018	5.6286	5.7485	5.8631
	v	—	—	—	0.0738	0.0780	0.0819	0.0857	0.0927	0.0993	0.1057	0.1119	0.1180
1800	h	—	—	—	1487.9	1521.4	1552.7	1582.2	1638.0	1691.2	1743.1	1794.5	1845.7
(45.37)	s	—	—	—	4.8614	4.9637	5.0561	5.1410	5.2948	5.4337	5.5624	5.6838	5.7995
	v	—	—	—	0.0647	0.0687	0.0725	0.0760	0.0825	0.0886	0.0945	0.1002	0.1057
2000	h	—	—	—	1473.9	1509.8	1542.7	1573.5	1631.1	1685.5	1738.2	1790.2	1842.0
(49.36)	s	—	—	—	4.7754	4.8848	4.9821	5.0707	5.2294	5.3714	5.5022	5.6251	5.7420

TABLE A.2E Thermodynamic Properties of Ammonia (English Units)

TABLE A.2.1E Saturated Ammonia (English Units)

Temp. F	Abs. Press. lbf/in.^{2} P	Specific Volume ft^3/lbm Sat. Liquid v_f	Specific Volume ft^3/lbm Evap. v_{fg}	Specific Volume ft^3/lbm Sat. Vapor v_g	Enthalpy Btu/lbm Sat. Liquid h_f	Enthalpy Btu/lbm Evap. h_{fg}	Enthalpy Btu/lbm Sat. Vapor h_g	Entropy Btu/lbm R Sat. Liquid s_f	Entropy Btu/lbm R Evap. s_{fg}	Entropy Btu/lbm R Sat. Vapor s_g
−60	5.547	0.022 77	44.7335	44.756	−20.89	610.19	589.30	−0.0510	1.5267	1.4758
−55	6.535	0.022 88	38.3792	38.402	−15.69	606.99	591.29	−0.0380	1.4999	1.4619
−50	7.664	0.022 99	33.0685	33.091	−10.48	603.73	593.26	−0.0252	1.4737	1.4485
−45	8.948	0.023 11	28.6093	28.632	−5.25	600.43	595.19	−0.0126	1.4480	1.4354
−40	10.403	0.023 22	24.8485	24.872	0.00	597.08	597.08	0.0000	1.4228	1.4228
−35	12.046	0.023 34	21.6629	21.686	5.26	593.68	598.95	0.0124	1.3980	1.4105
−30	13.894	0.023 45	18.9535	18.977	10.54	590.23	600.77	0.0248	1.3737	1.3985
−25	15.967	0.023 57	16.6399	16.663	15.84	586.72	602.56	0.0370	1.3498	1.3869
−20	18.282	0.023 69	14.6567	14.680	21.15	583.16	604.31	0.0492	1.3264	1.3756
−15	20.861	0.023 82	12.9505	12.974	26.49	579.54	606.03	0.0612	1.3033	1.3645
−10	23.725	0.023 94	11.4773	11.501	31.84	575.86	607.70	0.0731	1.2807	1.3538
−5	26.896	0.024 07	10.2011	10.225	37.21	572.12	609.33	0.0850	1.2584	1.3434
0	30.397	0.024 20	9.0918	9.116	42.60	568.33	610.92	0.0967	1.2364	1.3332
5	34.251	0.024 33	8.1245	8.149	48.00	564.47	612.47	0.1084	1.2148	1.3232
10	38.483	0.024 46	7.2784	7.303	53.43	560.54	613.97	0.1200	1.1936	1.3135
15	43.120	0.024 60	6.5363	6.561	58.88	556.56	615.43	0.1315	1.1726	1.3040
20	48.186	0.024 74	5.8833	5.908	64.34	552.51	616.85	0.1429	1.1519	1.2948
25	53.709	0.024 88	5.3073	5.332	69.83	548.39	618.21	0.1542	1.1315	1.2857
30	59.717	0.025 02	4.7978	4.823	75.33	544.20	619.53	0.1654	1.1114	1.2769
35	66.239	0.025 17	4.3460	4.371	80.86	539.93	620.80	0.1766	1.0916	1.2682

40	73.303	0.025 32	3.9443	3.970	86.41	535.60	622.01	0.1877	1.0720	1.2597
45	80.940	0.025 48	3.5863	3.612	91.98	531.19	623.17	0.1987	1.0526	1.2513
50	89.180	0.025 64	3.2666	3.292	97.58	526.70	624.28	0.2097	1.0335	1.2431
55	98.055	0.025 80	2.9803	3.006	103.20	522.12	625.32	0.2206	1.0145	1.2351
60	107.596	0.025 97	2.7234	2.749	108.84	517.47	626.31	0.2314	0.9958	1.2272
65	117.836	0.026 14	2.4924	2.519	114.51	512.73	627.24	0.2422	0.9773	1.2194
70	128.808	0.026 31	2.2843	2.311	120.21	507.90	628.10	0.2529	0.9589	1.2118
75	140.546	0.026 49	2.0964	2.123	125.93	502.97	628.90	0.2635	0.9407	1.2042
80	153.084	0.026 68	1.9264	1.953	131.68	497.95	629.63	0.2741	0.9227	1.1968
85	166.457	0.026 87	1.7724	1.799	137.45	492.83	630.29	0.2846	0.9048	1.1895
90	180.700	0.027 06	1.6325	1.660	143.26	487.61	630.87	0.2951	0.8871	1.1822
95	195.850	0.027 26	1.5053	1.533	149.10	482.28	631.37	0.3055	0.8695	1.1750
100	211.943	0.027 47	1.3894	1.417	154.97	476.83	631.80	0.3159	0.8520	1.1679
105	229.016	0.027 68	1.2836	1.311	160.87	471.27	632.14	0.3263	0.8346	1.1609
110	247.107	0.027 90	1.1869	1.215	166.80	465.59	632.40	0.3366	0.8173	1.1539
115	266.254	0.028 13	1.0983	1.126	172.78	459.78	632.56	0.3468	0.8001	1.1469
120	286.496	0.028 36	1.0171	1.045	178.79	453.84	632.63	0.3571	0.7829	1.1400
125	307.872	0.028 60	0.9425	0.971	184.84	447.76	632.60	0.3673	0.7658	1.1331

Source: Consistent with values presented in L. Haar and J. Gallagher, "Thermodynamic Properties of Ammonia," *J. Phys. Chem. Ref. Data*, 7, 3 (1978).

TABLE A.2.2E Superheated Ammonia (English Units)

Abs. Press. lbf/in.^{2} (Sat. Temp.)		Temperature, F											
		0	20	40	60	80	100	120	140	160	180	200	220
	v	28.567	29.881	31.185	32.481	33.770	35.055	36.336	37.613	38.889	40.162	41.434	—
10	h	617.9	628.1	638.3	648.6	658.8	669.1	679.4	689.8	700.2	710.7	721.3	—
(−41.32)	s	1.475	1.496	1.517	1.537	1.557	1.575	1.593	1.611	1.628	1.645	1.661	—
	v	18.909	19.804	20.688	21.564	22.434	23.298	24.159	25.017	25.872	26.726	27.577	—
15	h	616.2	626.7	637.2	647.5	657.9	668.3	678.7	689.1	699.6	710.2	720.8	—
(−27.26)	s	1.425	1.447	1.468	1.489	1.508	1.527	1.545	1.563	1.580	1.597	1.613	—
	v	14.077	14.763	15.439	16.105	16.765	17.420	18.071	18.719	19.364	20.007	20.649	21.290
20	h	614.5	625.3	635.9	646.5	657.0	667.5	678.0	688.5	699.1	709.7	720.4	731.1
(−16.61)	s	1.388	1.411	1.433	1.454	1.473	1.492	1.511	1.529	1.546	1.563	1.579	1.595
	v	11.177	11.738	12.288	12.829	13.363	13.893	14.418	14.940	15.459	15.976	16.492	17.006
25	h	612.8	623.9	634.7	645.5	656.1	666.7	677.3	687.9	698.5	709.2	719.9	730.7
(−7.93)	s	1.359	1.383	1.405	1.426	1.446	1.465	1.484	1.502	1.519	1.536	1.553	1.569
	v	9.242	9.721	10.187	10.645	11.095	11.541	11.982	12.420	12.855	13.289	13.721	14.151
30	h	611.1	622.4	633.5	644.4	655.2	665.9	676.6	687.3	698.0	708.7	719.5	730.3
(−0.54)	s	1.335	1.359	1.382	1.403	1.424	1.443	1.462	1.480	1.497	1.514	1.531	1.547

	v	—	8.279	8.686	9.084	9.475	9.861	10.242	10.620	10.996	11.369	11.741	12.111
35	*h*	—	620.9	632.2	643.3	654.3	665.1	675.9	686.7	697.4	708.2	719.0	729.9
(5.92)	*s*	—	1.339	1.362	1.384	1.404	1.424	1.443	1.461	1.479	1.496	1.513	1.529
	v	—	7.196	7.560	7.913	8.260	8.600	8.937	9.270	9.601	9.929	10.256	10.582
40	*h*	—	619.4	631.0	642.3	653.4	664.3	675.2	686.0	696.9	707.7	718.5	729.4
(11.69)	*s*	—	1.321	1.344	1.366	1.387	1.407	1.426	1.445	1.463	1.480	1.497	1.513
	v	—	6.354	6.683	7.002	7.314	7.620	7.922	8.220	8.516	8.809	9.101	9.392
45	*h*	—	617.8	629.7	641.2	652.4	663.5	674.5	685.4	696.3	707.2	718.1	729.0
(16.91)	*s*	—	1.304	1.329	1.351	1.372	1.393	1.412	1.430	1.448	1.465	1.482	1.499
	v	—	—	5.981	6.273	6.557	6.836	7.110	7.380	7.648	7.914	8.177	8.440
50	*h*	—	—	628.4	640.1	651.5	662.7	673.8	684.8	695.7	706.7	717.6	728.6
(21.69)	*s*	—	—	1.314	1.337	1.359	1.379	1.399	1.417	1.435	1.453	1.469	1.486
	v	—	—	4.928	5.179	5.422	5.659	5.891	6.120	6.346	6.569	6.791	7.012
60	*h*	—	—	625.7	637.8	649.6	661.1	672.3	683.5	694.6	705.6	716.7	727.7
(30.23)	*s*	—	—	1.289	1.313	1.335	1.356	1.375	1.394	1.413	1.430	1.447	1.464

(*Continued*)

TABLE A.2.2E *(Continued)* Superheated Ammonia (English Units)

Abs Press. lbf/in.^{2} (Sat. Temp.)		Temperature, F											
		60	80	100	120	140	160	180	200	240	280	320	360
	v	4.396	4.610	4.817	5.020	5.219	5.415	5.609	5.801	6.182	6.558	—	—
70	h	635.5	647.6	659.4	670.9	682.2	693.4	704.6	715.7	738.0	760.5	—	—
(37.71)	s	1.291	1.314	1.335	1.356	1.375	1.393	1.411	1.428	1.461	1.492	—	—
	v	3.808	4.001	4.186	4.367	4.544	4.717	4.889	5.059	5.394	5.725	—	—
80	h	633.2	645.6	657.7	669.4	680.9	692.3	703.6	714.8	737.2	759.8	—	—
(44.40)	s	1.272	1.296	1.318	1.338	1.358	1.376	1.394	1.412	1.445	1.476	—	—
	v	3.350	3.526	3.695	3.858	4.018	4.174	4.329	4.481	4.782	5.078	—	—
90	h	630.7	643.6	655.9	667.9	679.6	691.1	702.5	713.8	736.4	759.1	—	—
(50.48)	s	1.255	1.279	1.301	1.322	1.342	1.361	1.379	1.397	1.430	1.462	—	—
	v	2.983	3.146	3.301	3.451	3.597	3.740	3.880	4.019	4.291	4.560	—	—
100	h	628.3	641.5	654.2	666.4	678.2	689.9	701.4	712.9	735.6	758.4	—	—
(56.05)	s	1.239	1.264	1.287	1.308	1.328	1.347	1.366	1.383	1.417	1.449	—	—
	v	—	2.164	2.287	2.403	2.514	2.622	2.727	2.830	3.031	3.228	3.421	—
140	h	—	632.7	646.8	660.0	672.7	685.0	697.1	709.0	732.4	755.6	779.0	—
(74.77)	s	—	1.212	1.237	1.261	1.282	1.302	1.321	1.340	1.374	1.407	1.437	—

	v	—	—	1.719	1.818	1.910	1.999	2.085	2.168	2.330	2.487	2.641	—
180	*h*	—	—	638.7	653.3	666.9	680.0	692.6	704.9	729.0	752.8	776.5	—
(89.76)	*s*	—	—	1.197	1.222	1.245	1.267	1.287	1.306	1.341	1.374	1.406	—
	v	—	—	—	1.443	1.524	1.602	1.676	1.747	1.884	2.016	2.145	2.208
220	*h*	—	—	—	646.0	660.8	674.7	687.9	700.8	725.6	749.9	774.1	786.1
(102.40)	*s*	—	—	—	1.189	1.214	1.237	1.258	1.278	1.314	1.348	1.380	1.395
	v	—	—	—	1.301	1.379	1.452	1.522	1.588	1.716	1.839	1.958	2.017
240	*h*	—	—	—	642.2	657.6	671.9	685.6	698.7	723.9	748.5	772.8	785.0
(108.07)	*s*	—	—	—	1.174	1.200	1.223	1.245	1.265	1.302	1.337	1.369	1.384
	v	—	—	—	1.180	1.256	1.325	1.391	1.454	1.575	1.689	1.801	1.855
260	*h*	—	—	—	638.2	654.3	669.1	683.1	696.5	722.2	747.0	771.6	783.8
(113.40)	*s*	—	—	—	1.159	1.186	1.211	1.233	1.253	1.291	1.326	1.358	1.374
	v	—	—		1.076	1.149	1.216	1.279	1.339	1.453	1.561	1.665	1.717
280	*h*	—	—	—	634.0	650.9	666.2	680.6	694.3	720.4	745.6	770.3	782.6
(118.43)	*s*	—	—	—	1.145	1.173	1.198	1.221	1.242	1.281	1.316	1.348	1.364

TABLE A.3SI Thermodynamic Properties of Refrigerant-12 (Dichlorodifluoromethane)

TABLE A.3.1SI Saturated R-12 (SI Units)

		Specific Volume m^3/kg			Enthalpy kJ/kg			Entropy kJ/kg K		
Temp. °C	Abs. Press. MPa P	Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
−90	0.0028	0.000 608	4.414 937	4.415 545	−43.243	189.618	146.375	−0.2084	1.0352	0.8268
−85	0.0042	0.000 612	3.036 704	3.037 316	−38.968	187.608	148.640	−0.1854	0.9970	0.8116
−80	0.0062	0.000 617	2.137 728	2.138 345	−34.688	185.612	150.924	−0.1630	0.9609	0.7979
−75	0.0088	0.000 622	1.537 030	1.537 651	−30.401	183.625	153.224	−0.1411	0.9266	0.7855
−70	0.0123	0.000 627	1.126 654	1.127 280	−26.103	181.640	155.536	−0.1197	0.8940	0.7744
−65	0.0168	0.000 632	0.840 534	0.841 166	−21.793	179.651	157.857	−0.0987	0.8630	0.7643
−60	0.0226	0.000 637	0.637 274	0.637 910	−17.469	177.653	160.184	−0.0782	0.8334	0.7552
−55	0.0300	0.000 642	0.490 358	0.491 000	−13.129	175.641	162.512	−0.0581	0.8051	0.7470
−50	0.0391	0.000 648	0.382 457	0.383 105	−8.772	173.611	164.840	−0.0384	0.7779	0.7396
−45	0.0504	0.000 654	0.302 029	0.302 682	−4.396	171.558	167.163	−0.0190	0.7519	0.7329
−40	0.0642	0.000 659	0.241 251	0.241 910	−0.000	169.479	169.479	−0.0000	0.7269	0.7269
−35	0.0807	0.000 666	0.194 732	0.195 398	4.416	167.368	171.784	0.0187	0.7027	0.7214
−30	0.1004	0.000 672	0.158 703	0.159 375	8.854	165.222	174.076	0.0371	0.6795	0.7165
−25	0.1237	0.000 679	0.130 487	0.131 166	13.315	163.037	176.352	0.0552	0.6570	0.7121
−20	0.1509	0.000 685	0.108 162	0.108 847	17.800	160.810	178.610	0.0730	0.6352	0.7082
−15	0.1826	0.000 693	0.090 326	0.091 018	22.312	158.534	180.846	0.0906	0.6141	0.7046
−10	0.2191	0.000 700	0.075 946	0.076 646	26.851	156.207	183.058	0.1079	0.5936	0.7014
−5	0.2610	0.000 708	0.064 255	0.064 963	31.420	153.823	185.243	0.1250	0.5736	0.6986

0	0.3086	0.000 716	0.054 673	0.055 389	36.022	151.376	187.397	0.1418	0.5542	0.6960
5	0.3626	0.000 724	0.046 761	0.047 485	40.659	148.859	189.518	0.1585	0.5351	0.6937
10	0.4233	0.000 733	0.040 180	0.040 914	45.337	146.265	191.602	0.1750	0.5165	0.6916
15	0.4914	0.000 743	0.034 671	0.035 413	50.058	143.586	193.644	0.1914	0.4983	0.6897
20	0.5673	0.000 752	0.030 028	0.030 780	54.828	140.812	195.641	0.2076	0.4803	0.6879
25	0.6516	0.000 763	0.026 091	0.026 854	59.653	137.933	197.586	0.2237	0.4626	0.6863
30	0.7449	0.000 774	0.022 734	0.023 508	64.539	134.936	199.475	0.2397	0.4451	0.6848
35	0.8477	0.000 786	0.019 855	0.020 641	69.494	131.805	201.299	0.2557	0.4277	0.6834
40	0.9607	0.000 798	0.017 373	0.018 171	74.527	128.525	203.051	0.2716	0.4104	0.6820
45	1.0843	0.000 811	0.015 220	0.016 032	79.647	125.074	204.722	0.2875	0.3931	0.6806
50	1.2193	0.000 826	0.013 344	0.014 170	84.868	121.430	206.298	0.3034	0.3758	0.6792
55	1.3663	0.000 841	0.011 701	0.012 542	90.201	117.565	207.766	0.3194	0.3582	0.6777
60	1.5259	0.000 858	0.010 253	0.011 111	95.665	113.443	209.109	0.3355	0.3405	0.6760
65	1.6988	0.000 877	0.008 971	0.009 847	101.279	109.024	210.303	0.3518	0.3224	0.6742
70	1.8858	0.000 897	0.007 828	0.008 725	107.067	104.255	211.321	0.3683	0.3038	0.6721
75	2.0874	0.000 920	0.006 802	0.007 723	113.058	99.068	212.126	0.3851	0.2845	0.6697
80	2.3046	0.000 946	0.005 875	0.006 821	119.291	93.373	212.665	0.4023	0.2644	0.6667
85	2.5380	0.000 976	0.005 029	0.006 005	125.818	87.047	212.865	0.4201	0.2430	0.6631
90	2.7885	0.001 012	0.004 246	0.005 258	132.708	79.907	212.614	0.4385	0.2200	0.6585
95	3.0569	0.001 056	0.003 508	0.004 563	140.068	71.658	211.726	0.4579	0.1946	0.6526
100	3.3440	0.001 113	0.002 790	0.003 903	148.076	61.768	209.843	0.4788	0.1655	0.6444
105	3.6509	0.001 197	0.002 045	0.003 242	157.085	49.014	206.099	0.5023	0.1296	0.6319
110	3.9784	0.001 364	0.001 098	0.002 462	168.059	28.425	196.484	0.5322	0.0742	0.6064
112	4.1155	0.001 792	0.000 005	0.001 797	174.920	0.151	175.071	0.5651	0.0004	0.5655

Source: Consistent with values presented in "Thermodynamic Properties of Freon-12," E. I. du Pont de Nemours and Company, Inc., 1956.

TABLE A.3.2SI Superheated R-12 (SI Units)

Temp. °C	v m³/kg	h kJ/kg	s kJ/kg K	v m³/kg	h kJ/kg	s kJ/kg K	v m³/kg	h kJ/kg	s kJ/kg K
	0.05 MPa			**0.10 MPa**			**0.15 MPa**		
−20.0	0.341 857	181.042	0.7912	0.167 701	179.861	0.7401			
−10.0	0.356 227	186.757	0.8133	0.175 222	185.707	0.7628	0.114 716	184.619	0.7318
0.0	0.370 508	192.567	0.8350	0.182 647	191.628	0.7849	0.119 866	190.660	0.7543
10.0	0.384 716	198.471	0.8562	0.189 994	197.628	0.8064	0.124 932	196.762	0.7763
20.0	0.398 863	204.469	0.8770	0.197 277	203.707	0.8275	0.129 930	202.927	0.7977
30.0	0.412 959	210.557	0.8974	0.204 506	209.866	0.8482	0.134 873	209.160	0.8186
40.0	0.427 012	216.733	0.9175	0.211 691	216.104	0.8684	0.139 768	215.463	0.8390
50.0	0.441 030	222.997	0.9372	0.218 839	222.421	0.8883	0.144 625	221.835	0.8591
60.0	0.455 017	229.344	0.9565	0.225 955	228.815	0.9078	0.149 450	228.277	0.8787
70.0	0.468 978	235.774	0.9755	0.233 044	235.285	0.9269	0.154 247	234.789	0.8980
80.0	0.482 917	242.282	0.9942	0.240 111	241.829	0.9457	0.159 020	241.371	0.9169
90.0	0.496 838	248.868	1.0126	0.247 159	248.446	0.9642	0.163 774	248.020	0.9354
	0.20 MPa			**0.25 MPa**			**0.30 MPa**		
0.0	0.088 608	189.669	0.7320	0.069 752	188.644	0.7139	0.057 150	187.583	0.6984
10.0	0.092 550	195.878	0.7543	0.073 024	194.969	0.7366	0.059 984	194.034	0.7216
20.0	0.096 418	202.135	0.7760	0.076 218	201.322	0.7587	0.062 734	200.490	0.7440
30.0	0.100 228	208.446	0.7972	0.079 350	207.715	0.7801	0.065 418	206.969	0.7658
40.0	0.103 989	214.814	0.8178	0.082 431	214.153	0.8010	0.068 049	213.480	0.7869
50.0	0.107 710	221.243	0.8381	0.085 470	220.642	0.8214	0.070 635	220.030	0.8075
60.0	0.111 397	227.735	0.8578	0.088 474	227.185	0.8413	0.073 185	226.627	0.8276
70.0	0.115 055	234.291	0.8772	0.091 449	233.785	0.8608	0.075 705	233.273	0.8473
80.0	0.118 690	240.910	0.8962	0.094 398	240.443	0.8800	0.078 200	239.971	0.8665
90.0	0.122 304	247.593	0.9149	0.097 327	247.160	0.8987	0.080 673	246.723	0.8853
100.0	0.125 901	254.339	0.9332	0.100 238	253.936	0.9171	0.083 127	253.530	0.9038
110.0	0.129 483	261.147	0.9512	0.103 134	260.770	0.9352	0.085 566	260.391	0.9220

	0.40 MPa			0.50 MPa			0.60 MPa		
20.0	0.045 836	198.762	0.7199	0.035 646	196.935	0.6999			
30.0	0.047 971	205.428	0.7423	0.037 464	203.814	0.7230	0.030 422	202.116	0.7063
40.0	0.050 046	212.095	0.7639	0.039 214	210.656	0.7452	0.031 966	209.154	0.7291
50.0	0.052 072	218.779	0.7849	0.040 911	217.484	0.7667	0.033 450	216.141	0.7511
60.0	0.054 059	225.488	0.8054	0.042 565	224.315	0.7875	0.034 887	223.104	0.7723
70.0	0.056 014	232.230	0.8253	0.044 184	231.161	0.8077	0.036 285	230.062	0.7929
80.0	0.057 941	239.012	0.8448	0.045 774	238.031	0.8275	0.037 653	237.027	0.8129
90.0	0.059 846	245.837	0.8638	0.047 340	244.932	0.8467	0.038 995	244.009	0.8324
100.0	0.061 731	252.707	0.8825	0.048 886	251.869	0.8656	0.040 316	251.016	0.8514
110.0	0.063 600	259.624	0.9008	0.050 415	258.845	0.8840	0.041 619	258.053	0.8700
120.0	0.065 455	266.590	0.9187	0.051 929	265.862	0.9021	0.042 907	265.124	0.8882
130.0	0.067 298	273.605	0.9364	0.053 430	272.923	0.9198	0.044 181	272.231	0.9061
	0.70 MPa			0.80 MPa			0.90 MPa		
40.0	0.026 761	207.580	0.7148	0.022 830	205.924	0.7016	0.019 744	204.170	0.6982
50.0	0.028 100	214.745	0.7373	0.024 068	213.290	0.7248	0.020 912	211.765	0.7131
60.0	0.029 387	221.854	0.7590	0.025 247	220.558	0.7469	0.022 012	219.212	0.7358
70.0	0.030 632	228.931	0.7799	0.026 380	227.766	0.7682	0.023 062	226.564	0.7575
80.0	0.031 843	235.997	0.8002	0.027 477	234.941	0.7888	0.024 072	233.856	0.7785
90.0	0.033 027	243.066	0.8199	0.028 545	242.101	0.8088	0.025 051	241.113	0.7987
100.0	0.034 189	250.146	0.8392	0.029 588	249.260	0.8283	0.026 005	248.355	0.8184
110.0	0.035 332	257.247	0.8579	0.030 612	256.428	0.8472	0.026 937	255.593	0.8376
120.0	0.036 458	264.374	0.8763	0.031 619	263.613	0.8657	0.027 851	262.839	0.8562
130.0	0.037 572	271.531	0.8943	0.032 612	270.820	0.8838	0.028 751	270.100	0.8745
140.0	0.038 673	278.720	0.9119	0.033 592	278.055	0.9016	0.029 639	277.381	0.8923
150.0	0.039 764	285.946	0.9292	0.034 563	285.320	0.9189	0.030 515	284.687	0.9098

(*Continued*)

TABLE A.3.2SI *(Continued)* Superheated R-12 (SI Units)

Temp. °C	v m³/kg	h kJ/kg	s kJ/kg K	v m³/kg	h kJ/kg	s kJ/kg K	v m³/kg	h kJ/kg	s kJ/kg K
		1.00 MPa			**1.20 MPa**			**1.40 MPa**	
50.0	0.018 366	210.162	0.7021	0.014 483	206.661	0.6812			
60.0	0.019 410	217.810	0.7254	0.015 463	214.805	0.7060	0.012 579	211.457	0.6876
70.0	0.020 397	225.319	0.7476	0.016 368	222.687	0.7293	0.013 448	219.822	0.7123
80.0	0.021 341	232.739	0.7689	0.017 221	230.398	0.7514	0.014 247	227.891	0.7355
90.0	0.022 251	240.101	0.7895	0.018 032	237.995	0.7727	0.014 997	235.766	0.7575
100.0	0.023 133	247.430	0.8094	0.018 812	245.518	0.7931	0.015 710	243.512	0.7785
110.0	0.023 993	254.743	0.8287	0.019 567	252.993	0.8129	0.016 393	251.170	0.7988
120.0	0.024 835	262.053	0.8475	0.020 301	260.441	0.8320	0.017 053	258.770	0.8183
130.0	0.025 661	269.369	0.8659	0.021 018	267.875	0.8507	0.017 695	266.334	0.8373
140.0	0.026 474	276.699	0.8839	0.021 721	275.307	0.8689	0.018 321	273.877	0.8558
150.0	0.027 275	284.047	0.9015	0.022 412	282.745	0.8867	0.018 934	281.411	0.8738
160.0	0.028 068	291.419	0.9187	0.023 093	290.195	0.9041	0.019 535	288.946	0.8914
		1.60 MPa			**1.80 MPa**			**2.00 MPa**	
70.0	0.011 208	216.650	0.6959	0.009 406	213.049	0.6794			
80.0	0.011 984	225.177	0.7204	0.010 187	222.198	0.7057	0.008 704	218.859	0.6909
90.0	0.012 698	233.390	0.7433	0.010 884	230.835	0.7298	0.009 406	228.056	0.7166
100.0	0.013 366	241.397	0.7651	0.011 526	239.155	0.7524	0.010 035	236.760	0.7402
110.0	0.014 000	249.264	0.7859	0.012 126	247.264	0.7739	0.010 615	245.154	0.7624
120.0	0.014 608	257.035	0.8059	0.012 697	255.228	0.7944	0.011 159	253.341	0.7835
130.0	0.015 195	264.742	0.8253	0.013 244	263.094	0.8141	0.011 676	261.384	0.8037
140.0	0.015 765	272.406	0.8440	0.013 772	270.891	0.8332	0.012 172	269.327	0.8232
150.0	0.016 320	280.044	0.8623	0.014 284	278.642	0.8518	0.012 651	277.201	0.8420
160.0	0.016 864	287.669	0.8801	0.014 784	286.364	0.8698	0.013 116	285.027	0.8603
170.0	0.017 398	295.290	0.8975	0.015 272	294.069	0.8874	0.013 570	292.822	0.8781
180.0	0.017 923	302.914	0.9145	0.015 752	301.767	0.9046	0.014 013	300.598	0.8955

	2.50 MPa			3.00 MPa			3.50 MPa		
90.0	0.006 595	219.562	0.6823						
100.0	0.007 264	229.852	0.7103	0.005 231	220.529	0.6770			
110.0	0.007 837	239.271	0.7352	0.005 886	232.068	0.7075	0.004 324	222.121	0.6750
120.0	0.008 351	248.192	0.7582	0.006 419	242.208	0.7336	0.004 959	234.875	0.7078
130.0	0.008 827	256.794	0.7798	0.006 887	251.632	0.7573	0.005 456	245.661	0.7349
140.0	0.009 273	265.180	0.8003	0.007 313	260.620	0.7793	0.005 884	255.524	0.7591
150.0	0.009 697	273.414	0.8200	0.007 709	269.319	0.8001	0.006 270	264.846	0.7814
160.0	0.010 104	281.540	0.8390	0.008 083	277.817	0.8200	0.006 626	273.817	0.8023
170.0	0.010 497	289.589	0.8574	0.008 439	286.171	0.8391	0.006 961	282.545	0.8222
180.0	0.010 879	297.583	0.8752	0.008 782	294.422	0.8575	0.007 279	291.100	0.8413
190.0	0.011 250	305.540	0.8926	0.009 114	302.597	0.8753	0.007 584	299.528	0.8597
200.0	0.011 614	313.472	0.9095	0.009 436	310.718	0.8927	0.007 878	307.864	0.8775
	4.00 MPa								
120.0	0.003 736	224.863	0.6771						
130.0	0.004 325	238.443	0.7111						
140.0	0.004 781	249.703	0.7386						
150.0	0.005 172	259.904	0.7630						
160.0	0.005 522	269.492	0.7854						
170.0	0.005 845	278.684	0.8063						
180.0	0.006 147	287.602	0.8262						
190.0	0.006 434	296.326	0.8453						
200.0	0.006 708	304.906	0.8636						
210.0	0.006 972	313.380	0.8813						
220.0	0.007 228	321.774	0.8985						
230.0	0.007 477	330.108	0.9152						

TABLE A.3E *Thermodynamic Properties of Refrigerant-12 (Dichlorodifluoromethane)*

TABLE A.3.1E *Saturated R-12 (English Units)*

Temp. F T	Abs. Press. lbf/in.^{2} P	Specific Volume ft^3/lbm Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Enthalpy Btu/lbm Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Entropy Btu/lbm R Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
−130	0.412 24	0.009 736	70.7203	70.730	−18.609	81.577	62.968	−0.049 83	0.247 43	0.197 60
−120	0.641 90	0.009 816	46.7312	46.741	−16.565	80.617	64.052	−0.043 72	0.237 31	0.193 59
−110	0.970 34	0.009 899	31.7671	31.777	−14.518	79.663	65.145	−0.037 79	0.227 80	0.190 02
−100	1.4280	0.009 985	21.1541	22.164	−12.466	78.714	66.248	−0.032 00	0.218 83	0.186 83
−90	2.0509	0.010 073	15.8109	15.821	−10.409	77.764	67.355	−0.026 37	0.210 34	0.183 98
−80	2.8807	0.010 164	11.5228	11.533	−8.3451	76.812	68.467	−0.020 86	0.202 29	0.181 43
−70	3.9651	0.010 259	8.5584	8.5687	−6.2730	75.853	69.580	−0.015 48	0.194 64	0.179 16
−60	5.3575	0.010 357	6.4670	6.4774	−4.1919	74.885	70.693	−0.010 21	0.187 16	0.177 14
−50	7.1168	0.010 459	4.9637	4.9742	−2.1011	73.906	71.805	−0.005 06	0.180 38	0.175 33
−40	9.3076	0.010 564	3.8644	3.8750	0	72.913	72.913	0	0.173 73	0.173 73
−30	11.999	0.010 674	3.0478	3.0585	2.1120	71.903	74.015	0.004 96	0.167 33	0.172 29
−20	15.267	0.010 788	2.4321	2.4429	4.2357	70.874	75.110	0.009 83	0.161 19	0.171 02
−10	19.189	0.010 906	1.9628	1.9727	6.3716	69.824	76.196	0.014 62	0.155 27	0.169 89
0	23.849	0.011 030	1.5979	1.6089	8.5207	68.750	77.271	0.019 32	0.149 56	0.168 88
10	29.335	0.011 160	1.3129	1.3241	10.684	67.651	78.335	0.023 95	0.144 03	0.167 98
20	35.736	0.011 296	1.0875	1.0988	12.863	66.522	79.385	0.028 52	0.138 67	0.167 19
30	43.148	0.011 438	0.907 36	0.918 80	15.058	65.361	80.419	0.033 01	0.133 47	0.166 48
40	51.667	0.011 588	0.761 98	0.773 57	17.273	64.163	81.436	0.037 45	0.128 41	0.165 86
50	61.394	0.011 746	0.643 62	0.655 37	19.507	62.926	82.433	0.041 84	0.123 46	0.165 30
60	72.433	0.011 913	0.546 48	0.558 39	21.766	61.643	83.409	0.046 18	0.118 61	0.164 79

70	84.88	0.012 089	0.466 09	0.478 18	24.050	60.309	84.359	0.050 48	0.113 86	0.164 34
80	98.870	0.012 277	0.399 07	0.411 35	26.365	58.917	85.282	0.054 75	0.109 17	0.163 92
90	114.49	0.012 478	0.342 81	0.355 29	28.713	57.461	86.174	0.059 00	0.104 53	0.163 53
100	131.86	0.012 693	0.295 25	0.307 94	31.100	55.929	87.029	0.063 23	0.099 92	0.163 15
110	151.11	0.012 924	0.255 77	0.267 69	33.531	54.313	87.844	0.067 45	0.095 34	0.162 79
120	172.35	0.013 174	0.220 19	0.233 26	36.013	52.597	88.610	0.071 68	0.090 73	0.162 41
130	195.71	0.013 447	0.190 19	0.203 64	38.553	50.768	89.321	0.075 83	0.086 09	0.162 02
140	221.32	0.013 746	0.164 24	0.177 99	41.162	48.805	89.967	0.080 21	0.081 38	0.161 59
150	249.31	0.014 078	0.141 56	0.155 64	43.850	46.684	90.534	0.084 53	0.076 57	0.161 10
160	279.82	0.014 449	0.121 59	0.136 04	46.633	44.373	91.006	0.088 93	0.072 60	0.160 53
170	313.00	0.014 871	0.103 86	0.118 73	49.529	41.830	91.359	0.093 42	0.066 43	0.159 85
180	349.00	0.015 360	0.087 94	0.103 30	52.562	38.999	91.561	0.098 04	0.060 96	0.159 00
190	387.98	0.015 942	0.073 476	0.089 418	55.769	35.792	91.561	0.102 84	0.055 11	0.157 93
200	430.09	0.016 659	0.060 069	0.076 728	59.203	32.075	91.278	0.107 89	0.048 62	0.156 51
210	475.52	0.017 601	0.047 242	0.064 843	62.959	27.599	90.558	0.113 32	0.039 21	0.154 53
220	524.43	0.018 986	0.035 154	0.053 140	67.246	21.790	89.036	0.119 43	0.032 06	0.151 49
230	577.03	0.021 854	0.017 581	0.039 435	72.893	12.229	85.122	0.127 39	0.017 73	0.145 12
233.6 (critical)	596.9	0.028 70	0	0.028 70	78.86	0	78.86	0.135 90	0	0.135 90

Source: Consistent with values presented in "Thermodynamic Properties of Freon-12," E. I. du Pont de Nemours and Company Inc., 1956.

TABLE A.3.2E Superheated R-12 (English Units)

Temp. F	v	h	s	v	h	s	v	h	s
		5 lbf/in.²			10 lbf/in.²			15 lbf/in.²	
0	8.0611	78.582	0.196 63	3.9809	78.246	0.184 71	2.6201	77.902	0.177 51
20	8.4265	81.309	0.202 44	4.1691	81.014	0.190 61	2.7494	80.712	0.183 49
40	8.7903	84.090	0.208 12	4.3556	83.828	0.196 35	2.8770	83.561	0.189 31
60	9.1528	86.922	0.213 67	4.5408	86.689	0.201 97	3.0031	86.451	0.194 98
80	9.5142	89.806	0.219 12	4.7248	89.596	0.207 46	3.1281	89.383	0.200 51
100	9.8747	92.738	0.224 45	4.9079	92.548	0.212 83	3.2521	92.357	0.205 93
120	10.234	95.717	0.229 68	5.0903	95.546	0.218 09	3.3754	95.373	0.211 22
140	10.594	98.743	0.234 81	5.2720	98.586	0.223 25	3.4981	98.429	0.216 40
160	10.952	101.812	0.239 85	5.4533	101.669	0.228 30	3.6202	101.525	0.221 48
180	11.311	104.925	0.244 79	5.6341	104.793	0.233 26	3.7419	104.661	0.226 46
200	11.668	108.079	0.249 64	5.8145	107.957	0.238 13	3.8632	107.835	0.231 35
220	12.026	111.272	0.254 41	5.9946	111.159	0.242 91	3.9841	111.046	0.236 14
		20 lbf/in.²			25 lbf/in.²			30 lbf/in.²	
20	2.0391	80.403	0.178 29	1.6125	80.088	0.174 14	1.3278	79.765	0.170 65
40	2.1373	83.289	0.184 19	1.6932	83.012	0.180 12	1.3969	82.730	0.176 71
60	2.2340	86.210	0.189 92	1.7723	85.965	0.185 91	1.4644	85.716	0.182 57
80	2.3295	89.168	0.195 50	1.8502	88.950	0.191 55	1.5306	88.729	0.188 26
100	2.4241	92.164	0.200 95	1.9271	91.968	0.197 04	1.5957	91.770	0.193 79
120	2.5179	95.198	0.206 28	2.0032	95.021	0.202 40	1.6600	94.843	0.199 18
140	2.6110	98.270	0.211 49	2.0786	98.110	0.207 63	1.7237	97.948	0.204 45
160	2.7036	101.380	0.216 59	2.1535	101.234	0.212 76	1.7868	101.086	0.209 60
180	2.7957	104.528	0.221 59	2.2279	104.393	0.217 78	1.8494	104.258	0.214 63
200	2.8874	107.712	0.226 49	2.3019	107.588	0.222 69	1.9116	107.464	0.219 57
220	2.9789	110.932	0.231 30	2.3756	110.817	0.227 52	1.9735	110.702	0.224 40
240	3.0700	114.186	0.236 02	2.4491	114.080	0.232 25	2.0351	113.973	0.229 15

	35 lbf/in.²			40 lbf/in.²			50 lbf/in.²		
40	1.1850	82.442	0.173 75	1.0258	82.148	0.171 12	0.802 48	81.540	0.166 55
60	1.2442	85.463	0.179 68	1.0789	85.206	0.17712	0.847 13	84.676	0.172 71
80	1.3021	88.504	0.185 42	1.1306	88.277	0.182 92	0.890 25	87.811	0.178 62
100	1.3589	91.570	0.191 00	1.1812	91.367	0.188 54	0.932 16	90.953	0.184 34
120	1.4148	94.663	0.196 43	1.2309	94.480	0.194 01	0.973 13	94.110	0.189 88
140	1.4701	97.785	0.201 72	1.2798	97.620	0.199 33	1.0133	97.286	0.195 27
160	1.5248	100.938	0.206 89	1.3282	100.788	0.204 53	1.0529	100.485	0.200 51
180	1.5789	104.122	0.211 95	1.3761	103.985	0.209 61	1.0920	103.708	0.205 63
200	1.6327	107.338	0.216 90	1.4236	107.212	0.214 57	1.1307	106.958	0.210 64
220	1.6862	110.586	0.221 75	1.4707	110.469	0.219 44	1.1690	110.235	0.215 53
240	1.7394	113.865	0.226 51	1.5176	113.757	0.224 20	1.2070	113.539	0.220 32
260	1.7923	117.175	0.231 17	1.5642	117.074	0.228 88	1.2447	116.871	0.225 02
	60 lbf/in.²			**70 lbf/in.²**			**80 lbf/in.²**		
60	0.692 10	84.126	0.168 92	0.580 88	83.552	0.165 56	—	—	—
80	0.729 64	87.330	0.174 97	0.614 58	86.832	0.171 75	0.527 95	86.316	0.168 85
100	0.765 88	90.528	0.180 79	0.646 85	90.091	0.177 68	0.557 34	89.640	0.174 89
120	0.801 10	93.731	0.186 41	0.678 03	93.343	0.183 39	0.585 56	92.945	0.180 70
140	0.835 51	96.945	0.191 86	0.708 36	96.597	0.188 91	0.612 86	96.242	0.186 29
160	0.869 28	100.776	0.197 16	0.738 00	99.862	0.194 27	0.639 43	99.542	0.191 70
180	0.902 52	103.427	0.202 33	0.767 08	103.141	0.199 48	0.665 43	102.851	0.196 96
200	0.935 31	106.700	0.207 36	0.975 71	106.439	0.204 55	0.690 95	106.174	0.202 07
220	0.967 75	109.997	0.212 29	0.823 97	109.756	0.209 51	0.716 09	109.513	0.207 06
240	0.999 88	113.319	0.217 10	0.851 91	113.096	0.214 35	0.740 90	112.872	0.211 93
260	1.031 80	116.666	0.221 82	0.879 59	116.459	0.219 09	0.765 44	116.251	0.216 69
280	1.063 40	120.039	0.226 44	0.907 05	119.846	0.223 73	0.789 75	119.652	0.221 35

(*Continued*)

TABLE A.3.2E *(Continued)* Superheated R-12 (English Units)

Temp. F	v	h	s	v	h	s	v	h	s
		90 lbf/in.²			**100 lbf/in.²**			**125 lbf/in.²**	
100	0.487 49	89.175	0.172 34	0.431 38	88.694	0.169 96	0.329 43	87.407	0.164 55
120	0.513 46	92.536	0.178 24	0.455 62	92.116	0.175 97	0.350 86	91.008	0.170 87
140	0.538 45	95.879	0.183 91	0.478 81	95.507	0.181 72	0.370 98	94.537	0.176 86
160	0.562 68	99.216	0.189 38	0.501 18	98.884	0.187 26	0.390 15	98.023	0.182 58
180	0.586 29	102.557	0.194 69	0.522 91	102.257	0.192 62	0.408 57	101.484	0.188 07
200	0.609 41	105.905	0.199 84	0.544 13	105.633	0.197 82	0.426 42	104.934	0.193 38
220	0.632 13	109.267	0.204 86	0.564 92	109.018	0.202 87	0.443 80	108.380	0.198 53
240	0.654 51	112.644	0.209 76	0.585 38	112.415	0.207 80	0.460 81	111.829	0.203 53
260	0.676 62	116.040	0.214 55	0.605 54	115.828	0.212 61	0.477 50	115.287	0.208 40
280	0.698 49	119.456	0.219 23	0.625 46	119.258	0.217 31	0.493 94	118.756	0.213 16
300	0.720 16	122.892	0.223 81	0.645 18	122.707	0.221 91	0.510 16	122.238	0.217 80
320	0.741 66	126.349	0.228 30	0.664 72	126.176	0.226 41	0.526 19	125.737	0.222 35
		150 lbf/in.²			**175 lbf/in.²**			**200 lbf/in.²**	
120	0.280 07	89.800	0.166 29	—	—	—	—	—	—
140	0.298 45	93.498	0.172 56	0.245 95	92.373	0.168 59	0.205 79	91.137	0.164 80
160	0.315 66	97.112	0.178 49	0.261 98	96.142	0.174 78	0.221 21	95.100	0.171 30
180	0.332 00	100.675	0.184 15	0.276 97	99.823	0.180 62	0.235 35	98.921	0.177 37
200	0.347 69	104.206	0.189 58	0.291 20	103.447	0.186 20	0.248 60	102.652	0.183 11
220	0.362 85	107.720	0.194 83	0.304 85	107.036	0.191 56	0.261 17	106.325	0.188 60
240	0.377 61	111.226	0.199 92	0.318 04	110.605	0.196 74	0.273 23	109.962	0.193 87
260	0.392 03	114.732	0.204 85	0.330 87	114.162	0.201 75	0.284 89	113.576	0.198 96
280	0.406 17	118.242	0.209 67	0.343 39	117.717	0.206 62	0.296 23	117.178	0.203 90
300	0.420 08	121.761	0.214 36	0.355 67	121.273	0.211 37	0.307 30	120.775	0.208 70
320	0.433 79	125.290	0.218 94	0.367 73	124.835	0.215 99	0.318 15	124.373	0.213 37
340	0.447 33	128.833	0.223 43	0.379 63	128.407	0.220 52	0.328 81	127.974	0.217 93

	250 lbf/in.²			300 lbf/in.²			400 lbf/in.²		
160	0.162 49	92.717	0.164 62	—	—	—	—	—	—
180	0.176 05	96.925	0.171 30	0.134 82	94.556	0.165 37	—	—	—
200	0.188 24	100.930	0.177 47	0.146 97	98.975	0.172 17	0.091 005	93.718	0.160 92
220	0.199 52	104.809	0.183 26	0.157 74	103.136	0.178 38	0.103 16	99.046	0.168 88
240	0.210 14	108.607	0.188 77	0.167 61	107.140	0.184 19	0.113 00	103.735	0.175 68
260	0.220 27	112.351	0.194 04	0.176 85	111.043	0.189 69	0.121 63	108.105	0.181 83
280	0.230 01	116.060	0.199 13	0.185 62	114.879	0.194 95	0.129 49	112.286	0.187 56
300	0.239 44	119.747	0.204 05	0.194 02	118.670	0.200 00	0.136 80	116.343	0.192 98
320	0.248 62	123.420	0.208 82	0.202 14	122.430	0.204 89	0.143 72	120.318	0.198 14
340	0.257 59	127.088	0.213 46	0.210 02	126.171	0.209 63	0.150 32	124.235	0.203 10
360	0.266 39	130.754	0.217 99	0.217 70	129.900	0.214 23	0.156 68	128.112	0.207 89
380	0.275 04	134.423	0.222 41	0.225 22	133.624	0.218 72	0.162 85	131.961	0.212 58

	500 lbf/in.²			600 lbf/in.²		
220	0.064 207	92.397	0.156 83	—	—	—
240	0.077 620	99.218	0.166 72	0.047 488	91.024	0.153 35
260	0.087 054	104.526	0.174 21	0.061 922	99.741	0.165 66
280	0.094 923	109.277	0.180 72	0.070 859	105.637	0.173 74
300	0.101 90	113.729	0.186 66	0.078 059	110.729	0.180 53
320	0.108 29	117.997	0.192 21	0.084 333	115.420	0.186 63
340	0.114 26	122.143	0.197 46	0.090 017	119.871	0.192 27
360	0.119 92	126.205	0.202 47	0.095 289	124.167	0.197 57
380	0.125 33	130.207	0.207 30	0.100 25	128.355	0.202 62
400	0.130 54	134.166	0.211 96	0.104 98	132.466	0.207 46
420	0.135 59	138.096	0.216 48	0.109 52	136.523	0.212 13
440	0.140 51	142.004	0.220 87	0.113 91	140.539	0.216 64

TABLE A.4SI *Thermodynamic Properties of Refrigerant-22 (Chlorodifluoromethane)*

TABLE A.4.1SI Saturated *R-22 (SI Units)*

Temp. °C	Abs. Press. MPa P	Specific Volume m^3/kg			Enthalpy kJ/kg			Entropy kJ/kg K		
		Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
−70	0.0205	0.000 670	0.940 268	0.940 938	−30.607	249.425	218.818	−0.1401	1.2277	1.0876
−65	0.0280	0.000 676	0.704 796	0.705 472	−25.658	246.925	221.267	−0.1161	1.1862	1.0701
−60	0.0375	0.000 682	0.536 470	0.537 152	−20.652	244.354	223.702	−0.0924	1.1463	1.0540
−55	0.0495	0.000 689	0.414 138	0.414 827	−15.585	241.703	226.117	−0.0689	1.1079	1.0390
−50	0.0644	0.000 695	0.323 862	0.324 557	−10.456	238.965	228.509	−0.0457	1.0708	1.0251
−45	0.0827	0.000 702	0.256 288	0.256 990	−5.262	236.132	230.870	−0.0227	1.0349	1.0122
−40	0.1049	0.000 709	0.205 036	0.205 745	0.000	233.198	233.197	0.0000	1.0002	1.0002
−35	0.1317	0.000 717	0.165 683	0.166 400	5.328	230.156	235.484	0.0225	0.9664	0.9889
−30	0.1635	0.000 725	0.135 120	0.135 844	10.725	227.001	237.726	0.0449	0.9335	0.9784
−25	0.2010	0.000 733	0.111 126	0.111 859	16.191	223.727	239.918	0.0670	0.9015	0.9685
−20	0.2448	0.000 741	0.092 102	0.092 843	21.728	220.327	242.055	0.0890	0.8703	0.9593
−15	0.2957	0.000 750	0.076 876	0.077 625	27.334	216.798	244.132	0.1107	0.8398	0.9505
−10	0.3543	0.000 759	0.064 581	0.065 340	33.012	213.132	246.144	0.1324	0.8099	0.9422
−5	0.4213	0.000 768	0.054 571	0.055 339	38.762	209.323	248.085	0.1538	0.7806	0.9344
0	0.4976	0.000 778	0.046 357	0.047 135	44.586	205.364	249.949	0.1751	0.7518	0.9269

5	0.5838	0.000 789	0.039 567	0.040 356	50.485	201.246	251.731	0.1963	0.7235	0.9197
10	0.6807	0.000 800	0.033 914	0.034 714	56.463	196.960	253.423	0.2173	0.6956	0.9129
15	0.7891	0.000 812	0.029 176	0.029 988	62.523	192.495	255.018	0.2382	0.6680	0.9062
20	0.9099	0.000 824	0.025 179	0.026 003	68.670	187.836	256.506	0.2590	0.6407	0.8997
25	1.0439	0.000 838	0.021 787	0.022 624	74.910	182.968	257.877	0.2797	0.6137	0.8934
30	1.1919	0.000 852	0.018 890	0.019 742	81.250	177.869	259.119	0.3004	0.5867	0.8871
35	1.3548	0.000 867	0.016 401	0.017 269	87.700	172.516	260.216	0.3210	0.5598	0.8809
40	1.5335	0.000 884	0.014 251	0.015 135	94.272	166.877	261.149	0.3417	0.5329	0.8746
45	1.7290	0.000 902	0.012 382	0.013 284	100.982	160.914	261.896	0.3624	0.5058	0.8682
50	1.9423	0.000 922	0.010 747	0.011 669	107.851	154.576	262.428	0.3832	0.4783	0.8615
55	2.1744	0.000 944	0.009 308	0.010 252	114.905	147.800	262.705	0.4042	0.4504	0.8546
60	2.4266	0.000 969	0.008 032	0.009 001	122.180	140.497	262.678	0.4255	0.4217	0.8472
65	2.6999	0.000 997	0.006 890	0.007 887	129.729	132.547	262.276	0.4472	0.3920	0.8391
70	2.9959	0.001 030	0.005 859	0.006 889	137.625	123.772	261.397	0.4695	0.3607	0.8302
75	3.3161	0.001 069	0.004 914	0.005 983	145.986	113.902	259.888	0.4927	0.3272	0.8198
80	3.6623	0.001 118	0.004 031	0.005 149	155.011	102.475	257.486	0.5173	0.2902	0.8075
85	4.0368	0.001 183	0.003 175	0.004 358	165.092	88.598	253.690	0.5445	0.2474	0.7918
90	4.4425	0.001 282	0.002 282	0.003 564	177.204	70.037	247.241	0.5767	0.1929	0.7695
95	4.8835	0.001 521	0.001 030	0.002 551	196.359	34.925	231.284	0.6273	0.0949	0.7222
96.006	4.9773	0.001 906	0.000 000	0.001 906	212.546	0.000	212.546	0.6708	0.0000	0.6708

Source: Consistent with values presented in "Thermodynamic Properties of Freon-22," E. I. du Pont de Nemours and Company, Inc., 1964.

TABLE A.4.2SI Superheated Vapor R-22 (SI Units)

Temp. °C	v m³/kg	h kJ/kg	s kJ/kg K	v m³/kg	h kJ/kg	s kJ/kg K	v m³/kg	h kJ/kg	s kJ/kg K
	0.05 MPa			**0.10 MPa**			**0.15 MPa**		
−40	0.440 633	234.724	1.076 16	0.216 331	233.337	1.005 23	—	—	—
−30	0.460 641	240.602	1.100 84	0.226 754	239.359	1.030 52	0.148 723	238.078	0.987 73
−20	0.480 543	246.586	1.124 95	0.237 064	245.466	1.055 13	0.155 851	244.319	1.012 88
−10	0.500 357	252.676	1.148 55	0.247 279	251.665	1.079 14	0.162 879	250.631	1.037 33
0	0.520 095	258.874	1.171 66	0.257 415	257.956	1.102 61	0.169 823	257.022	1.061 16
10	0.539 771	265.180	1.194 33	0.267 485	264.345	1.125 58	0.176 699	263.496	1.084 44
20	0.559 393	271.594	1.216 59	0.277 500	270.831	1.148 09	0.183 516	270.057	1.107 21
30	0.578 970	278.115	1.238 46	0.287 467	277.416	1.170 17	0.190 284	276.709	1.129 52
40	0.598 507	284.743	1.259 98	0.297 394	284.101	1.191 87	0.197 011	283.452	1.151 40
50	0.618 011	291.478	1.281 14	0.307 287	290.887	1.213 20	0.203 702	290.289	1.172 89
60	0.637 485	298.319	1.301 99	0.317 149	297.772	1.234 18	0.210 362	297.220	1.194 02
70	0.656 935	305.265	1.322 53	0.326 986	304.757	1.254 84	0.216 997	304.246	1.214 79
80	0.676 362	312.314	1.342 78	0.336 801	311.842	1.275 19	0.223 608	311.368	1.235 25
90	0.695 771	319.465	1.362 75	0.346 596	319.026	1.295 24	0.230 200	318.584	1.255 40
	0.20 MPa			**0.25 MPa**			**0.30 MPa**		
−20	0.115 203	243.140	0.981 84	—	—	—	—	—	—
−10	0.120 647	249.574	1.006 76	0.095 280	248.492	0.982 31	0.078 344	247.382	0.961 70
0	0.126 003	256.069	1.030 98	0.099 689	255.097	1.006 95	0.082 128	254.104	0.986 77
10	0.131 286	262.633	1.054 58	0.104 022	261.755	1.030 89	0.085 832	260.861	1.011 06
20	0.136 509	269.273	1.077 63	0.108 292	268.476	1.054 21	0.089 469	267.667	1.034 68
30	0.141 681	275.992	1.100 16	0.112 508	275.267	1.076 99	0.093 051	274.531	1.057 71
40	0.146 809	282.796	1.122 24	0.116 681	282.132	1.099 27	0.096 588	281.460	1.080 19
50	0.151 902	289.686	1.143 90	0.120 815	289.076	1.121 09	0.100 085	288.460	1.102 20
60	0.156 963	296.664	1.165 16	0.124 918	296.102	1.142 50	0.103 550	295.535	1.123 76
70	0.161 997	303.731	1.186 07	0.128 993	303.212	1.163 53	0.106 986	302.689	1.144 91
80	0.167 008	310.890	1.206 63	0.133 044	310.409	1.184 20	0.110 399	309.924	1.165 69
90	0.171 999	318.139	1.226 87	0.137 075	317.692	1.204 54	0.113 790	317.241	1.186 12
100	0.176 972	325.480	1.246 81	0.141 089	325.063	1.224 56	0.117 164	324.643	1.206 23
110	0.181 931	332.912	1.266 46	0.145 086	332.522	1.244 28	0.120 522	332.129	1.226 03

	0.40 MPa			0.50 MPa			0.60 MPa		
0	0.060 131	252.051	0.953 59	—	—	—	—	—	—
10	0.063 060	259.023	0.978 66	0.049 355	257.108	0.952 23	0.040 180	255.109	0.929 45
20	0.065 915	266.010	1.002 91	0.051 751	264.295	0.977 17	0.042 280	262.517	0.955 17
30	0.068 710	273.029	1.026 46	0.054 081	271.483	1.001 28	0.044 307	269.888	0.979 89
40	0.071 455	280.092	1.049 38	0.056 358	278.690	1.024 67	0.046 276	277.250	1.003 78
50	0.074 160	287.209	1.071 75	0.058 590	285.930	1.047 43	0.048 198	284.622	1.026 95
60	0.076 830	294.386	1.093 62	0.060 786	293.215	1.069 63	0.050 081	292.020	1.049 50
70	0.079 470	301.630	1.115 04	0.062 951	300.552	1.091 33	0.051 931	299.456	1.071 49
80	0.082 085	308.944	1.136 05	0.065 090	307.949	1.112 57	0.053 754	306.938	1.092 98
90	0.084 679	316.332	1.156 68	0.067 206	315.410	1.133 40	0.055 553	314.475	1.114 03
100	0.087 254	323.796	1.176 95	0.069 303	322.939	1.153 86	0.057 332	322.071	1.134 66
110	0.089 813	331.339	1.196 90	0.071 384	330.539	1.173 95	0.059 094	329.731	1.154 92
120	0.092 358	338.961	1.216 54	0.073 450	338.213	1.193 73	0.060 842	337.458	1.174 82
130	0.094 890	346.664	1.235 88	0.075 503	345.963	1.213 19	0.062 576	345.255	1.194 41
	0.70 MPa			**0.80 MPa**			**0.90 MPa**		
20	0.035 487	260.667	0.935 65	0.030 366	258.737	0.917 87	0.026 355	256.713	0.90132
30	0.037 305	268.240	0.961 05	0.032 034	266.533	0.944 02	0.027 915	264.760	0.928 31
40	0.039 059	275.769	0.985 49	0.033 632	274.243	0.969 05	0.029 397	272.670	0.953 98
50	0.040 763	283.282	1.009 10	0.035 175	281.907	0.993 14	0.030 819	280.497	0.978 59
60	0.042 424	290.800	1.032 01	0.036 674	289.553	1.016 44	0.032 193	288.278	1.002 30
70	0.044 052	298.339	1.054 31	0.038 136	297.202	1.039 06	0.033 528	296.042	1.025 26
80	0.045 650	305.912	1.076 06	0.039 568	304.868	1.061 08	0.034 832	303.807	1.047 57
90	0.047 224	313.527	1.097 32	0.040 974	312.565	1.082 57	0.036 108	311.590	1.069 30
100	0.048 778	321.192	1.118 15	0.042 359	320.303	1.103 59	0.037 363	319.401	1.090 52
110	0.050 313	328.914	1.138 56	0.043 725	328.087	1.124 17	0.038 598	327.251	1.111 28
120	0.051 834	336.696	1.158 61	0.045 076	335.925	1.144 37	0.039 817	335.147	1.131 62
130	0.053 341	344.541	1.178 32	0.046 413	343.821	1.164 20	0.041 022	343.094	1.151 58
140	0.054 836	352.454	1.197 70	0.047 738	351.778	1.183 69	0.042 215	351.097	1.171 19
150	0.056 321	360.435	1.216 79	0.049 052	359.799	1.202 88	0.043 398	359.159	1.190 47

(*Continued*)

TABLE A.4.2SI *(Continued)* Superheated Vapor R-22 (SI Units)

Temp. °C	v m³/kg	h kJ/kg	s kJ/kg K	v m³/kg	h kJ/kg	s kJ/kg K	v m³/kg	h kJ/kg	s kJ/kg K
		1.00 MPa			**1.20 MPa**			**1.40 MPa**	
30	0.024 600	262.912	0.913 58	—	—	—	—	—	—
40	0.025 995	271.042	0.939 96	0.020 851	267.602	0.914 11	0.017 120	263.861	0.890 10
50	0.027 323	279.046	0.965 12	0.022 051	276.011	0.940 55	0.018 247	272.766	0.918 09
60	0.028 601	286.973	0.989 28	0.023 191	284.263	0.965 70	0.019 299	281.401	0.944 41
70	0.029 836	294.859	1.012 60	0.024 282	292.415	0.989 81	0.020 295	289.858	0.969 42
80	0.031 038	302.727	1.035 20	0.025 336	300.508	1.013 05	0.021 248	298.202	0.993 39
90	0.032 213	310.599	1.057 18	0.026 359	308.570	1.035 56	0.022 167	306.473	1.016 49
100	0.033 364	318.488	1.078 61	0.027 357	316.623	1.057 44	0.023 058	314.703	1.038 84
110	0.034 495	326.405	1.099 55	0.028 334	324.682	1.078 75	0.023 926	322.916	1.060 56
120	0.035 609	334.360	1.120 04	0.029 292	332.762	1.099 57	0.024 775	331.128	1.081 72
130	0.036 709	342.360	1.140 14	0.030 236	340.871	1.119 94	0.025 608	339.354	1.102 38
140	0.037 797	350.410	1.159 86	0.031 166	349.019	1.139 90	0.026 426	347.603	1.122 59
150	0.038 873	358.514	1.179 24	0.032 084	357.210	1.159 49	0.027 233	355.885	1.142 40
160	0.039 940	366.677	1.198 31	0.032 993	365.450	1.178 73	0.028 029	364.206	1.161 83
		1.60 MPa			**1.80 MPa**			**2.00 MPa**	
50	0.015 351	269.262	0.896 89	0.013 052	265.423	0.876 25	—	—	—
60	0.016 351	278.358	0.924 61	0.014 028	275.097	0.905 73	0.012 135	271.563	0.887 29
70	0.017 284	287.171	0.950 68	0.014 921	284.331	0.933 04	0.013 008	281.310	0.916 12
80	0.018 167	295.797	0.975 46	0.015 755	293.282	0.958 76	0.013 811	290.640	0.942 92
90	0.019 011	304.301	0.999 20	0.016 546	302.046	0.983 23	0.014 563	299.697	0.968 21
100	0.019 825	312.725	1.022 09	0.017 303	310.683	1.006 69	0.015 277	308.571	0.992 32
110	0.020 614	321.103	1.044 24	0.018 032	319.239	1.029 32	0.015 960	317.322	1.015 46
120	0.021 382	329.457	1.065 76	0.018 738	327.745	1.051 23	0.016 619	325.991	1.037 80
130	0.022 133	337.805	1.086 73	0.019 427	336.224	1.072 53	0.017 258	334.610	1.059 44
140	0.022 869	346.162	1.107 21	0.020 099	344.695	1.093 29	0.017 881	343.201	1.080 49
150	0.023 592	354.540	1.127 24	0.020 759	353.172	1.113 56	0.018 490	351.783	1.101 02
160	0.024 305	362.945	1.146 88	0.021 407	361.666	1.133 40	0.019 087	360.369	1.121 07
170	0.025 008	371.386	1.166 14	0.022 045	370.186	1.152 84	0.019 673	368.970	1.140 70
180	0.025 703	379.869	1.185 07	0.022 675	378.738	1.171 93	0.020 251	377.595	1.159 95

	2.50 MPa			3.00 MPa			3.50 MPa		
70	0.009 459	272.677	0.874 76	—	—	—	—	—	—
80	0.010 243	283.332	0.905 37	0.007 747	274.530	0.867 80	0.005 765	262.739	0.824 89
90	0.010 948	293.338	0.933 32	0.008 465	286.042	0.899 95	0.006 597	277.268	0.865 48
100	0.011 598	302.935	0.959 39	0.009 098	296.663	0.928 81	0.007 257	289.504	0.898 72
110	0.012 208	312.261	0.984 05	0.009 674	306.744	0.955 47	0.007 829	300.640	0.928 18
120	0.012 788	321.400	1.007 60	0.010 211	316.470	0.980 53	0.008 346	311.129	0.955 20
130	0.013 343	330.412	1.030 23	0.010 717	325.955	1.004 35	0.008 825	321.196	0.980 49
140	0.013 880	339.336	1.052 10	0.011 200	335.270	1.027 18	0.009 276	330.976	1.004 45
150	0.014 400	348.205	1.073 31	0.011 665	344.467	1.049 18	0.009 704	340.554	1.027 36
160	0.014 907	357.040	1.093 95	0.012 114	353.584	1.070 47	0.010 114	349.989	1.049 40
170	0.015 402	365.860	1.114 08	0.012 550	362.647	1.091 16	0.010 510	359.324	1.070 71
180	0.015 887	374.679	1.133 76	0.012 976	371.679	1.111 31	0.010 894	368.590	1.091 38
190	0.016 364	383.508	1.153 03	0.013 392	380.695	1.130 99	0.011 268	377.810	1.111 51
200	0.016 834	392.354	1.171 92	0.013 801	389.708	1.150 24	0.011 634	387.004	1.131 15
	4.00 MPa			**5.00 MPa**			**6.00 MPa**		
90	0.005 037	265.629	0.825 44	—	—	—	—	—	—
100	0.005 804	280.997	0.867 21	0.003 334	253.042	0.780 05	—	—	—
110	0.006 405	293.748	0.900 94	0.004 255	275.919	0.840 64	0.002 432	243.278	0.746 74
120	0.006 924	305.273	0.930 64	0.004 851	291.362	0.880 45	0.003 333	272.385	0.821 85
130	0.007 391	316.080	0.957 78	0.005 335	304.469	0.913 37	0.003 899	290.253	0.866 75
140	0.007 822	326.422	0.983 12	0.005 757	316.379	0.942 56	0.004 345	304.757	0.902 30
150	0.008 226	336.446	1.007 10	0.006 139	327.563	0.969 31	0.004 728	317.633	0.933 10
160	0.008 610	346.246	1.029 99	0.006 493	338.266	0.994 31	0.005 071	329.553	0.960 94
170	0.008 978	355.885	1.051 99	0.006 826	348.633	1.017 97	0.005 386	340.849	0.986 73
180	0.009 332	365.409	1.073 24	0.007 142	358.760	1.040 57	0.005 680	351.715	1.010 98
190	0.009 675	374.853	1.093 86	0.007 444	368.713	1.062 30	0.005 958	362.271	1.034 02
200	0.010 009	384.240	1.113 91	0.007 735	378.537	1.083 28	0.006 222	372.602	1.056 09
210	0.010 335	393.593	1.133 47	0.008 018	388.268	1.103 63	0.006 477	382.764	1.077 34
220	0.010 654	402.925	1.152 59	0.008 292	397.932	1.123 43	0.006 722	392.801	1.097 90

TABLE A.4E Thermodynamic Properties of Refrigerant-22 (Chlorodifluoromethane)

TABLE A.4.1E Saturated R-22 (English Units)

Temp. F	Abs. Press. lbf/in.^{2} P	Specific Volume ft^3/lbm			Enthalpy Btu/lbm			Entropy Btu/lbm R		
		Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
−100	2.398	0.010 664	18.421 932	18.432 596	−14.564	107.935	93.371	−0.037 34	0.300 08	0.262 74
−90	3.422	0.010 771	13.224 284	13.235 055	−12.216	106.759	94.544	−0.030 91	0.288 78	0.257 87
−80	4.782	0.010 881	9.683 986	9.694 867	−9.838	105.548	95.710	−0.024 57	0.277 99	0.253 42
−70	6.552	0.010 995	7.220 800	7.231 795	−7.429	104.297	96.868	−0.018 32	0.267 64	0.249 32
−60	8.817	0.011 113	5.473 304	5.484 417	−4.988	103.001	98.014	−0.012 14	0.257 70	0.245 56
−50	11.673	0.011 235	4.211 144	4.222 380	−2.512	101.656	99.144	−0.006 04	0.248 13	0.242 09
−40	15.221	0.011 363	3.284 362	3.295 724	0.000	100.257	100.257	0.000 00	0.238 88	0.238 88
−30	19.572	0.011 495	2.593 397	2.604 892	2.547	98.801	101.348	0.005 98	0.229 94	0.235 91
−20	24.844	0.011 634	2.070 938	2.082 572	5.131	97.285	102.415	0.011 89	0.221 26	0.233 15
−10	31.162	0.011 778	1.670 698	1.682 477	7.751	95.704	103.455	0.017 76	0.212 82	0.230 58
0	38.656	0.011 930	1.360 344	1.372 274	10.409	94.056	104.465	0.023 56	0.204 61	0.228 17
10	47.464	0.012 088	1.116 953	1.129 042	13.104	92.338	105.442	0.029 32	0.196 59	0.225 92
20	57.727	0.012 255	0.924 053	0.936 309	15.837	90.545	106.383	0.035 03	0.188 76	0.223 79
30	69.590	0.012 431	0.769 651	0.782 082	18.609	88.674	107.284	0.040 70	0.181 08	0.221 78

40	83.206	0.012 618	0.644 909	0.657 527	21.421	86.720	108.142	0.046 32	0.173 55	0.219 86
50	98.727	0.012 815	0.543 244	0.556 059	24.275	84.678	108.953	0.051 90	0.166 14	0.218 03
60	116.311	0.013 025	0.459 693	0.472 719	27.172	82.540	109.712	0.057 45	0.158 82	0.216 27
70	136.122	0.013 251	0.390 483	0.403 734	30.116	80.298	110.414	0.062 96	0.151 59	0.214 56
80	158.326	0.013 492	0.332 713	0.346 206	33.109	77.943	111.052	0.068 46	0.144 42	0.212 88
90	183.094	0.013 754	0.284 134	0.297 887	36.158	75.461	111.619	0.073 94	0.137 28	0.211 22
100	210.604	0.014 038	0.242 983	0.257 021	39.267	72.838	112.105	0.079 42	0.130 14	0.209 56
110	241.042	0.014 350	0.207 871	0.222 220	42.446	70.052	112.498	0.084 91	0.122 96	0.207 87
120	274.603	0.014 694	0.177 684	0.192 379	45.705	67.077	112.782	0.090 42	0.115 71	0.206 13
130	311.495	0.015 080	0.151 526	0.166 606	49.059	63.877	112.936	0.095 98	0.108 32	0.204 31
140	351.943	0.015 518	0.128 658	0.144 176	52.528	60.403	112.931	0.101 63	0.100 72	0.202 35
150	396.194	0.016 025	0.108 459	0.124 484	56.143	56.585	112.728	0.107 39	0.092 81	0.200 20
160	444.525	0.016 627	0.090 384	0.107 011	59.948	52.316	112.263	0.113 34	0.084 42	0.197 76
170	497.258	0.017 367	0.073 912	0.091 279	64.019	47.419	111.438	0.119 59	0.075 31	0.194 90
180	554.782	0.018 332	0.058 458	0.076 790	68.498	41.570	110.068	0.126 35	0.064 98	0.191 33
190	617.590	0.019 733	0.043 104	0.062 837	73.711	34.023	107.734	0.134 09	0.523 37	0.186 46
200	686.356	0.022 436	0.025 002	0.047 438	80.862	21.990	102.853	0.144 60	0.033 33	0.177 94
204.81	721.906	0.030 525	0.000 000	0.030 525	91.378	0.000	91.378	0.160 22	0.000 00	0.160 22

Source: Consistent with values presented in "Thermodynamic Properties of Freon-22," E. I. du Pont de Nemours and Company, Inc., 1964.

TABLE A.4.2E Superheated Vapor R-22 (English Units)

Temp. F	v ft^3/lbm	h Btu/lbm	s Btu/lbm R	v ft^3/lbm	h Btu/lbm	s Btu/lbm R	v ft^3/lbm	h Btu/lbm	s Btu/lbm R
	5.00 lbf/in.^{2}			**10.00 lbf/in.^{2}**			**15.00 lbf/in.^{2}**		
−20	10.803 437	103.885	0.272 38	5.345 980	103.526	0.255 88	3.526 127	103.159	0.245 96
0	11.311 411	106.735	0.278 72	5.606 006	106.414	0.262 30	3.703 682	106.088	0.252 48
20	11.817 729	109.643	0.284 91	5.864 306	109.356	0.268 56	3.879 438	109.065	0.258 82
40	12.322 672	112.611	0.290 97	6.121 184	112.353	0.274 68	4.053 721	112.091	0.265 00
60	12.826 471	115.638	0.296 91	6.376 884	115.404	0.280 67	4.226 790	115.168	0.271 03
80	13.329 310	118.724	0.302 74	6.631 601	118.512	0.286 54	4.398 851	118.298	0.276 94
100	13.831 342	121.867	0.308 45	6.885 493	121.674	0.292 29	4.570 068	121.480	0.282 73
120	14.332 691	125.069	0.314 07	7.138 689	124.892	0.297 94	4.740 576	124.715	0.288 41
140	14.833 460	128.327	0.319 60	7.391 295	128.165	0.303 49	4.910 485	128.003	0.293 99
160	15.333 734	131.642	0.325 04	7.643 400	131.493	0.308 95	5.079 885	131.344	0.299 47
180	15.833 586	135.012	0.330 39	7.895 077	134.875	0.314 32	5.248 850	134.737	0.304 86
200	16.333 073	138.437	0.335 66	8.146 385	138.310	0.319 61	5.417 443	138.183	0.310 16
220	16.832 247	141.916	0.340 86	8.397 376	141.799	0.324 82	5.585 717	141.680	0.315 38
240	17.331 150	145.449	0.345 98	8.648 094	145.339	0.329 95	5.753 713	145.229	0.320 53
	20.00 lbf/in.^{2}			**25.00 lbf/in.^{2}**			**30.00 lbf/in.^{2}**		
0	2.752 110	105.756	0.245 35	2.180 820	105.419	0.239 70	1.799 655	105.076	0.234 97
20	2.886 696	108.769	0.251 77	2.290 794	108.469	0.246 19	1.893 302	108.165	0.241 54
40	3.019 756	111.826	0.258 01	2.399 184	111.558	0.252 50	1.985 301	111.286	0.247 92
60	3.151 564	114.930	0.264 10	2.506 281	114.689	0.258 64	2.075 964	114.445	0.254 12
80	3.282 337	118.082	0.270 05	2.612 314	117.865	0.264 64	2.165 535	117.645	0.260 16
100	3.412 247	121.284	0.275 88	2.717 465	121.087	0.270 50	2.254 201	120.888	0.266 06
120	3.541 434	124.536	0.281 59	2.821 879	124.357	0.276 24	2.342 116	124.176	0.271 83
140	3.670 012	127.840	0.287 19	2.925 673	127.675	0.281 87	2.429 400	127.510	0.277 48
160	3.798 073	131.194	0.292 69	3.028 942	131.043	0.287 39	2.516 151	130.891	0.283 03
180	3.925 694	134.599	0.298 10	3.131 765	134.460	0.292 82	2.602 450	134.320	0.288 48
200	4.052 938	138.055	0.303 42	3.234 207	137.926	0.298 15	2.688 363	137.797	0.293 83
220	4.179 859	141.562	0.308 65	3.336 323	141.443	0.303 40	2.773 946	141.323	0.299 09
240	4.306 501	145.119	0.313 81	3.438 156	145.008	0.308 57	2.859 245	144.897	0.304 27
260	4.432 902	148.725	0.318 89	3.539 746	148.622	0.313 67	2.944 298	148.518	0.309 38

	40.00 lbf/in.^{2}			50.00 lbf/in.^{2}			60.00 lbf/in.^{2}		
20	1.395 901	107.541	0.233 99	1.096 839	106.897	0.227 88	—	—	—
40	1.467 550	110.732	0.240 51	1.156 446	110.163	0.234 55	0.948 632	109.577	0.229 50
60	1.537 770	113.950	0.246 82	1.214 515	113.443	0.240 99	0.998 710	112.923	0.236 07
80	1.606 832	117.199	0.252 96	1.271 354	116.745	0.247 22	1.047 477	116.281	0.242 41
100	1.674 945	120.485	0.258 93	1.327 196	120.075	0.253 28	1.095 191	119.658	0.248 55
120	1.742 275	123.810	0.264 77	1.382 218	123.438	0.259 18	1.142 049	123.061	0.254 53
140	1.808 950	127.176	0.270 48	1.436 562	126.838	0.264 95	1.188 201	126.495	0.260 35
160	1.875 076	130.585	0.276 07	1.490 339	130.276	0.270 59	1.233 767	129.963	0.266 04
180	1.940 738	134.039	0.281 56	1.543 637	133.755	0.276 11	1.278 840	133.468	0.271 61
200	2.006 005	137.538	0.286 94	1.596 531	137.276	0.281 53	1.323 499	137.012	0.277 06
220	2.070 933	141.082	0.292 23	1.649 080	140.840	0.286 86	1.367 805	140.596	0.282 41
240	2.135 572	144.673	0.297 44	1.701 333	144.448	0.292 09	1.411 809	144.221	0.287 67
260	2.199 961	148.310	0.302 57	1.753 331	148.100	0.297 23	1.455 553	147.889	0.292 84
280	2.264 133	151.992	0.307 61	1.805 109	151.797	0.302 30	1.499 074	151.600	0.297 92
	70.00 lbf/in.^{2}			80.00 lbf/in.^{2}			100.00 lbf/in.^{2}		
40	0.799 807	108.972	0.225 07	0.687 816	108.347	0.221 07	—	—	—
60	0.844 285	112.391	0.231 78	0.728 202	111.843	0.227 93	0.564 977	110.700	0.221 17
80	0.887 358	115.807	0.238 23	0.767 077	115.323	0.234 50	0.598 178	114.319	0.228 01
100	0.929 319	119.234	0.244 46	0.804 771	118.801	0.240 83	0.630 034	117.911	0.234 54
120	0.970 381	122.679	0.250 51	0.841 521	122.290	0.246 96	0.660 842	121.492	0.240 83
140	1.010 709	126.148	0.256 39	0.877 507	125.796	0.252 90	0.690 814	125.077	0.246 91
160	1.050 430	129.647	0.262 13	0.912 863	129.326	0.258 69	0.720 109	128.674	0.252 81
180	1.089 644	133.178	0.267 74	0.947 697	132.885	0.264 35	0.748 847	132.290	0.258 55
200	1.128 433	136.745	0.273 23	0.982 094	136.476	0.269 87	0.777 122	135.931	0.264 15
220	1.166 860	140.350	0.278 62	1.016 120	140.101	0.275 29	0.805 010	139.599	0.269 63
240	1.204 979	143.993	0.283 90	1.049 833	143.763	0.280 60	0.832 570	143.299	0.275 00
260	1.242 834	147.677	0.289 09	1.083 276	147.463	0.285 81	0.859 850	147.032	0.280 26
280	1.280 461	151.401	0.294 19	1.116 488	151.202	0.290 94	0.886 890	150.800	0.285 42
300	1.317 892	155.167	0.299 22	1.149 500	154.981	0.295 98	0.913 725	154.605	0.290 50

(*Continued*)

TABLE A.4.2E (*Continued*) Superheated Vapor R-22 (English Units)

Temp. F	v ft^3/lbm	h Btu/lbm	s Btu/lbm R	v ft^3/lbm	h Btu/lbm	s Btu/lbm R	v ft^3/lbm	h Btu/lbm	s Btu/lbm R
	125.00 lbf/in.^{2}			**150.00 lbf/in.^{2}**			**175.00 lbf/in.^{2}**		
80	0.462 187	112.989	0.221 04	0.370 548	111.556	0.214 84	—	—	—
100	0.489 623	116.743	0.227 87	0.395 343	115.504	0.222 02	0.327 308	114.180	0.216 68
120	0.515 842	120.456	0.234 39	0.418 698	119.368	0.228 80	0.348 835	118.221	0.223 78
140	0.541 119	124.148	0.240 65	0.440 974	123.181	0.235 27	0.369 104	122.172	0.230 48
160	0.565 647	127.835	0.246 70	0.462 413	126.968	0.241 48	0.388 428	126.069	0.236 87
180	0.589 569	131.528	0.252 56	0.483 188	130.744	0.247 48	0.407 018	129.935	0.243 01
200	0.612 993	135.234	0.258 27	0.503 424	134.520	0.253 29	0.425 024	133.787	0.248 94
220	0.636 004	138.959	0.263 83	0.523 219	138.305	0.258 95	0.442 555	137.637	0.254 69
240	0.658 668	142.708	0.269 27	0.542 646	142.107	0.264 46	0.459 695	141.493	0.260 28
260	0.681 039	146.485	0.274 59	0.561 765	145.929	0.269 84	0.476 509	145.363	0.265 73
280	0.703 159	150.292	0.279 80	0.580 621	149.775	0.275 12	0.493 050	149.251	0.271 06
300	0.725 065	154.130	0.284 93	0.599 254	153.649	0.280 28	0.509 357	153.162	0.276 28
320	0.746 785	158.003	0.289 96	0.617 695	157.553	0.285 36	0.525 464	157.098	0.281 39
340	0.768 345	161.911	0.294 91	0.635 970	161.489	0.290 34	0.541 400	161.062	0.286 41
	200.00 lbf/in.^{2}			**250.00 lbf/in.^{2}**			**300.00 lbf/in.^{2}**		
100	0.275 532	112.750	0.211 65	—	—	—	—	—	—
120	0.295 948	117.004	0.219 11	0.220 383	114.297	0.210 36	—	—	—
140	0.314 866	121.114	0.226 08	0.237 948	118.818	0.218 03	0.185 201	116.199	0.210 42
160	0.332 701	125.134	0.232 68	0.254 012	123.141	0.225 12	0.200 622	120.938	0.218 20
180	0.349 717	129.100	0.238 98	0.269 023	127.340	0.231 79	0.214 601	125.436	0.225 34
200	0.366 094	133.034	0.245 03	0.283 251	131.461	0.238 14	0.227 586	129.784	0.232 04
220	0.381 960	136.953	0.250 89	0.296 876	135.533	0.244 22	0.239 842	134.035	0.238 39
240	0.397 409	140.867	0.256 56	0.310 023	139.576	0.250 08	0.251 540	138.225	0.244 46
260	0.412 513	144.787	0.262 09	0.322 782	143.604	0.255 76	0.262 797	142.375	0.250 31
280	0.427 330	148.719	0.267 47	0.335 222	147.629	0.261 27	0.273 699	146.503	0.255 97
300	0.441 904	152.668	0.272 74	0.347 397	151.659	0.266 65	0.284 308	150.621	0.261 46
320	0.456 270	156.637	0.277 90	0.359 347	155.699	0.271 90	0.294 673	154.738	0.266 81
340	0.470 459	160.631	0.282 96	0.371 107	159.756	0.277 04	0.304 833	158.861	0.272 03
360	0.484 493	164.652	0.287 92	0.382 702	163.831	0.282 07	0.314 819	162.995	0.277 14
380	0.498 394	168.700	0.292 80	0.394 156	167.929	0.287 01	0.324 654	167.145	0.282 14
400	0.512 178	172.779	0.297 60	0.405 487	172.052	0.291 86	0.334 360	171.314	0.287 05

	400.00 lbf/in.²			500.00 lbf/in.²			600.00 lbf/in.²		
160	0.130 528	115.516	0.204 59	—	—	—	—	—	—
180	0.144 597	121.014	0.213 32	0.098 744	115.064	0.200 54	—	—	—
200	0.156 738	126.023	0.221 04	0.112 200	121.432	0.210 34	0.079 113	115.116	0.198 10
220	0.167 697	130.755	0.228 10	0.123 190	126.954	0.218 59	0.091 943	122.320	0.208 87
240	0.177 846	135.315	0.234 71	0.132 847	132.051	0.225 98	0.101 966	128.295	0.217 53
260	0.187 402	139.761	0.240 98	0.141 644	136.894	0.232 81	0.110 605	133.705	0.225 16
280	0.196 502	144.131	0.246 97	0.149 835	141.572	0.239 22	0.118 386	138.790	0.232 13
300	0.205 243	148.451	0.252 73	0.157 571	146.141	0.245 32	0.125 576	143.668	0.238 63
320	0.213 694	152.741	0.258 31	0.164 954	150.634	0.251 15	0.132 329	148.407	0.244 79
340	0.221 905	157.012	0.263 72	0.172 055	155.077	0.256 78	0.138 746	153.050	0.250 67
360	0.229 916	161.275	0.268 98	0.178 925	159.487	0.262 23	0.144 896	157.628	0.256 33
380	0.237 758	165.538	0.274 12	0.185 605	163.877	0.267 52	0.150 830	162.160	0.261 79
400	0.245 455	169.807	0.279 14	0.192 123	168.257	0.272 67	0.156 584	166.662	0.267 09
420	0.253 028	174.087	0.284 07	0.198 505	172.634	0.277 71	0.162 187	171.146	0.272 25
440	0.260 493	178.381	0.288 89	0.204 768	177.014	0.282 63	0.167 662	175.621	0.277 27
	700.00 lbf/in.²			800.00 lbf/in.²			900.00 lbf/in.²		
220	0.067 104	116.048	0.197 48	0.042 152	104.391	0.178 83	—	—	—
240	0.078 820	123.792	0.208 72	0.059 974	118.024	0.198 65	0.043 352	109.908	0.185 68
260	0.087 856	130.088	0.217 59	0.070 151	125.882	0.209 73	0.055 694	120.852	0.201 13
280	0.095 590	135.733	0.225 33	0.078 163	132.339	0.218 58	0.064 298	128.530	0.211 65
300	0.102 525	141.007	0.232 37	0.085 058	138.131	0.226 31	0.071 320	135.010	0.220 30
320	0.108 911	146.046	0.238 92	0.091 252	143.538	0.233 33	0.077 446	140.872	0.227 92
340	0.114 893	150.925	0.245 10	0.096 959	148.696	0.239 87	0.082 984	146.359	0.234 87
360	0.120 566	155.695	0.250 99	0.102 306	153.686	0.246 03	0.088 104	151.600	0.241 34
380	0.125 992	160.387	0.256 64	0.107 373	158.557	0.251 90	0.092 910	156.672	0.247 45
400	0.131 218	165.025	0.262 10	0.112 219	163.344	0.257 53	0.097 471	161.623	0.253 28
420	0.136 279	169.625	0.267 39	0.116 884	168.071	0.262 97	0.101 836	166.487	0.258 88
440	0.141 201	174.201	0.272 53	0.121 399	172.756	0.268 24	0.106 039	171.289	0.264 27
460	0.146 005	178.761	0.277 55	0.125 787	177.412	0.273 35	0.110 108	176.046	0.269 50
480	0.150 707	183.315	0.282 45	0.130 067	182.049	0.278 34	0.114 063	180.771	0.274 58
500	0.155 321	187.867	0.287 24	0.134 254	186.675	0.283 21	0.117 920	185.475	0.279 54

TABLE A.5SI Thermodynamic Properties of Nitrogen

TABLE A.5.1SI Saturated Nitrogen (SI Units)

Temp. K	Abs. Press. MPa P	Specific Volume m^3/kg Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Enthalpy kJ/kg Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Entropy kJ/kg K Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
63.148	0.012 52	0.001 150	1.480 099	1.481 249	−150.911	215.392	64.482	2.4234	3.4108	5.8342
65	0.017 41	0.001 160	1.092 665	1.093 825	−147.172	213.384	66.212	2.4816	3.2829	5.7646
70	0.038 58	0.001 191	0.525 015	0.526 206	−137.088	207.788	70.700	2.6307	2.9683	5.5991
75	0.076 10	0.001 223	0.280 499	0.281 722	−126.949	201.816	74.867	2.7700	2.6909	5.4609
77.348	0.101 325	0.001 240	0.215 145	0.216 385	−122.150	198.839	76.689	2.8326	2.5707	5.4033
80	0.136 99	0.001 259	0.162 485	0.163 744	−116.689	195.319	78.630	2.9014	2.4415	5.3429
85	0.229 03	0.001 299	0.100 204	0.101 503	−106.252	188.149	81.898	3.0266	2.2136	5.2401
90	0.360 66	0.001 343	0.064 803	0.066 146	−95.577	180.137	84.560	3.1466	2.0016	5.1482
95	0.540 82	0.001 393	0.043 398	0.044 792	−84.593	171.075	86.482	3.2627	1.8009	5.0636
100	0.778 81	0.001 452	0.029 764	0.031 216	−73.199	160.691	87.493	3.3761	1.6070	4.9831
105	1.084 23	0.001 522	0.020 673	0.022 195	−61.238	148.597	87.359	3.4883	1.4153	4.9036
110	1.467 17	0.001 610	0.014 342	0.015 952	−48.446	134.165	85.719	3.6017	1.2197	4.8215
115	1.938 75	0.001 729	0.009 717	0.011 445	−34.308	116.212	81.904	3.7204	1.0106	4.7310
120	2.512 48	0.001 915	0.006 083	0.007 998	−17.605	91.930	74.324	3.8536	0.7661	4.6197
125	3.208 86	0.002 353	0.002 530	0.004 883	6.677	48.762	55.438	4.0395	0.3901	4.4296
126.193	3.397 80	0.003 194	0.000 000	0.003 194	29.791	0.000	29.791	4.2193	0.0000	4.2193

Source: Consistent with values presented in R. Jacobsen, R. Stewart and M. Jahangiri, "Thermodynamic Properties of Nitrogen . . . ," *J. Phys. Chem. Ref. Data*, 15, (1986).

TABLE A.5.2SI *Superheated Nitrogen (SI Units)*

Abs. Press. MPa		Temperature, K								
		100	125	150	175	200	225	250	275	300
	v	0.291 030	0.367 236	0.442 612	0.517 577	0.592 311	0.666 904	0.741 404	0.815 839	0.890 229
0.1	h	101.938	128.423	154.695	180.860	206.967	233.039	259.090	285.128	311.160
	s	5.6944	5.9308	6.1225	6.2838	6.4232	6.5461	6.6559	6.7551	6.8457
	v	0.142 521	0.181 711	0.220 007	0.257 878	0.295 515	0.333 008	0.370 408	0.407 743	0.445 033
0.2	h	100.238	127.294	153.876	180.236	206.476	232.644	258.766	284.861	310.938
	s	5.4775	5.7191	5.9130	6.0755	6.2157	6.3390	6.4491	6.5486	6.6393
	v	0.053 062	0.070 328	0.086 429	0.102 059	0.117 442	0.132 677	0.147 817	0.162 892	0.177 921
0.5	h	94.460	123.776	151.376	178.349	204.998	231.458	257.799	284.063	310.276
	s	5.1660	5.4282	5.6296	5.7959	5.9383	6.0629	6.1740	6.2741	6.3653
	v	—	0.033 064	0.041 876	0.050 120	0.058 093	0.065 911	0.073 631	0.081 285	0.088 893
1.0	h	—	117.397	147.062	175.156	202.522	229.482	256.194	282.743	309.182
	s	—	5.1872	5.4039	5.5772	5.7234	5.8504	5.9630	6.0642	6.1562
	v	—	0.014 030	0.019 541	0.024 153	0.028 436	0.032 548	0.036 558	0.040 500	0.044 395
2.0	h	—	101.541	137.779	168.584	197.528	225.543	253.014	280.140	307.034
	s	—	4.8887	5.1541	5.3443	5.4989	5.6310	5.7467	5.8502	5.9438
	v	—	—	0.008 231	0.011 185	0.013 650	0.015 912	0.018 063	0.020 145	0.022 179
4.0	h	—	—	115.595	154.672	187.417	217.740	246.800	275.098	302.898
	s	—	—	4.8379	5.0797	5.2548	5.3978	5.5203	5.6282	5.7250

	v	—	—	0.004 421	0.006 909	0.008 771	0.010 412	0.011 937	0.013 393	0.014 803
6.0	h	—	—	87.298	139.945	177.293	210.125	240.822	270.294	298.988
	s	—	—	4.5685	4.8956	5.0955	5.2503	5.3797	5.4921	5.5920
	v	—	—	0.002 914	0.004 861	0.006 387	0.007 701	0.008 905	0.010 042	0.011 135
8.0	h	—	—	61.924	125.326	167.469	202.833	235.145	265.761	295.318
	s	—	—	4.3522	4.7460	4.9717	5.1385	5.2748	5.3916	5.4945
	v	—	—	0.002 388	0.003 752	0.005 014	0.006 112	0.007 113	0.008 053	0.008 952
10.0	h	—	—	48.659	112.363	158.353	196.022	229.841	261.532	291.902
	s	—	—	4.2290	4.6233	4.8697	5.0474	5.1901	5.3109	5.4167
	v	—	—	0.001 955	0.002 598	0.003 365	0.004 109	0.004 804	0.005 461	0.006 088
15.0	h	—	—	36.805	91.928	140.599	181.908	218.586	252.470	284.565
	s	—	—	4.0790	4.4191	4.6796	4.8745	5.0292	5.1585	5.2702
	v	—	—	0.001 782	0.002 187	0.002 687	0.003 213	0.003 729	0.004 226	0.004 704
20.0	h	—	—	33.644	83.317	130.168	172.324	210.434	245.699	279.007
	s	—	—	3.9960	4.3024	4.5529	4.7517	4.9124	5.0469	5.1629

TABLE A.6SI Thermodynamic Properties of Methane

TABLE A.6.1SI Saturated Methane (SI Units)

Temp. K	Abs. Press. MPa P	Specific Volume $m^3/kmol$ Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Enthalpy kJ/kmol Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Entropy kJ/kmol K Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
90.685	0.011 69	0.035 53	63.843 87	63.879 40	−5744.6	8713.3	2968.8	67.804	96.083	163.888
95	0.019 83	0.035 99	39.277 08	39.313 07	−5514.8	8618.0	3103.2	70.276	90.715	160.991
100	0.034 41	0.036 55	23.688 68	23.725 22	−5243.3	8499.0	3255.8	73.056	84.990	158.047
105	0.056 43	0.037 13	15.046 89	15.084 02	−4967.8	8371.5	3403.7	75.736	79.729	155.465
110	0.088 20	0.037 76	9.981 79	10.019 54	−4689.2	8234.7	3545.5	78.317	74.863	153.180
115	0.132 32	0.038 42	6.867 71	6.906 13	−4407.6	8087.6	3680.0	80.806	70.328	151.134
120	0.191 58	0.039 12	4.872 41	4.911 53	−4122.7	7928.5	3805.8	83.211	66.072	149.283
125	0.268 96	0.039 88	3.547 15	3.587 03	−3834.1	7755.9	3921.8	85.542	62.047	147.590
130	0.367 60	0.040 70	2.638 75	2.679 45	−3541.0	7567.8	4026.7	87.810	58.214	146.023
135	0.490 72	0.041 59	1.998 52	2.040 11	−3242.8	7362.2	4119.3	90.022	54.534	144.556
140	0.641 65	0.042 56	1.535 98	1.578 53	−2938.4	7136.7	4198.3	92.190	50.976	143.166
145	0.823 79	0.043 63	1.194 25	1.237 88	−2626.7	6888.5	4261.9	94.323	47.506	141.829
150	1.040 65	0.044 82	0.936 59	0.981 41	−2306.1	6614.2	4308.1	96.431	44.094	140.525
155	1.295 80	0.046 16	0.738 58	0.784 75	−1974.7	6309.1	4334.4	98.528	40.703	139.231
160	1.592 96	0.047 71	0.583 61	0.631 31	−1630.1	5967.2	4337.1	100.627	37.295	137.992
165	1.936 07	0.049 51	0.460 04	0.509 55	−1268.7	5579.9	4311.2	102.749	33.817	136.566

170	2.329 36	0.051 69	0.359 51	0.411 21	−885.1	5133.9	4248.9	104.920	30.200	135.120
175	2.777 62	0.054 43	0.275 67	0.330 11	−470.5	4607.5	4137.0	107.185	26.329	133.514
180	3.286 55	0.058 12	0.203 12	0.261 25	−8.5	3958.8	3950.4	109.627	21.993	131.620
185	3.863 61	0.063 80	0.135 59	0.199 39	542.6	3082.0	3624.6	112.453	16.659	129.112
190	4.520 82	0.080 00	0.047 76	0.127 76	1479.6	1280.2	2759.8	117.195	6.737	123.932
190.551	4.599 20	0.098 63	0.000 00	0.098 63	2081.4	0.0	2081.4	120.320	0.000	120.320

Source: Consistent with values presented in D. Friend, J. Ely, and H. Ingham, "Thermophysical Properties of Methane," *J. Phys. Chem. Ref. Data*, 18, (1989).

TABLE A.6.2SI Superheated Methane (SI Units)

Abs. Press. MPa		Temperature, K									
		150	175	200	225	250	275	300	350	400	450
	v	24.7596	28.9640	33.1526	37.3323	41.5065	45.6769	49.8447	58.1749	66.5006	—
0.05	h	4948.5	5788.5	6628.6	7472.7	8325.3	9191.4	10 076.0	11 918.9	13 883.3	—
	s	168.7248	173.9043	178.3910	182.3676	185.9606	189.2621	192.3404	198.0177	203.2600	—
	v	12.2866	14.4131	16.5234	18.6246	20.7202	22.8120	24.9011	29.0741	33.2425	—
0.10	h	4921.5	5768.4	6612.8	7459.8	8314.6	9182.3	10 068.2	11 913.0	13 878.7	—
	s	162.8426	168.0653	172.5753	176.5658	180.1678	183.4755	186.5583	192.2415	197.4873	—
	v	2.2986	2.7686	3.2184	3.6577	4.0909	4.5200	4.9464	5.7937	6.6363	—
0.50	h	4689.4	5601.0	6483.5	7355.5	8228.1	9109.2	10 005.6	11 865.7	13 842.2	—
	s	148.4215	154.0457	158.7602	162.8690	166.5462	169.9050	173.0243	178.7551	184.0297	—
	v	—	1.3073	1.5531	1.7860	2.0119	2.2335	2.4522	2.8838	3.3107	—
1.00	h	—	5372.4	6313.5	7221.2	8118.0	9016.8	9926.8	11 806.6	13 796.7	—
	s	—	147.3890	152.4185	156.6959	160.4756	163.9022	167.0690	172.8607	178.1718	—
	v	—	0.8147	0.9961	1.1614	1.3187	1.4713	1.6208	1.9140	2.2023	—
1.50	h	—	5114.7	6132.6	7081.9	8005.5	8923.3	9847.5	11 747.6	13 751.4	—
	s	—	142.9776	148.4207	152.8954	156.7882	160.2872	163.5037	169.3581	174.7060	—
	v	—	0.5621	0.7160	0.8486	0.9720	1.0903	1.2053	1.4292	1.6482	—
2.00	h	—	4812.5	5938.6	6937.4	7890.7	8828.7	9767.8	11 688.5	13 706.2	—
	s	—	139.3163	145.3437	150.0529	154.0712	157.6475	160.9159	166.8345	172.2196	—

	v	—	—	0.4316	0.5346	0.6250	0.7093	0.7899	0.9447	1.0944	1.2411
3.00	h	—	—	5497.9	6630.4	7653.5	8636.2	9607.0	11 570.7	13 616.6	15 778.3
	s	—	—	140.3639	145.7075	150.0216	153.7688	157.1478	163.1998	168.6605	173.7498
	v	—	—	0.2829	0.3765	0.4514	0.5190	0.5825	0.7028	0.8178	0.9297
4.00	h	—	—	4945.0	6295.1	7406.0	8439.7	9445.0	11 453.5	13 528.0	15 709.8
	s	—	—	135.8446	142.2255	146.9118	150.8541	154.3533	160.5444	166.0819	171.2188
	v	—	—	0.1832	0.2806	0.3473	0.4050	0.4584	0.5579	0.6520	0.7431
5.00	h	—	—	4143.8	5925.3	7148.0	8239.6	9282.0	11 337.1	13 440.6	15 642.5
	s	—	—	130.6851	139.1374	144.2980	148.4620	152.0907	158.4263	164.0415	169.2259
	v	—	—	0.0980	0.2160	0.2780	0.3293	0.3759	0.4615	0.5417	0.6188
6.00	h	—	—	2571.6	5514.6	6879.9	8036.7	9118.7	11 221.8	13 354.4	15 576.4
	s	—	—	122.1278	136.2170	141.9837	146.3974	150.1644	156.6491	162.3425	167.5742
	v	—	—	0.0661	0.1357	0.1923	0.2356	0.2736	0.3417	0.4042	0.4638
8.00	h	—	—	1420.5	4572.0	6319.6	7626.6	8793.9	10 995.8	13 186.6	15 448.1
	s	—	—	115.6201	130.5008	137.8958	142.8853	146.9501	153.7417	159.5914	164.9164
	v	—	—	0.0603	0.0954	0.1430	0.1808	0.2133	0.2705	0.3223	0.3712
10.00	h	—	—	1158.7	3679.0	5753.0	7220.7	8476.6	10 777.7	13 025.6	15 325.4
	s	—	—	113.6831	125.5287	134.3053	139.9107	144.2850	151.3850	157.3880	162.8037

TABLE A.7SI *Critical Constants (SI Units)*

Substance	Formula	Molec. Weight	Temp. K	Press. MPa	Vol. m^3/kmol	Acentric Factor
Ammonia	NH_3	17.031	405.5	11.35	0.0725	0.250
Argon	Ar	39.948	150.8	4.87	0.0749	0.001
Bromine	Br_2	159.808	588	10.30	0.1272	0.108
Carbon dioxide	CO_2	44.01	304.1	7.38	0.0939	0.239
Carbon monoxide	CO	28.01	132.9	3.50	0.0932	0.066
Chlorine	Cl_2	70.906	416.9	7.98	0.1238	0.090
Deuterium (normal)	D_2	4.032	38.4	1.66	—	−0.160
Fluorine	F_2	37.997	144.3	5.22	0.0663	0.054
Helium	He	4.003	5.19	0.227	0.0574	−0.365
Helium[3]	He	3.017	3.31	0.114	0.0729	−0.473
Hydrogen (normal)	H_2	2.016	33.2	1.30	0.0651	−0.218
Krypton	Kr	83.80	209.4	5.50	0.0912	0.005
Neon	Ne	20.183	44.4	2.76	0.0416	−0.029
Nitric oxide	NO	30.006	180	6.48	0.0577	0.588
Nitrogen	N_2	28.013	126.2	3.39	0.0898	0.039
Nitrogen dioxide	NO_2	46.006	431	10.1	0.1678	0.834
Nitrous oxide	N_2O	44.013	309.6	7.24	0.0974	0.165
Oxygen	O_2	31.999	154.6	5.04	0.0734	0.025
Sulfur dioxide	SO_2	64.063	430.8	7.88	0.1222	0.256
Water	H_2O	18.015	647.3	22.12	0.0571	0.344
Xenon	Xe	131.30	289.7	5.84	0.1184	0.008
Acetylene	C_2H_2	26.038	308.3	6.14	0.1127	0.190
Benzene	C_6H_6	78.114	562.2	4.89	0.2590	0.212
n-Butane	C_4H_{10}	58.124	425.2	3.80	0.2550	0.199
Carbon tetrachloride	CCL_4	153.823	556.4	4.56	0.2759	0.193
Chlorodifluoroethane[a]	CH_3CCLF_2	100.495	410.3	4.25	0.2310	0.250
Chlorodifluoromethane	$CHCLF_2$	86.469	369.3	4.97	0.1656	0.221
Chloroform	$CHCL_3$	119.378	536.4	5.37	0.2389	0.218
Dichlorodifluoromethane	CCL_2F_2	120.914	385.0	4.14	0.2167	0.204
Dichlorofluoroethane[a]	CH_3CCL_2F	116.95	481.5	4.54	0.2520	0.215
Dichlorofluoromethane	$CHCL_2F$	102.923	451.6	5.18	0.1964	0.210
Dichlorotrifluoroethane[a]	$CHCL_2CF_3$	152.93	456.9	3.67	0.2781	0.282
Difluoroethane[a]	CHF_2CH_3	66.05	386.4	4.52	0.1795	0.275
Ethane	C_2H_6	30.070	305.4	4.88	0.1483	0.099
Ethyl alcohol	C_2H_5OH	46.069	513.9	6.14	0.1671	0.644
Ethylene	C_2H_4	28.054	282.4	5.04	0.1304	0.089
n-Heptane	C_7H_{16}	100.205	540.3	2.74	0.4320	0.349
n-Hexane	C_6H_{14}	86.178	507.5	3.01	0.3700	0.299
Methane	CH_4	16.043	190.4	4.60	0.0992	0.011
Methyl alcohol	CH_3OH	32.042	512.6	8.09	0.1180	0.556
Methyl chloride	CH_3CL	50.488	416.3	6.70	0.1389	0.153
n-Octane	C_8H_{18}	114.232	568.8	2.49	0.4920	0.398
n-Pentane	C_5H_{16}	72.151	469.7	3.37	0.3040	0.251
Propane	C_3H_8	44.094	369.8	4.25	0.2030	0.153
Propene	C_3H_6	42.081	364.9	4.60	0.1810	0.144
Propyne	C_3H_4	40.065	402.4	5.63	0.1640	0.215
Tetrafluoroethane[a]	CF_3CH_2F	102.03	374.2	4.06	0.1980	0.327

Source: R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, fourth edition, McGraw-Hill Book Company, New York, 1987.

[a] Data from M. O. McLinden, NIST Thermophysics Division, 1989.

TABLE A.8SI *Properties of Various Solids and Liquids*[a] *(SI Units)*

Solid	C_p, kJ/kg K	ρ, kg/m^3	Liquid	C_p, kJ/kg K	ρ, kg/m^3
Aluminum	0.900	2700	Ammonia	4.800	602
Concrete	0.65	2300	Ethanol	2.456	783
Copper	0.386	8900	R-12	0.977	1310
Granite	1.017	2700	Mercury	0.139	13 560
Graphite	0.711	2500	Methanol	2.550	787
Iron	0.450	7840	Oil (light)	1.800	910
Lead	0.128	11 310	Water	4.184	997
Rubber (soft)	1.840	1100			
Sand (dry)	0.80	1450–1750			
Silver	0.235	10 470			
Tin	0.217	5730			
Wood (most)	1.760	350–700			

[a] Values at 25°C.

TABLE A.8E *Properties of Various Solids and Liquids*[a] *(English Units)*

Solid	C_p, Btu/lbm R	ρ, lbm/ft^3	Liquid	C_p, Btu/lbm R	ρ, lbm/ft^3
Aluminum	0.215	170	Ammonia	1.146	38
Concrete	0.155	155	Ethanol	0.587	49
Copper	0.092	555	R–12	0.233	82
Granite	0.243	170	Mercury	0.033	847
Graphite	0.170	155	Methanol	0.609	49
Iron	0.107	490	Oil (light)	0.430	57
Lead	0.030	705	Water	1.000	62
Rubber (soft)	0.439	70			
Sand (dry)	0.19	90–110			
Silver	0.056	655			
Tin	0.052	360			
Wood (most)	0.420	22–45			

[a] Values at 80 F.

TABLE A.9SI Properties of Various Ideal Gases[a] (SI Units)

Gas	Chemical Formula	Molecular Mass	R, kJ/kg K	C_{p0}, kJ/kg K	C_{v0}, kJ/kg K	k
Air		28.97	0.287 00	1.0035	0.7165	1.400
Ammonia	NH_3	17.031	0.488 19	2.1300	1.6418	1.297
Argon	Ar	39.948	0.208 13	0.5203	0.3122	1.667
Butane	C_4H_{10}	58.124	0.143 04	1.7164	1.5734	1.091
Carbon dioxide	CO_2	44.01	0.188 92	0.8418	0.6529	1.289
Carbon monoxide	CO	28.01	0.296 83	1.0413	0.7445	1.400
Ethane	C_2H_6	30.07	0.276 50	1.7662	1.4897	1.186
Ethanol	C_2H_5OH	46.069	0.180 48	2.4963	2.3158	1.078
Ethylene	C_2H_4	28.054	0.296 37	1.5482	1.2518	1.237
Helium	He	4.003	2.077 03	5.1926	3.1156	1.667
Hydrogen	H_2	2.016	4.124 18	14.2091	10.0849	1.409
Methane	CH_4	16.04	0.518 35	2.2537	1.7354	1.299
Methanol	CH_3OH	32.042	0.259 48	1.4050	1.1455	1.227
Neon	Ne	20.183	0.411 95	1.0299	0.6179	1.667
Nitrogen	N_2	28.013	0.296 80	1.0416	0.7448	1.400
Octane	C_8H_{18}	114.23	0.072 79	1.7113	1.6385	1.044
Oxygen	O_2	31.999	0.259 83	0.9216	0.6618	1.393
Propane	C_3H_8	44.097	0.188 55	1.6794	1.4909	1.126
Steam	H_2O	18.015	0.461 52	1.8723	1.4108	1.327

[a] C_{p0}, C_{v0}, and k are at 300 K.

TABLE A9E Properties of Various Ideal Gases[a] (English Units)

Gas	Chemical Formula	Molecular Mass	R, ft-lbf/ lbm R	C_{p0}, Btu/ lbm R	C_{v0}, Btu/ lbm R	k
Air		28.97	53.34	0.240	0.171	1.400
Ammonia	NH_3	17.031	90.72	0.509	0.392	1.297
Argon	Ar	39.948	38.68	0.1253	0.0756	1.667
Butane	C_4H_{10}	58.124	26.58	0.415	0.381	1.09
Carbon dioxide	CO_2	44.01	35.10	0.203	0.158	1.285
Carbon monoxide	CO	28.01	55.16	0.249	0.178	1.399
Ethane	C_2H_6	30.07	51.38	0.427	0.361	1.183
Ethanol	C_2H_5OH	46.069	33.54	0.596	0.553	1.078
Ethylene	C_2H_4	28.054	55.07	0.411	0.340	1.208
Helium	He	4.003	386.0	1.25	0.753	1.667
Hydrogen	H_2	2.016	766.4	3.43	2.44	1.404
Methane	CH_4	16.04	96.35	0.532	0.403	1.32
Methanol	CH_3OH	32.042	48.22	0.336	0.274	1.227
Neon	Ne	20.183	76.55	0.246	0.1477	1.667
Nitrogen	N_2	28.013	55.15	0.248	0.177	1.400
Octane	C_8H_{18}	114.23	13.53	0.409	0.392	1.044
Oxygen	O_2	31.999	48.28	0.219	0.157	1.395
Propane	C_3H_8	44.097	35.04	0.407	0.362	1.124
Steam	H_2O	18.015	85.76	0.445	0.335	1.329

[a] C_{p0}, C_{v0}, and k are at 80 F.

TABLE A.10SI Constant-Pressure Specific Heats of Various Ideal Gases (SI Units)

$$\bar{C}_{po} = \frac{\text{Btu}}{\text{lb mole R}} \qquad \theta = \frac{T(\text{Rankine})}{180}$$

Gas		Range R	Max Error %
N_2	$\bar{C}_{po} = 9.3355 - 122.56\theta^{-1.5} + 256.38\theta^{-2} - 196.08\theta^{-3}$	540–6300	0.43
O_2	$\bar{C}_{po} = 8.9465 + 4.8044 \times 10^{-3}\theta^{1.5} - 42.679\theta^{-1.5} + 56.615\theta^{-2}$	540–6300	0.30
H_2	$\bar{C}_{po} = 13.505 - 167.96\theta^{-0.75} + 278.44\theta^{-1} - 134.01\theta^{-1.5}$	540–6300	0.60
CO	$\bar{C}_{po} = 16.526 - 0.16841\theta^{0.75} - 47.985\theta^{-0.5} + 42.246\theta^{-0.75}$	540–6300	0.42
OH	$\bar{C}_{po} = 19.490 - 14.185\theta^{0.25} + 4.1418\theta^{0.75} - 1.0196\theta$	540–6300	0.43
NO	$\bar{C}_{po} = 14.169 - 0.40861\theta^{0.5} - 16877\theta^{-0.5} + 17.899\theta^{-1.5}$	540–6300	0.34
H_2O	$\bar{C} = 34.190 - 43.868\theta^{0.25} + 19.778\theta^{0.5} - 0.88407\theta$	540–6300	0.43
CO_2	$\bar{C}_{po} = -0.89286 + 7.2967\theta^{0.5} - 0.98074\theta + 5.7835 \times 10^{-3}\theta^2$	540–6300	0.19
NO_2	$\bar{C}_{po} = 11.005 + 51.650\theta^{-0.5} - 86.916\theta^{-0.75} + 55.580\theta^{-2}$	540–6300	0.26
CH_4	$\bar{C}_{po} = -160.82 + 105.10\theta^{0.25} - 5.9452\theta^{0.75} + 77.408\theta^{-0.5}$	540–3600	0.15
C_2H_4	$\bar{C}_{po} = -22.800 + 29.433\theta^{0.5} - 8.5185\theta^{0.75} + 43.683\theta^{-3}$	540–3600	0.07
C_2H_6	$\bar{C}_{po} = 1.648 + 4.124\theta - 0.153\theta^2 + 1.74 \times 10^{-3}\theta^3$	540–2700	0.83
C_3H_8	$\bar{C}_{po} = -0.966 + 7.2790 - 0.3755\theta^2 + 7.58 \times 10^{-3}\theta^3$	540–2700	0.40
C_4H_{10}	$\bar{C}_{po} = 0.945 + 8.873\theta - 0.438\theta^2 + 8.36 \times 10^{-3}\theta^3$	540–2700	0.54

TABLE A.10E Constant-Pressure Specific Heats of Various Ideal Gases (English Units)

$$C_{po} = \text{kJ/kmol K} \qquad \theta = T(\text{Kelvin})/100$$

Gas		Range K	Max. Error %
N_2	$\bar{C}_{po} = 39.060 - 512.79\theta^{-1.5} + 1072.7\theta^{-2} - 820.40\theta^{-3}$	300–3500	0.43
O_2	$\bar{C}_{po} = 37.432 + 0.020\,102\theta^{1.5} - 178.57\theta^{-1.5} + 236.88\theta^{-2}$	300–3500	0.30
H_2	$\bar{C}_{po} = 56.505 - 702.74\theta^{-0.75} + 1165.0\theta^{-1} - 560.70\theta^{-1.5}$	300–3500	0.60
CO	$\bar{C}_{po} = 69.145 - 0.704\,63\theta^{0.75} - 200.77\theta^{-0.5} + 176.76\theta^{-0.75}$	300–3500	0.42
OH	$\bar{C}_{po} = 81.546 - 59.350\theta^{0.25} + 17.329\theta^{0.75} - 4.2660\theta$	300–3500	0.43
NO	$\bar{C}_{po} = 59.283 - 1.7096\theta^{0.5} - 70.613\theta^{-0.5} + 74.889\theta^{-1.5}$	300–3500	0.34
H_2O	$\bar{C}_{po} = 143.05 - 183.54\theta^{0.25} + 82.751\theta^{0.5} - 3.6989\theta$	300–3500	0.43
CO_2	$\bar{C}_{po} = -3.7357 + 30.529\theta^{0.5} - 4.1034\theta + 0.024\,198\theta^2$	300–3500	0.19
NO_2	$\bar{C}_{po} = 46.045 + 216.10\theta^{-0.5} - 363.66\theta^{-0.75} + 232.550\theta^{-2}$	300–3500	0.26
CH_4	$\bar{C}_{po} = -672.87 + 439.74\theta^{0.25} - 24.875\theta^{0.75} + 323.88\theta^{-0.5}$	300–2000	0.15
C_2H_4	$\bar{C}_{po} = -95.395 + 123.15\theta^{0.5} - 35.641\theta^{0.75} + 182.77\theta^{-3}$	300–2000	0.07
C_2H_6	$\bar{C}_{po} = 6.895 + 17.26\theta - 0.6402\theta^2 + 0.007\,28\theta^3$	300–1500	0.83
C_3H_8	$\bar{C}_{po} = -4.042 + 30.46\theta - 1.571\theta^2 + 0.031\,71\theta^3$	300–1500	0.40
C_4H_{10}	$\bar{C}_{po} = 3.954 + 37.12\theta - 1.833\theta^2 + 0.034\,98\theta^3$	300–1500	0.54

Source: From T. C. Scott and R. E. Sonntag. University of Michigan, unpublished 1971, except C_2H_6, C_3H_8, and C_4H_{10} from K. A. Kobe, *Petroleum Refiner*, 28, No. 2, 113 (1949).

TABLE A.11SI Ideal-Gas Properties of Air (SI Units)

T, K	u, kJ/kg	h, kJ/kg	s°, kJ/kg K	P_r	v_r
200	142.768	200.174	6.462 60	0.270 27	493.466 1
220	157.071	220.218	6.558 12	0.377 00	389.149 4
240	171.379	240.267	6.645 35	0.510 88	313.273 5
260	185.695	260.323	6.725 62	0.675 73	256.584 0
280	200.022	280.390	6.799 98	0.875 56	213.256 6
300	214.364	300.473	6.869 26	1.114 58	179.490 6
320	228.726	320.576	6.934 13	1.397 22	152.727 7
340	243.113	340.704	6.995 15	1.728 14	131.199 4
360	257.532	360.863	7.052 76	2.112 26	113.654 2
380	271.988	381.060	7.107 35	2.554 79	99.188 24
400	286.487	401.299	7.159 26	3.061 19	87.136 65
420	301.035	421.589	7.208 75	3.637 27	77.002 50
440	315.640	441.934	7.256 07	4.289 16	68.408 81
460	330.306	462.340	7.301 42	5.023 33	61.065 77
480	345.039	482.814	7.344 99	5.846 63	54.747 87
500	359.844	503.360	7.386 92	6.766 29	49.277 71
520	374.726	523.982	7.427 36	7.789 97	44.514 26
540	389.689	544.686	7.466 42	8.925 69	40.344 39
560	404.736	565.474	7.504 22	10.181 97	36.676 49
580	419.871	586.350	7.540 84	11.567 71	33.435 81
600	435.097	607.316	7.576 38	13.092 32	30.560 89
620	450.415	628.375	7.610 90	14.765 64	28.000 82
640	465.828	649.528	7.644 48	16.598 01	25.713 15
660	481.335	670.776	7.677 17	18.600 25	23.662 28
680	496.939	692.120	7.709 03	20.783 67	21.818 16
700	512.639	713.561	7.740 10	23.160 10	20.155 29
720	528.435	735.098	7.770 44	25.741 88	18.651 92
740	544.328	756.731	7.800 08	28.541 88	17.289 43
760	560.316	778.460	7.829 05	31.573 47	16.051 76
780	576.400	800.284	7.857 40	34.850 61	14.925 04
800	592.577	822.202	7.885 14	38.387 77	13.897 24
820	608.847	844.212	7.912 32	42.199 98	12.957 85
840	625.208	866.314	7.938 95	46.302 83	12.097 71
860	641.659	888.506	7.965 06	50.712 50	11.308 76
880	658.198	910.786	7.990 68	55.445 70	10.583 91
900	674.824	933.152	8.015 81	60.519 77	9.916 92
920	691.534	955.603	8.040 48	65.952 61	9.302 23
940	708.328	978.138	8.064 72	71.762 72	8.734 95
960	725.203	1000.753	8.088 53	77.969 20	8.210 69
980	742.157	1023.448	8.111 93	84.591 78	7.725 55
1000	759.189	1046.221	8.134 93	91.650 77	7.276 04
1020	776.297	1069.069	8.157 56	99.167 15	6.859 05
1040	793.478	1091.991	8.179 81	107.162 5	6.471 75
1060	810.731	1114.984	8.201 71	115.659 0	6.111 64
1080	828.054	1138.048	8.223 27	124.679 6	5.776 43

TABLE A.11SI *(Continued)*

T, K	u, kJ/kg	h, kJ/kg	s°, kJ/kg K	P_r	v_r
1100	845.445	1161.180	8.244 49	134.247 8	5.464 08
1120	862.903	1184.379	8.265 39	144.387 8	5.172 72
1140	880.426	1207.642	8.285 98	155.124 4	4.900 68
1160	898.012	1230.969	8.306 26	166.483 3	4.646 42
1180	915.660	1254.357	8.326 25	178.490 7	4.408 57
1200	933.367	1277.805	8.345 96	191.173 5	4.185 86
1250	977.888	1336.677	8.394 02	226.019 2	3.688 04
1300	1022.751	1395.892	8.440 46	265.714 4	3.262 57
1350	1067.936	1455.429	8.485 39	310.742 6	2.897 11
1400	1113.426	1515.270	8.528 91	361.619 1	2.581 71
1450	1159.202	1575.398	8.571 11	418.894 2	2.308 31
1500	1205.253	1635.800	8.612 08	483.155 4	2.070 31
1550	1251.547	1696.446	8.651 85	554.957 7	1.862 53
1600	1298.079	1757.329	8.690 51	634.967 0	1.680 35
1650	1344.834	1818.436	8.728 11	723.856 0	1.520 07
1700	1391.801	1879.755	8.764 72	822.332 0	1.378 58
1750	1438.970	1941.275	8.800 39	931.137 6	1.253 30
1800	1486.331	2002.987	8.835 16	1051.051	1.142 30
1850	1533.873	2064.882	8.869 08	1182.887	1.042 04
1900	1581.591	2126.951	8.902 19	1327.498	0.954 45
1950	1629.474	2189.186	8.934 52	1485.772	0.875 21
2000	1677.518	2251.581	8.966 11	1658.635	0.804 10
2050	1725.714	2314.128	8.996 99	1847.076	0.740 12
2100	1774.057	2376.823	9.027 21	2052.108	0.682 42
2150	1822.541	2439.659	9.056 78	2274.788	0.630 27
2200	1871.161	2502.630	9.085 73	2516.216	0.583 05
2250	1919.912	2565.733	9.114 09	2777.537	0.540 20
2300	1968.790	2628.962	9.141 89	3059.939	0.501 24
2350	2017.789	2692.313	9.169 13	3364.657	0.465 76
2400	2066.907	2755.782	9.195 86	3692.973	0.433 38
2450	2116.138	2819.366	9.222 08	4046.215	0.403 78
2500	2165.480	2883.059	9.247 81	4425.759	0.376 69
2550	2214.929	2946.859	9.273 08	4833.030	0.351 85
2600	2264.481	3010.763	9.297 90	5269.504	0.329 03
2650	2314.133	3074.767	9.322 28	5736.707	0.308 05
2700	2363.883	3138.868	9.346 25	6236.214	0.288 72
2750	2413.727	3203.064	9.369 80	6769.656	0.270 89
2800	2463.663	3267.351	9.392 97	7338.714	0.254 43
2850	2513.687	3331.726	9.415 76	7945.124	0.239 21
2900	2563.797	3396.188	9.438 18	8590.676	0.225 11
2950	2613.990	3460.733	9.460 25	9277.216	0.212 05
3000	2664.265	3525.359	9.481 98	10 006.645	0.199 92

Source: Consistent with thermodynamic data in *JANAF Thermochemical Tables*, third edition, Thermal Group, Dow Chemical U.S.A., Midland, MI, 1985.

TABLE A.11E *Ideal-Gas Properties of Air (English Units)*

T, R	u, Btu/lbm	h, Btu/lbm	s°, Btu/lbm R	P_r	v_r
400	68.212	95.634	1.568 79	56.631 93	6079.381
440	75.047	105.212	1.591 61	79.002 01	4793.749
480	81.887	114.794	1.612 45	107.074 53	3858.476
520	88.733	124.383	1.631 64	141.657 73	3159.539
560	95.589	133.980	1.649 42	183.606 32	2625.192
600	102.457	143.590	1.666 00	233.824 98	2208.620
640	109.340	153.216	1.681 53	293.272 55	1878.318
680	116.242	162.860	1.696 15	362.966 61	1612.512
720	123.167	172.528	1.709 96	443.988 34	1395.795
760	130.118	182.221	1.723 06	537.487 44	1217.043
800	137.099	191.944	1.735 53	644.687 00	1068.075
840	144.114	201.701	1.747 43	766.888 16	942.774 9
880	151.165	211.494	1.758 82	905.474 52	836.502 4
920	158.255	221.327	1.769 74	1061.916 3	745.689 9
960	165.388	231.202	1.780 25	1237.774 2	667.560 4
1000	172.564	241.121	1.790 37	1434.702 9	599.927 5
1040	179.787	251.086	1.800 14	1654.454 3	541.052 4
1080	187.058	261.099	1.809 59	1898.880 7	489.538 4
1120	194.378	271.161	1.818 74	2169.937 5	444.254 2
1160	201.748	281.273	1.827 61	2469.685 7	404.275 1
1200	209.168	291.436	1.836 22	2800.294 5	368.840 2
1240	216.640	301.650	1.844 59	3164.043 5	337.318 3
1280	224.163	311.915	1.852 74	3563.325 0	309.182 7
1320	231.737	322.231	1.860 67	4000.645 9	283.991 0
1360	239.362	332.598	1.868 41	4478.629 7	261.369 2
1400	247.037	343.016	1.875 96	5000.018 7	241.000 0
1440	254.762	353.483	1.883 33	5567.675 3	222.612 4
1480	262.537	364.000	1.890 54	6184.584 4	205.973 7
1520	270.359	374.565	1.897 58	6853.854 7	190.883 9
1560	278.230	385.177	1.904 47	7578.720 7	177.169 7
1600	286.146	395.837	1.911 22	8362.544 1	164.680 5
1640	294.109	406.541	1.917 83	9208.815 9	153.285 4
1680	302.116	417.290	1.924 31	10 121.157	142.869 6
1720	310.166	428.083	1.930 66	11 103.324	133.332 5
1760	318.259	438.918	1.936 88	12 159.203	124.585 7
1800	326.393	449.794	1.943 00	13 292.820	116.551 0
1840	334.567	460.710	1.948 99	14 508.337	109.159 3
1880	342.780	471.666	1.954 88	15 810.055	102.349 3
1920	351.031	482.659	1.960 67	17 202.419	96.066 61
1960	359.319	493.689	1.966 36	18 690.015	90.262 46

TABLE A.11E *(Continued)*

T, R	u, Btu/lbm	h, Btu/lbm	s°, Btu/lbm R	P_r	v_r
2000	367.642	504.755	1.971 95	20 277.577	84.893 55
2040	376.001	515.856	1.977 44	21 969.986	79.921 04
2080	384.393	526.990	1.982 85	23 772.274	75.310 13
2120	392.819	538.158	1.988 16	25 689.626	71.029 52
2160	401.276	549.357	1.993 40	27 727.382	67.051 06
2200	409.764	560.588	1.998 55	29 891.043	63.349 38
2300	431.114	588.793	2.011 08	35 888.602	55.160 99
2400	452.640	617.175	2.023 16	42 802.021	48.262 27
2500	474.330	645.721	2.034 81	50 731.334	42.415 49
2600	496.175	674.421	2.046 07	59 784.038	37.432 50
2700	518.165	703.267	2.056 96	70 075.770	33.163 22
2800	540.286	732.244	2.067 50	81 718.665	29.491 55
2900	562.532	761.345	2.077 71	94 844.293	26.317 68
3000	584.895	790.564	2.087 61	109 587.64	23.562 45
3100	607.369	819.894	2.097 23	126 091.36	21.161 04
3200	629.948	849.328	2.106 58	144 505.97	19.060 09
3300	652.625	878.861	2.115 67	164 989.93	17.215 41
3400	675.396	908.488	2.124 51	187 709.82	15.590 24
3500	698.257	938.204	2.133 12	212 840.41	14.153 85
3600	721.203	968.005	2.141 52	240 564.71	12.880 46
3700	744.230	997.888	2.149 70	271 078.39	11.748 10
3800	767.334	1027.848	2.157 69	304 583.58	10.738 36
3900	790.513	1057.882	2.165 50	341 292.04	9.835 56
4000	813.763	1087.988	2.173 12	381 425.11	9.026 34
4100	837.081	1118.162	2.180 57	425 213.89	8.299 22
4200	860.466	1148.402	2.187 85	472 899.49	7.644 36
4300	883.913	1178.705	2.194 99	524 733.17	7.053 27
4400	907.422	1209.069	2.201 97	580 976.62	6.518 61
4500	930.989	1239.492	2.208 80	641 902.07	6.033 99
4600	954.613	1269.972	2.215 50	707 792.58	5.593 87
4700	978.292	1300.506	2.222 07	778 942.17	5.193 42
4800	1002.023	1331.093	2.228 51	855 656.05	4.828 39
4900	1025.806	1361.732	2.234 83	938 250.84	4.495 08
5000	1049.638	1392.419	2.241 02	1027 054.7	4.190 22
5100	1073.518	1423.155	2.247 11	1122 407.6	3.910 93
5200	1097.444	1453.936	2.253 09	1224 661.5	3.654 67
5300	1121.414	1484.762	2.258 96	1334 180.5	3.419 18
5400	1145.428	1515.632	2.264 73	1451 341.1	3.202 47

Source: Consistent with thermodynamic data in *JANAF Thermochemical Tables*, third edition, Thermal Group, Dow Chemical U.S.A., Midland, MI, 1985.

TABLE A.12SI Ideal-Gas Properties of Various Substances (SI Units), Entropies at 0.1-MPa (1-bar) Pressure

	Nitrogen, Diatomic (N_2) (3/77)		Nitrogen, Monatomic (N) (12/82)	
	$(\bar{h}_f^\circ)_{298} = 0$ kJ/kmol $M = 28.013$		$(\bar{h}_f^\circ)_{298} = 472\,680$ kJ/kmol $M = 14.007$	
Temp. K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−8670	0	−6197	0
100	−5768	159.812	−4119	130.593
200	−2857	179.985	−2040	145.001
298	0	191.609	0	153.300
300	54	191.789	38	153.429
400	2971	200.181	2117	159.409
500	5911	206.740	4196	164.047
600	8894	212.177	6274	167.837
700	11 937	216.865	8353	171.041
800	15 046	221.016	10 431	173.816
900	18 223	224.757	12 510	176.265
1000	21 463	228.171	14 589	178.455
1100	24 760	231.314	16 667	180.436
1200	28 109	234.227	18 746	182.244
1300	31 503	236.943	20 825	183.908
1400	34 936	239.487	22 903	185.448
1500	38 405	241.881	24 982	186.883
1600	41 904	244.139	27 060	188.224
1700	45 430	246.276	29 139	189.484
1800	48 979	248.304	31 218	190.672
1900	52 549	250.234	33 296	191.796
2000	56 137	252.075	35 375	192.863
2200	63 362	255.518	39 534	194.845
2400	70 640	258.684	43 695	196.655
2600	77 963	261.615	47 860	198.322
2800	85 323	264.342	52 033	199.868
3000	92 715	266.892	56 218	201.311
3200	100 134	269.286	60 420	202.667
3400	107 577	271.542	64 646	203.948
3600	115 042	273.675	68 902	205.164
3800	122 526	275.698	73 194	206.325
4000	130 027	277.622	77 532	207.437
4400	145 078	281.209	86 367	209.542
4800	160 188	284.495	95 457	211.519
5200	175 352	287.530	104 843	213.397
5600	190 572	290.349	114 550	215.195
6000	205 848	292.984	124 590	216.926

Source: Consistent with thermodynamic data in *JANAF Thermochemical Tables*, third edition, Thermal Group, Dow Chemical U.S.A., Midland, MI, 1985.

TABLE A.12SI *(Continued)*

	Oxygen, Diatomic (O_2) (3/77)		Oxygen, Monatomic (O) (9/82)	
	$(\bar{h}_f^\circ)_{298} = 0$ kJ/kmol $M = 31.999$		$(\bar{h}_f^\circ)_{298} = 249\,170$ kJ/kmol $M = 16.00$	
Temp. K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−8683	0	−6725	0
100	−5777	173.308	−4518	135.947
200	−2868	193.483	−2186	152.153
298	0	205.148	0	161.059
300	54	205.329	41	161.194
400	3027	213.873	2207	167.431
500	6086	220.693	4343	172.198
600	9245	226.450	6462	176.060
700	12 499	231.465	8570	179.310
800	15 836	235.920	10 671	182.116
900	19 241	239.931	12 767	184.585
1000	22 703	243.579	14 860	186.790
1100	26 212	246.923	16 950	188.783
1200	29 761	250.011	19 039	190.600
1300	33 345	252.878	21 126	192.270
1400	36 958	255.556	23 212	193.816
1500	40 600	258.068	25 296	195.254
1600	44 267	260.434	27 381	196.599
1700	47 959	262.673	29 464	197.862
1800	51 674	264.797	31 547	199.053
1900	55 414	266.819	33 630	200.179
2000	59 176	268.748	35 713	201.247
2200	66 770	272.366	39 878	203.232
2400	74 453	275.708	44 045	205.045
2600	82 225	278.818	48 216	206.714
2800	90 080	281.729	52 391	208.262
3000	98 013	284.466	56 574	209.705
3200	106 022	287.050	60 767	211.058
3400	114 101	289.499	64 971	212.332
3600	122 245	291.826	69 190	213.538
3800	130 447	294.043	73 424	214.682
4000	138 705	296.161	77 675	215.773
4400	155 374	300.133	86 234	217.812
4800	172 240	303.801	94 873	219.691
5200	189 312	307.217	103 592	221.435
5600	206 618	310.423	112 391	223.066
6000	224 210	313.457	121 264	224.597

(Continued)

TABLE A.12SI *(Continued)* Ideal-Gas Properties of Various Substances (SI Units), Entropies at 0.1-MPa (1-bar) Pressure

	Carbon Dioxide (CO_2) (9/65)		Carbon Monoxide (CO) (9/65)	
	$(\bar{h}_f^\circ)_{298} = -393\,522$ kJ/kmol $M = 44.01$		$(\bar{h}_f^\circ)_{298} = -110\,527$ kJ/kmol $M = 28.01$	
Temp. K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−9364	0	−8671	0
100	−6457	179.010	−5772	165.852
200	−3413	199.976	−2860	186.024
298	0	213.794	0	197.651
300	69	214.024	54	197.831
400	4003	225.314	2977	206.240
500	8305	234.902	5932	212.833
600	12 906	243.284	8942	218.321
700	17 754	250.752	12 021	223.067
800	22 806	257.496	15 174	227.277
900	28 030	263.646	18 397	231.074
1000	33 397	269.299	21 686	234.538
1100	38 885	274.528	25 031	237.726
1200	44 473	279.390	28 427	240.679
1300	50 148	283.931	31 867	243.431
1400	55 895	288.190	35 343	246.006
1500	61 705	292.199	38 852	248.426
1600	67 569	295.984	42 388	250.707
1700	73 480	299.567	45 948	252.866
1800	79 432	302.969	49 529	254.913
1900	85 420	306.207	53 128	256.860
2000	91 439	309.294	56 743	258.716
2200	103 562	315.070	64 012	262.182
2400	115 779	320.384	71 326	265.361
2600	128 074	325.307	78 679	268.302
2800	140 435	329.887	86 070	271.044
3000	152 853	334.170	93 504	273.607
3200	165 321	338.194	100 962	276.012
3400	177 836	341.988	108 440	278.279
3600	190 394	345.576	115 938	280.422
3800	202 990	348.981	123 454	282.454
4000	215 624	352.221	130 989	284.387
4400	240 992	358.226	146 108	287.989
4800	266 488	363.812	161 285	291.290
5200	292 112	368.939	176 510	294.337
5600	317 870	373.711	191 782	297.167
6000	343 782	378.180	207 105	299.809

TABLE A.12SI *(Continued)*

	Water (H_2O) (3/79)		Hydroxyl (OH) (6/77)	
	$(\bar{h}_f^\circ)_{298} = -241\,826$ kJ/kmol $M = 18.015$		$(\bar{h}_f^\circ)_{298} = 38\,987$ kJ/kmol $M = 17.007$	
Temp. K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−9904	0	−9172	0
100	−6617	152.386	−6140	149.591
200	−3282	175.488	−2975	171.592
298	0	188.835	0	183.709
300	62	189.043	55	183.894
400	3450	198.787	3034	192.466
500	6922	206.532	5991	199.066
600	10 499	213.051	8943	204.448
700	14 190	218.739	11 902	209.008
800	18 002	223.826	14 881	212.984
900	21 937	228.460	17 889	216.526
1000	26 000	232.739	20 935	219.735
1100	30 190	236.732	24 024	222.680
1200	34 506	240.485	27 159	225.408
1300	38 941	244.035	30 340	227.955
1400	43 491	247.406	33 567	230.347
1500	48 149	250.620	36 838	232.604
1600	52 907	253.690	40 151	234.741
1700	57 757	256.631	43 502	236.772
1800	62 693	259.452	46 890	238.707
1900	67 706	262.162	50 311	240.556
2000	72 788	264.769	53 763	242.328
2200	83 153	269.706	60 751	245.659
2400	93 741	274.312	67 840	248.743
2600	104 520	278.625	75 018	251.614
2800	115 463	282.680	82 268	254.301
3000	126 548	286.504	89 585	256.825
3200	137 756	290.120	96 960	259.205
3400	149 073	293.550	104 388	261.456
3600	160 484	296.812	111 864	263.592
3800	171 981	299.919	119 382	265.625
4000	183 552	302.887	126 940	267.563
4400	206 892	308.448	142 165	271.191
4800	230 456	313.573	157 522	274.531
5200	254 216	318.328	173 002	277.629
5600	278 161	322.764	188 598	280.518
6000	302 295	326.926	204 309	283.227

(Continued)

TABLE A.12SI *(Continued)* Ideal-Gas Properties of Various Substances (SI Units), Entropies at 0.1-MPa (1-bar) Pressure

	Hydrogen, Diatomic (H_2) (3/77)		Hydrogen, Monatomic (H) (3/82)	
	$(\bar{h}_f^\circ)_{298} = 0$ kJ/kmol $M = 2.016$		$(\bar{h}_f^\circ)_{298} = 217\,999$ kJ/kmol $M = 1.008$	
Temp. K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−8467	0	−6197	0
100	−5467	100.727	−4119	92.009
200	−2774	119.410	−2040	106.417
298	0	130.678	0	114.716
300	53	130.856	38	114.845
400	2961	139.219	2117	120.825
500	5883	145.738	4196	125.463
600	8799	151.078	6274	129.253
700	11 730	155.609	8353	132.457
800	14 681	159.554	10 431	135.233
900	17 657	163.060	12 510	137.681
1000	20 663	166.225	14 589	139.871
1100	23 704	169.121	16 667	141.852
1200	26 785	171.798	18 746	143.661
1300	29 907	174.294	20 825	145.324
1400	33 073	176.637	22 903	146.865
1500	36 281	178.849	24 982	148.299
1600	39 533	180.946	27 060	149.640
1700	42 826	182.941	29 139	150.900
1800	46 160	184.846	31 218	152.089
1900	49 532	186.670	33 296	153.212
2000	52 942	188.419	35 375	154.279
2200	59 865	191.719	39 532	156.260
2400	66 915	194.789	43 689	158.069
2600	74 082	197.659	47 847	159.732
2800	81 355	200.355	52 004	161.273
3000	88 725	202.898	56 161	162.707
3200	96 187	205.306	60 318	164.048
3400	103 736	207.593	64 475	165.308
3600	111 367	209.773	68 633	166.497
3800	119 077	211.856	72 790	167.620
4000	126 864	213.851	76 947	168.687
4400	142 658	217.612	85 261	170.668
4800	158 730	221.109	93 576	172.476
5200	175 057	224.379	101 890	174.140
5600	191 607	227.447	110 205	175.681
6000	208 332	230.322	118 519	177.114

TABLE A.12SI *(Continued)*

	Nitric Oxide (NO) (6/63)		Nitrogen Dioxide (NO_2) (6/64)	
	$(\bar{h}_f^\circ)_{298} = 90\,291$ kJ/kmol $M = 30.006$		$(\bar{h}_f^\circ)_{298} = 33\,100$ kJ/kmol $M = 46.005$	
Temp. K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K	$(\bar{h}^\circ - \bar{h}_{298}^\circ)$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol K
0	−9192	0	−10 186	0
100	−6073	177.031	−6861	202.563
200	−2951	198.747	−3495	225.852
298	0	210.759	0	240.034
300	55	210.943	68	240.263
400	3040	219.529	3927	251.342
500	6059	226.263	8099	260.638
600	9144	231.886	12 555	268.755
700	12 308	236.762	17 250	275.988
800	15 548	241.088	22 138	282.513
900	18 858	244.985	27 180	288.450
1000	22 229	248.536	32 344	293.889
1100	25 653	251.799	37 606	298.904
1200	29 120	254.816	42 946	303.551
1300	32 626	257.621	48 351	307.876
1400	36 164	260.243	53 808	311.920
1500	39 729	262.703	59 309	315.715
1600	43 319	265.019	64 846	319.289
1700	46 929	267.208	70 414	322.664
1800	50 557	269.282	76 008	325.861
1900	54 201	271.252	81 624	328.898
2000	57 859	273.128	87 259	331.788
2200	65 212	276.632	98 578	337.182
2400	72 606	279.849	109 948	342.128
2600	80 034	282.822	121 358	346.695
2800	87 491	285.585	132 800	350.934
3000	94 973	288.165	144 267	354.890
3200	102 477	290.587	155 756	358.597
3400	110 000	292.867	167 262	362.085
3600	117 541	295.022	178 783	365.378
3800	125 099	297.065	190 316	368.495
4000	132 671	299.007	201 860	371.456
4400	147 857	302.626	224 973	376.963
4800	163 094	305.940	248 114	381.997
5200	178 377	308.998	271 276	386.632
5600	193 703	311.838	294 455	390.926
6000	209 070	314.488	317 648	394.926

TABLE A.13 The Reduced Second Virial Coefficent $B^*(T^*)$ and Force Constants for the Lennard–Jones (6–12) Potential

TABLE A.13.1 The Reduced Second Virial Coefficient

T^*	$B^*(T^*)$	T^*	$B^*(T^*)$
0.3	−27.881	2.6	−0.266 13
0.4	−13.799	2.8	−0.184 51
0.5	−8.7202	3.0	−0.115 23
0.6	−6.1980	3.2	−0.055 79
0.7	−4.7100	3.4	−0.004 28
0.8	−3.7342	3.6	+0.040 72
0.9	−3.0471	3.8	0.080 33
1.0	−2.5381	4.0	0.115 42
1.1	−2.1464	4.2	0.146 68
1.2	−1.8359	4.4	0.174 69
1.3	−1.5841	4.6	0.199 90
1.4	−1.3758	4.8	0.222 68
1.5	−1.2009	5.0	0.243 34
1.6	−1.0519	6.0	0.322 90
1.7	−0.923 62	7.0	0.376 09
1.8	−0.812 03	8.0	0.413 43
1.9	−0.714 15	9.0	0.440 60
2.0	−0.627 63	10.0	0.460 88
2.2	−0.481 71	20.0	0.525 37
2.4	−0.363 58	30.0	0.526 93

TABLE A.13.2 Force Constants from Experimental Virial Coefficient Data

Substance	ϵ/k, K	b_0, m^3/kmol
Ne	35.8	0.0262
Ar	119.0	0.0502
Kr	173.0	0.0583
Xe	225.3	0.0854
N_2	95.05	0.0635
O_2	117.5	0.0578
CO	100.2	0.0675
NO	131.0	0.0402
CO_2	186.0	0.118
N_2O	193.0	0.118
CH_4	148.1	0.0698
CF_4	152	0.131

Source: From J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, second printing, corrected, with notes added, John Wiley and Sons, New York, March 1964.

TABLE A.14 Generalized Three-Parameter (T_r, P_r, ω) Compressibility Factor Tables

TABLE A.14.1 Generalized Saturation Pressure, Compressibility Factor, Fugacity Coefficient Table

$$XY = X^{(Y)},\ Y = 0 \text{ or } 1, \text{ and } X = X0 + \omega \times X1$$

where $X = \ln(P_r)$, Z_f, Z_g, or $\ln(f/P)$

T_r	$\ln(P_r)$ 0	$\ln(P_r)$ 1	Z_f0	Z_f1	Z_g0	Z_g1	$\ln(f/P)$ 0	$\ln(f/P)$ 1
0.30	−13.140 55	−20.250 52	0.000 00	0.000 01	0.999 98	−0.000 01	−0.000 02	−0.000 01
0.32	−11.890 25	−17.925 91	0.000 00	0.000 01	0.999 93	−0.000 02	−0.000 07	−0.000 02
0.34	−10.796 55	−15.916 85	0.000 01	−0.000 01	0.999 83	−0.000 06	−0.000 17	−0.000 06
0.36	−9.832 81	−14.169 98	0.000 02	0.000 00	0.999 63	−0.000 14	−0.000 37	−0.000 14
0.38	−8.978 01	−12.643 08	0.000 03	0.000 00	0.999 27	−0.000 30	−0.000 73	−0.000 30
0.40	−8.215 40	−11.302 30	0.000 06	0.000 00	0.998 65	−0.000 59	−0.001 34	−0.000 59
0.42	−7.531 40	−10.120 21	0.000 12	−0.000 01	0.997 70	−0.001 08	−0.002 30	−0.001 07
0.44	−6.914 92	−9.074 27	0.000 22	−0.000 02	0.996 28	−0.001 84	−0.003 71	−0.001 83
0.46	−6.356 83	−8.145 86	0.000 38	−0.000 04	0.994 30	−0.002 96	−0.005 68	−0.002 95
0.48	−5.849 50	−7.319 40	0.000 61	−0.000 07	0.991 65	−0.004 55	−0.008 32	−0.004 52
0.50	−5.386 53	−6.581 81	0.000 95	−0.000 13	0.988 20	−0.006 68	−0.011 73	−0.006 63
0.52	−4.962 53	−5.921 98	0.001 41	−0.000 21	0.983 89	−0.009 44	−0.016 00	−0.009 35
0.54	−4.572 89	−5.330 41	0.002 04	−0.000 34	0.978 62	−0.012 89	−0.021 18	−0.012 72
0.56	−4.213 67	−4.798 97	0.002 86	−0.000 52	0.972 33	−0.017 07	−0.027 34	−0.016 78
0.58	−3.881 46	−4.320 61	0.003 90	−0.000 76	0.964 98	−0.022 01	−0.034 49	−0.021 53

0.60	−3.573 31	−3.889 23	0.005 21	−0.001 09	0.956 52	−0.027 70	−0.042 65	−0.026 93
0.62	−3.286 66	−3.499 50	0.006 82	−0.001 52	0.946 95	−0.034 11	−0.051 82	−0.032 93
0.64	−3.019 26	−3.146 73	0.008 77	−0.002 07	0.936 23	−0.041 20	−0.061 98	−0.039 44
0.66	−2.769 13	−2.826 80	0.011 10	−0.002 76	0.924 36	−0.048 90	−0.073 12	−0.046 38
0.68	−2.534 52	−2.536 09	0.013 84	−0.003 61	0.911 33	−0.057 14	−0.085 19	−0.053 61
0.70	−2.313 88	−2.271 35	0.017 05	−0.004 65	0.897 11	−0.065 84	−0.098 17	−0.061 02
0.72	−2.105 84	−2.029 70	0.020 77	−0.005 89	0.881 70	−0.074 90	−0.112 03	−0.068 46
0.74	−1.909 15	−1.808 58	0.025 04	−0.007 36	0.865 06	−0.084 23	−0.126 74	−0.075 79
0.76	−1.722 72	−1.605 67	0.029 94	−0.009 09	0.847 12	−0.093 74	−0.142 27	−0.082 87
0.78	−1.545 54	−1.418 90	0.035 52	−0.011 12	0.827 82	−0.103 34	−0.158 61	−0.089 56
0.80	−1.376 72	−1.246 41	0.041 86	−0.013 46	0.807 04	−0.112 93	−0.175 76	−0.095 71
0.82	−1.215 45	−1.086 49	0.049 06	−0.016 19	0.784 63	−0.122 42	−0.193 73	−0.101 17
0.84	−1.060 97	−0.937 62	0.057 25	−0.019 34	0.760 36	−0.131 73	−0.212 54	−0.105 78
0.86	−0.912 63	−0.798 41	0.066 58	−0.023 02	0.733 94	−0.140 76	−0.232 24	−0.109 36
0.88	−0.769 80	−0.667 57	0.077 27	−0.027 32	0.704 91	−0.149 41	−0.252 90	−0.111 72
0.90	−0.631 92	−0.543 95	0.089 61	−0.032 43	0.672 62	−0.157 58	−0.274 61	−0.112 60
0.92	−0.498 47	−0.426 50	0.104 07	−0.038 64	0.636 05	−0.165 16	−0.297 50	−0.111 68
0.94	−0.368 98	−0.314 24	0.121 43	−0.046 49	0.593 47	−0.172 12	−0.321 76	−0.108 48
0.96	−0.243 01	−0.206 27	0.143 28	−0.057 26	0.541 46	−0.178 98	−0.347 66	−0.102 29
0.98	−0.120 14	−0.101 78	0.174 12	−0.075 57	0.471 12	−0.194 05	−0.375 60	−0.091 43
1.00	−0.160 08	−0.000 00	0.290 10	−0.087 90	0.290 10	−0.087 90	−0.406 39	−0.071 90

Source: Calculated using Lee–Kesler equation of state, Eq. 12.65.

(*Continued*)

TABLE A.14.1 *(Continued)* Generalized Saturation Enthalpy Departure and Entropy Departure Table

$$XY = X^{(Y)},\ Y = 0 \text{ or } 1, \text{ and } X = X0 + \omega \times X1$$

$$\text{where} \qquad X = dh_{f \text{ or } g} = \left(\frac{h^* - h}{RT_c}\right)_{f \text{ or } g}$$

$$\text{or} \qquad X = ds_{f \text{ or } g} = \left(\frac{s_P^* - s_P}{R}\right)_{f \text{ or } g}$$

T_r	dh_f0	dh_f1	dh_g0	dh_g1	ds_f0	ds_f1	ds_g0	ds_g1
0.30	6.046 16	11.101 62	0.000 02	0.000 01	20.099 53	6.484 13	0.000 05	0.000 02
0.32	5.990 61	10.929 42	0.000 07	0.000 03	18.065 62	14.044 51	0.000 14	0.000 07
0.34	5.935 15	10.747 80	0.000 18	0.000 09	16.518 69	17.047 28	0.000 35	0.000 19
0.36	5.878 95	10.552 73	0.000 40	0.000 22	16.018 37	15.585 14	0.000 76	0.000 46
0.38	5.821 77	10.343 11	0.000 85	0.000 49	15.311 91	12.460 79	0.001 50	0.001 00
0.40	5.763 67	10.119 67	0.001 63	0.001 03	14.411 29	12.878 08	0.002 72	0.001 98
0.42	5.704 81	9.884 17	0.002 91	0.001 98	13.583 78	13.106 85	0.004 63	0.003 65
0.44	5.645 39	9.638 85	0.004 89	0.003 57	12.820 92	13.002 70	0.007 41	0.006 29
0.46	5.585 58	9.386 07	0.007 81	0.006 07	12.137 84	12.279 12	0.011 29	0.010 25
0.48	5.525 53	9.128 08	0.011 91	0.009 81	11.503 44	11.731 30	0.016 48	0.015 91
0.50	5.465 34	8.866 95	0.017 45	0.015 14	10.918 01	11.200 36	0.023 17	0.023 64
0.52	5.405 09	8.604 46	0.024 72	0.022 46	10.376 36	10.686 01	0.031 55	0.033 84
0.54	5.344 81	8.342 13	0.033 99	0.032 17	9.873 61	10.190 96	0.041 76	0.046 86
0.56	5.284 47	8.081 20	0.045 52	0.044 68	9.405 54	9.721 97	0.053 95	0.063 00
0.58	5.224 03	7.822 69	0.059 58	0.060 35	8.968 10	9.264 60	0.068 23	0.082 53

0.60	5.163 43	7.567 39	0.076 41	0.079 55	8.558 83	8.829 93	0.084 70	0.105 66
0.62	5.102 55	7.315 91	0.096 26	0.102 59	8.174 15	8.416 73	0.103 44	0.132 54
0.64	5.041 26	7.068 70	0.119 38	0.129 76	7.811 56	8.023 57	0.124 55	0.163 30
0.66	4.979 40	6.826 07	0.146 01	0.161 31	7.468 73	7.649 48	0.148 11	0.198 03
0.68	4.916 78	6.588 22	0.176 40	0.197 48	7.143 58	7.293 51	0.174 23	0.236 80
0.70	4.853 18	6.355 24	0.210 84	0.238 51	6.834 15	6.954 71	0.203 02	0.279 71
0.72	4.788 32	6.127 17	0.249 61	0.284 63	6.538 67	6.631 80	0.234 65	0.326 87
0.74	4.721 90	5.903 94	0.293 09	0.336 13	6.255 49	6.324 58	0.269 34	0.378 44
0.76	4.653 55	5.685 43	0.341 70	0.393 33	5.983 04	6.031 43	0.307 34	0.434 67
0.78	4.582 83	5.471 46	0.395 95	0.456 66	5.719 81	5.751 41	0.349 02	0.495 90
0.80	4.509 22	5.261 80	0.456 50	0.526 70	5.464 32	5.483 49	0.394 86	0.562 66
0.82	4.432 03	5.056 14	0.524 18	0.604 19	5.215 08	5.226 70	0.445 52	0.635 65
0.84	4.350 43	4.854 10	0.600 10	0.690 22	4.970 49	4.979 97	0.501 87	0.715 91
0.86	4.263 29	4.655 20	0.685 74	0.786 28	4.728 80	4.742 21	0.565 14	0.804 91
0.88	4.169 06	4.458 83	0.783 19	0.894 57	4.487 93	4.512 21	0.637 09	0.904 84
0.90	4.065 48	4.264 19	0.895 50	1.018 50	4.245 17	4.288 62	0.720 40	1.019 07
0.92	3.949 04	4.070 17	1.027 44	1.163 67	3.996 68	4.069 80	0.819 28	1.153 18
0.94	3.813 58	3.875 20	1.187 19	1.340 53	3.736 13	3.853 63	0.941 20	1.317 61
0.96	3.646 43	3.677 04	1.391 16	1.573 46	3.450 88	3.637 35	1.101 46	1.536 73
0.98	3.411 36	3.475 96	1.683 60	1.970 79	3.105 21	3.420 52	1.342 35	1.919 59
1.00	2.584 38	2.470 76	2.584 38	2.470 76	2.177 99	2.398 87	2.177 99	2.398 87

Source: Calculated Using Lee–Kesler equation of state, Eq. 12.65.

TABLE A.14.2 Generalized Compressibility Factor Table $Z = Z0 + \omega \times Z1$; Notation, Table A.14.1

T_r	P_r	0.10	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.70	2.00	2.50	3.00	5.00	7.00	10.00
0.30	Z0	0.0290	0.0579	0.1158	0.1737	0.2315	0.2892	0.3470	0.4047	0.4911	0.5775	0.7213	0.8648	1.4366	2.0048	2.8507
	Z1	−0.0081	−0.0161	−0.0323	−0.0484	−0.0645	−0.0806	−0.0966	−0.1127	−0.1368	−0.1608	−0.2008	−0.2407	−0.3996	−0.5572	−0.7916
0.40	Z0	0.0239	0.0477	0.0953	0.1429	0.1904	0.2379	0.2853	0.3327	0.4036	0.4744	0.5921	0.7095	1.1758	1.6373	2.3211
	Z1	−0.0095	−0.0190	−0.0380	−0.0570	−0.0758	−0.0946	−0.1134	−0.1321	−0.1601	−0.1879	−0.2341	−0.2799	−0.4603	−0.6365	−0.8936
0.50	Z0	0.0207	0.0413	0.0825	0.1236	0.1647	0.2056	0.2465	0.2873	0.3483	0.4092	0.5103	0.6110	1.0094	1.4017	1.9801
	Z1	−0.0090	−0.0181	−0.0360	−0.0539	−0.0716	−0.0893	−0.1069	−0.1243	−0.1504	−0.1762	−0.2189	−0.2611	−0.4253	−0.5831	−0.8099
0.60	Z0	0.0186	0.0371	0.0741	0.1109	0.1476	0.1842	0.2207	0.2571	0.3115	0.3657	0.4554	0.5446	0.8959	1.2398	1.7440
	Z1	−0.0082	−0.0164	−0.0326	−0.0487	−0.0646	−0.0803	−0.0960	−0.1115	−0.1345	−0.1572	−0.1945	−0.2312	−0.3718	−0.5047	−0.6929
0.70	Z0	0.0172	0.0344	0.0687	0.1027	0.1366	0.1703	0.2038	0.2372	0.2869	0.3364	0.4181	0.4991	0.8161	1.1241	1.5729
	Z1	−0.0075	−0.0148	−0.0294	−0.0438	−0.0579	−0.0718	−0.0855	−0.0990	−0.1189	−0.1385	−0.1703	−0.2013	−0.3184	−0.4270	−0.5785
0.75	Z0	0.9165	0.0336	0.0670	0.1001	0.1330	0.1656	0.1981	0.2303	0.2784	0.3260	0.4046	0.4823	0.7854	1.0787	1.5047
	Z1	−0.0744	−0.0143	−0.0282	−0.0417	−0.0550	−0.0681	−0.0808	−0.0934	−0.1118	−0.1298	−0.1590	−0.1872	−0.2929	−0.3901	−0.5250
0.80	Z0	0.9319	0.8539	0.0661	0.0985	0.1307	0.1626	0.1942	0.2255	0.2721	0.3182	0.3942	0.4690	0.7598	1.0400	1.4456
	Z1	−0.0487	−0.1160	−0.0272	−0.0401	−0.0526	−0.0648	−0.0767	−0.0883	−0.1052	−0.1217	−0.1481	−0.1736	−0.2682	−0.3545	−0.4740
0.85	Z0	0.9436	0.8810	0.0661	0.0983	0.1301	0.1614	0.1924	0.2230	0.2684	0.3132	0.3868	0.4591	0.7388	1.0071	1.3943
	Z1	−0.0319	−0.0715	−0.0268	−0.0391	−0.0509	−0.0622	−0.0731	−0.0837	−0.0990	−0.1138	−0.1375	−0.1602	−0.2439	−0.3201	−0.4254
0.90	Z0	0.9528	0.9015	0.7800	0.1006	0.1321	0.1630	0.1935	0.2235	0.2678	0.3114	0.3828	0.4527	0.7220	0.9793	1.3496
	Z1	−0.0205	−0.0442	−0.1118	−0.0396	−0.0503	−0.0604	−0.0701	−0.0795	−0.0929	−0.1059	−0.1265	−0.1463	−0.2195	−0.2862	−0.3788
0.95	Z0	0.9600	0.9174	0.8206	0.6967	0.1410	0.1705	0.1998	0.2288	0.2717	0.3138	0.3827	0.4501	0.7092	0.9561	1.3108
	Z1	−0.0126	−0.0262	−0.0589	−0.1110	−0.0540	−0.0607	−0.0678	−0.0751	−0.0860	−0.0967	−0.1141	−0.1310	−0.1943	−0.2526	−0.3339
1.00	Z0	0.9659	0.9300	0.8509	0.7574	0.6353	0.2901	0.2237	0.2459	0.2839	0.3229	0.3880	0.4522	0.7004	0.9372	1.2772
	Z1	−0.0069	−0.0140	−0.0285	−0.0435	−0.0588	−0.0879	−0.0609	−0.0652	−0.0735	−0.0824	−0.0972	−0.1118	−0.1672	−0.2185	−0.2902
1.05	Z0	0.9707	0.9401	0.8743	0.8002	0.7130	0.6026	0.4437	0.3246	0.3182	0.3452	0.4014	0.4604	0.6956	0.9222	1.2481
	Z1	−0.0029	−0.0054	−0.0092	−0.0097	−0.0032	0.0220	0.1059	0.0951	−0.0117	−0.0432	−0.0671	−0.0838	−0.1370	−0.1835	−0.2476
1.10	Z0	0.9747	0.9485	0.8930	0.8323	0.7649	0.6880	0.5984	0.5003	0.4086	0.3953	0.4277	0.4770	0.6950	0.9110	1.2232
	Z1	0.0001	0.0007	0.0038	0.0106	0.0236	0.0476	0.0897	0.1468	0.1418	0.0698	−0.0033	−0.0373	−0.1021	−0.1469	−0.2056

1.15	Z0	0.9780	0.9554	0.9081	0.8576	0.8032	0.7443	0.6803	0.6129	0.5227	0.4760	0.4718	0.5042	0.6987	0.9033	1.2021
	Z1	0.0023	0.0052	0.0127	0.0237	0.0396	0.0625	0.0943	0.1345	0.1815	0.1667	0.0906	0.0332	−0.0611	−0.1084	−0.1642
1.20	Z0	0.9808	0.9611	0.9205	0.8779	0.8330	0.7858	0.7363	0.6856	0.6135	0.5605	0.5295	0.5425	0.7069	0.8990	1.1844
	Z1	0.0040	0.0084	0.0190	0.0326	0.0499	0.0719	0.0991	0.1310	0.1780	0.1990	0.1651	0.1095	−0.0141	−0.0678	−0.1231
1.30	Z0	0.9852	0.9702	0.9396	0.9083	0.8764	0.8438	0.8111	0.7784	0.7316	0.6908	0.6467	0.6344	0.7358	0.8998	1.1580
	Z1	0.0061	0.0125	0.0267	0.0429	0.0612	0.0819	0.1048	0.1294	0.1669	0.1991	0.2223	0.2079	0.0875	0.0176	−0.0423
1.40	Z0	0.9884	0.9768	0.9534	0.9298	0.9062	0.8827	0.8595	0.8367	0.8043	0.7753	0.7387	0.7202	0.7761	0.9112	1.1419
	Z1	0.0072	0.0147	0.0306	0.0477	0.0661	0.0857	0.1063	0.1276	0.1596	0.1894	0.2259	0.2397	0.1737	0.1008	0.0350
1.50	Z0	0.9909	0.9818	0.9636	0.9456	0.9278	0.9103	0.8933	0.8768	0.8536	0.8328	0.8052	0.7887	0.8200	0.9297	1.1339
	Z1	0.0078	0.0158	0.0323	0.0497	0.0677	0.0864	0.1055	0.1248	0.1535	0.1806	0.2186	0.2433	0.2309	0.1717	0.1058
1.60	Z0	0.9928	0.9856	0.9714	0.9575	0.9439	0.9308	0.9180	0.9059	0.8889	0.8738	0.8537	0.8410	0.8617	0.9518	1.1320
	Z1	0.0080	0.0162	0.0330	0.0501	0.0677	0.0855	0.1035	0.1214	0.1478	0.1729	0.2098	0.2381	0.2631	0.2255	0.1673
1.80	Z0	0.9955	0.9910	0.9823	0.9739	0.9659	0.9583	0.9511	0.9444	0.9353	0.9275	0.9176	0.9118	0.9297	0.9961	1.1391
	Z1	0.0081	0.0162	0.0325	0.0488	0.0652	0.0816	0.0978	0.1137	0.1370	0.1593	0.1932	0.2224	0.2846	0.2871	0.2576
2.00	Z0	0.9972	0.9944	0.9892	0.9842	0.9796	0.9754	0.9715	0.9680	0.9635	0.9599	0.9561	0.9550	0.9772	1.0328	1.1516
	Z1	0.0078	0.0155	0.0310	0.0464	0.0617	0.0767	0.0916	0.1061	0.1273	0.1476	0.1789	0.2069	0.2820	0.3097	0.3096
2.50	Z0	0.9994	0.9989	0.9981	0.9975	0.9971	0.9969	0.9970	0.9973	0.9982	0.9996	1.0031	1.0080	1.0395	1.0866	1.1763
	Z1	0.0068	0.0135	0.0268	0.0399	0.0528	0.0654	0.0778	0.0899	0.1075	0.1245	0.1511	0.1757	0.2542	0.3052	0.3475
3.00	Z0	1.0004	1.0008	1.0018	1.0030	1.0043	1.0057	1.0074	1.0091	1.0121	1.0153	1.0215	1.0284	1.0635	1.1075	1.1848
	Z1	0.0059	0.0117	0.0232	0.0345	0.0456	0.0565	0.0672	0.0776	0.0929	0.1076	0.1310	0.1529	0.2268	0.2817	0.3385
3.50	Z0	1.0008	1.0017	1.0035	1.0055	1.0075	1.0097	1.0120	1.0143	1.0181	1.0221	1.0292	1.0368	1.0723	1.1138	1.1834
	Z1	0.0052	0.0103	0.0204	0.0303	0.0401	0.0497	0.0591	0.0683	0.0818	0.0949	0.1158	0.1356	0.2042	0.2584	0.3194
4.00	Z0	1.0010	1.0021	1.0043	1.0066	1.0090	1.0115	1.0140	1.0166	1.0207	1.0249	1.0323	1.0401	1.0747	1.1136	1.1773
	Z1	0.0046	0.0091	0.0182	0.0270	0.0357	0.0443	0.0527	0.0610	0.0731	0.0849	0.1038	0.1219	0.1857	0.2378	0.2994
5.00	Z0	1.0012	1.0024	1.0048	1.0073	1.0098	1.0124	1.0150	1.0176	1.0217	1.0259	1.0331	1.0405	1.0722	1.1064	1.1611
	Z1	0.0038	0.0075	0.0149	0.0222	0.0294	0.0365	0.0434	0.0503	0.0604	0.0703	0.0863	0.1016	0.1573	0.2047	0.2637

Source: Calculated using Lee–Kesler equation of state, Eq. 12.65.

TABLE A.14.3 Generalized Enthalpy Departure Table [$dh = (h^* - h)/RT_c$]: $dh = dh0 + \omega \times dh1$; Notation, Table A.14.1

T_r	P_r	0.10	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.70	2.00	2.50	3.00	5.00	7.00	10.00
0.30	$dh0$	6.040	6.034	6.022	6.011	5.999	5.987	5.975	5.963	5.945	5.927	5.898	5.868	5.748	5.628	5.446
	$dh1$	11.098	11.095	11.088	11.081	11.074	11.067	11.061	11.054	11.044	11.034	11.017	11.001	10.936	10.873	10.782
0.40	$dh0$	5.757	5.751	5.738	5.726	5.713	5.700	5.687	5.675	5.655	5.636	5.604	5.572	5.442	5.311	5.113
	$dh1$	10.120	10.120	10.120	10.120	10.120	10.120	10.120	10.120	10.120	10.121	10.121	10.122	10.127	10.135	10.150
0.50	$dh0$	5.459	5.453	5.440	5.427	5.414	5.401	5.388	5.375	5.355	5.336	5.303	5.270	5.135	4.999	4.791
	$dh1$	8.869	8.871	8.875	8.879	8.883	8.887	8.891	8.895	8.902	8.908	8.919	8.931	8.979	9.030	9.111
0.60	$dh0$	5.159	5.153	5.141	5.129	5.116	5.104	5.091	5.079	5.060	5.041	5.008	4.976	4.842	4.704	4.492
	$dh1$	7.570	7.573	7.579	7.585	7.592	7.598	7.605	7.611	7.622	7.632	7.650	7.668	7.744	8.825	7.950
0.70	$dh0$	4.853	4.848	4.839	4.828	4.818	4.808	4.797	4.786	4.769	4.752	4.723	4.693	4.566	4.432	4.221
	$dh1$	6.356	6.360	6.366	6.373	6.381	6.388	6.396	6.404	6.417	6.430	6.452	6.475	6.573	6.677	6.837
0.75	$dh0$	0.183	4.687	4.679	4.672	4.664	4.655	4.646	4.637	4.622	4.607	4.581	4.554	4.434	4.303	4.095
	$dh1$	0.306	5.796	5.803	5.809	5.816	5.824	5.832	5.841	5.854	5.868	5.892	5.918	6.027	6.141	6.317
0.80	$dh0$	0.160	0.345	4.507	4.504	4.499	4.494	4.488	4.481	4.470	4.459	4.437	4.413	4.303	4.178	3.974
	$dh1$	0.234	0.542	5.266	5.271	5.277	5.285	5.292	5.301	5.315	5.330	5.356	5.384	5.506	5.632	5.824
0.85	$dh0$	0.141	0.300	4.308	4.313	4.316	4.316	4.316	4.314	4.309	4.302	4.287	4.269	4.173	4.056	3.857
	$dh1$	0.182	0.401	4.753	4.754	4.758	4.763	4.771	4.779	4.794	4.810	4.840	4.871	5.008	5.149	5.358
0.90	$dh0$	0.126	0.264	0.596	4.074	4.094	4.108	4.118	4.125	4.130	4.132	4.129	4.119	4.043	3.935	3.744
	$dh1$	0.144	0.308	0.751	4.254	4.248	4.249	4.255	4.263	4.279	4.298	4.333	4.371	4.530	4.688	4.916
0.95	$dh0$	0.113	0.235	0.516	0.885	3.763	3.825	3.865	3.893	3.922	3.939	3.955	3.958	3.910	3.815	3.634
	$dh1$	0.115	0.241	0.542	0.994	3.737	3.713	3.713	3.723	3.746	3.773	3.822	3.873	4.068	4.248	4.498
1.00	$dh0$	0.103	0.212	0.455	0.750	1.151	2.584	3.441	3.560	3.653	3.706	3.757	3.782	3.774	3.695	3.526
	$dh1$	0.093	0.191	0.410	0.675	1.034	2.471	2.952	3.033	3.119	3.186	3.279	3.358	3.615	3.825	4.100
1.05	$dh0$	0.094	0.192	0.407	0.654	0.955	1.359	2.034	2.831	3.243	3.398	3.521	3.583	3.632	3.575	3.420
	$dh1$	0.075	0.153	0.318	0.498	0.691	0.877	0.878	1.113	2.027	2.381	2.645	2.800	3.167	3.418	3.722
1.10	$dh0$	0.086	0.175	0.367	0.581	0.827	1.120	1.487	1.955	2.609	2.965	3.231	3.353	3.484	3.453	3.315
	$dh1$	0.061	0.123	0.251	0.381	0.507	0.617	0.673	0.631	0.780	1.261	1.853	2.167	2.720	3.023	3.362

1.15	*dh*0	0.079	0.160	0.334	0.523	0.732	0.968	1.239	1.550	2.059	2.479	2.888	3.091	3.329	3.329	3.211
	*dh*1	0.050	0.099	0.199	0.296	0.385	0.459	0.503	0.502	0.468	0.604	1.083	1.497	2.275	2.641	3.019
1.20	*dh*0	0.073	0.148	0.305	0.474	0.657	0.857	1.076	1.315	1.704	2.079	2.537	2.807	3.166	3.202	3.107
	*dh*1	0.040	0.080	0.158	0.232	0.297	0.349	0.381	0.388	0.358	0.361	0.591	0.934	1.840	2.273	2.692
1.30	*dh*0	0.063	0.127	0.259	0.399	0.545	0.698	0.860	1.029	1.293	1.560	1.964	2.274	2.825	2.942	2.899
	*dh*1	0.026	0.052	0.100	0.142	0.177	0.203	0.218	0.221	0.205	0.178	0.182	0.300	1.066	1.592	2.086
1.40	*dh*0	0.055	0.110	0.224	0.341	0.463	0.588	0.716	0.848	1.050	1.253	1.576	1.857	2.486	2.679	2.692
	*dh*1	0.016	0.032	0.060	0.083	0.100	0.111	0.115	0.112	0.096	0.070	0.034	0.044	0.504	1.012	1.547
1.50	*dh*0	0.048	0.097	0.196	0.297	0.400	0.505	0.611	0.719	0.883	1.046	1.309	1.549	2.175	2.421	2.486
	*dh*1	0.009	0.018	0.032	0.042	0.048	0.049	0.046	0.038	0.018	−0.008	−0.052	−0.078	0.142	0.556	1.080
1.60	*dh*0	0.043	0.086	0.173	0.261	0.350	0.440	0.531	0.622	0.759	0.894	1.114	1.318	1.904	2.177	2.285
	*dh*1	0.004	0.007	0.012	0.013	0.011	0.005	−0.004	−0.016	−0.038	−0.065	−0.113	−0.151	−0.082	0.217	0.689
1.80	*dh*0	0.034	0.068	0.137	0.206	0.275	0.344	0.413	0.481	0.583	0.683	0.844	0.996	1.476	1.751	1.908
	*dh*1	−0.003	−0.006	−0.015	−0.025	−0.037	−0.051	−0.067	−0.084	−0.113	−0.143	−0.194	−0.241	−0.317	−0.203	0.112
2.00	*dh*0	0.028	0.056	0.111	0.167	0.222	0.276	0.330	0.384	0.463	0.541	0.665	0.782	1.167	1.411	1.577
	*dh*1	−0.007	−0.015	−0.030	−0.047	−0.065	−0.085	−0.105	−0.125	−0.157	−0.190	−0.244	−0.295	−0.428	−0.424	−0.255
2.50	*dh*0	0.018	0.035	0.070	0.104	0.137	0.170	0.203	0.234	0.281	0.326	0.398	0.465	0.687	0.838	0.954
	*dh*1	−0.012	−0.025	−0.049	−0.075	−0.100	−0.125	−0.150	−0.176	−0.213	−0.250	−0.310	−0.367	−0.552	−0.661	−0.704
3.00	*dh*0	0.011	0.023	0.045	0.067	0.088	0.109	0.129	0.149	0.177	0.205	0.248	0.288	0.415	0.495	0.545
	*dh*1	−0.014	−0.029	−0.058	−0.086	−0.114	−0.142	−0.170	−0.198	−0.238	−0.278	−0.342	−0.403	−0.611	−0.763	−0.899
3.50	*dh*0	0.007	0.015	0.029	0.043	0.056	0.069	0.081	0.093	0.111	0.127	0.152	0.174	0.239	0.270	0.264
	*dh*1	−0.016	−0.031	−0.062	−0.092	−0.122	−0.152	−0.181	−0.210	−0.253	−0.294	−0.361	−0.425	−0.650	−0.827	−1.015
4.00	*dh*0	0.005	0.009	0.017	0.026	0.033	0.041	0.048	0.054	0.064	0.072	0.085	0.095	0.116	0.110	0.061
	*dh*1	−0.016	−0.032	−0.064	−0.096	−0.127	−0.158	−0.188	−0.218	−0.262	−0.306	−0.375	−0.442	−0.680	−0.874	−1.097
5.00	*dh*0	0.001	0.001	0.002	0.003	0.004	0.004	0.004	0.004	0.003	0.001	−0.003	−0.009	−0.045	−0.101	−0.213
	*dh*1	−0.017	−0.034	−0.068	−0.101	−0.133	−0.166	−0.198	−0.229	−0.276	−0.321	−0.395	−0.466	−0.726	−0.947	−1.219

Source: Calculated using Lee–Kesler equation of state, Eq. 12.65.

TABLE A.14.4 Generalized Entropy Departure Table $[ds = (s^* - s)/R]$: $ds = ds0 + \omega \times ds1$; Notation, Table A.14.1

T_r	P_r	0.10	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.70	2.00	2.50	3.00	5.00	7.00	10.00
0.30	*ds*0	9.319	8.635	7.961	7.574	7.304	7.099	6.935	6.799	6.633	6.497	6.319	6.182	5.847	5.683	5.578
	*ds*1	16.773	16.753	16.714	16.675	16.637	16.598	16.559	16.521	16.463	16.405	16.310	16.214	15.838	15.469	14.927
0.40	*ds*0	8.506	7.821	7.144	6.755	6.483	6.275	6.109	5.970	5.799	5.660	5.475	5.330	4.967	4.772	4.619
	*ds*1	13.980	13.971	13.951	13.932	13.914	13.895	13.876	13.858	13.830	13.803	13.757	13.713	13.540	13.376	13.144
0.50	*ds*0	7.842	7.156	6.479	6.089	5.816	5.608	5.441	5.302	5.130	4.989	4.802	4.656	4.282	4.074	3.899
	*ds*1	11.196	11.191	11.181	11.171	11.161	11.151	11.142	11.132	11.118	11.105	11.083	11.063	10.986	10.920	10.836
0.60	*ds*0	7.294	6.610	5.933	5.544	5.273	5.066	4.900	4.762	4.591	4.451	4.266	4.120	3.747	3.537	3.353
	*ds*1	8.827	8.823	8.817	8.811	8.806	8.800	8.795	8.790	8.784	8.777	8.768	8.759	8.735	8.723	8.720
0.70	*ds*0	6.823	6.140	5.467	5.082	4.814	4.610	4.446	4.310	4.143	4.007	3.826	3.684	3.322	3.117	2.935
	*ds*1	6.954	6.951	6.946	6.941	6.937	6.933	6.930	6.928	6.924	6.922	6.919	6.919	6.928	6.952	7.002
0.75	*ds*0	0.164	5.917	5.248	4.866	4.600	4.399	4.238	4.104	3.940	3.807	3.630	3.491	3.138	2.939	2.761
	*ds*1	0.340	6.173	6.167	6.162	6.158	6.155	6.152	6.150	6.148	6.146	6.147	6.149	6.174	6.213	6.285
0.80	*ds*0	0.134	0.294	5.026	4.649	4.388	4.191	4.034	3.904	3.744	3.615	3.444	3.310	2.970	2.777	2.605
	*ds*1	0.246	0.578	5.474	5.467	5.462	5.458	5.455	5.453	5.452	5.452	5.455	5.461	5.501	5.555	5.648
0.85	*ds*0	0.111	0.239	4.785	4.418	4.166	3.976	3.825	3.701	3.548	3.425	3.262	3.135	2.812	2.629	2.463
	*ds*1	0.183	0.408	4.853	4.841	4.832	4.826	4.822	4.820	4.820	4.822	4.828	4.839	4.898	4.969	5.083
0.90	*ds*0	0.094	0.199	0.463	4.145	3.912	3.738	3.599	3.484	3.344	3.231	3.081	2.963	2.663	2.491	2.334
	*ds*1	0.140	0.301	0.744	4.269	4.250	4.238	4.232	4.230	4.231	4.236	4.250	4.267	4.351	4.442	4.578
0.95	*ds*0	0.080	0.168	0.377	0.671	3.556	3.433	3.326	3.235	3.119	3.023	2.893	2.790	2.520	2.361	2.215
	*ds*1	0.109	0.228	0.517	0.961	3.697	3.658	3.647	3.646	3.655	3.669	3.697	3.728	3.851	3.966	4.125
1.00	*ds*0	0.069	0.144	0.315	0.532	0.847	2.178	2.893	2.893	2.843	2.784	2.690	2.609	2.380	2.239	2.105
	*ds*1	0.086	0.177	0.382	0.632	0.977	2.399	2.868	2.940	3.012	3.067	3.140	3.200	3.387	3.532	3.717
1.05	*ds*0	0.060	0.124	0.267	0.439	0.656	0.965	1.523	2.185	2.444	2.483	2.461	2.415	2.242	2.121	2.001
	*ds*1	0.069	0.140	0.292	0.460	0.642	0.820	0.831	1.073	1.951	2.283	2.522	2.655	2.949	3.134	3.348
1.10	*ds*0	0.053	0.108	0.230	0.371	0.537	0.742	1.012	1.368	1.855	2.081	2.191	2.202	2.104	2.007	1.903
	*ds*1	0.055	0.112	0.229	0.350	0.470	0.577	0.640	0.620	0.786	1.241	1.786	2.067	2.534	2.767	3.013

1.15	*ds*0	0.047	0.096	0.201	0.319	0.452	0.607	0.790	1.007	1.366	1.649	1.885	1.968	1.966	1.897	1.810
	*ds*1	0.045	0.091	0.183	0.275	0.361	0.437	0.489	0.506	0.507	0.654	1.100	1.471	2.138	2.428	2.708
1.20	*ds*0	0.042	0.085	0.177	0.277	0.389	0.512	0.651	0.807	1.063	1.308	1.587	1.727	1.827	1.789	1.722
	*ds*1	0.037	0.075	0.149	0.220	0.286	0.343	0.385	0.408	0.414	0.447	0.680	0.991	1.767	2.115	2.430
1.30	*ds*0	0.033	0.068	0.140	0.217	0.298	0.385	0.478	0.576	0.732	0.891	1.127	1.299	1.554	1.581	1.556
	*ds*1	0.026	0.052	0.102	0.148	0.190	0.226	0.254	0.275	0.291	0.300	0.351	0.481	1.147	1.569	1.944
1.40	*ds*0	0.027	0.056	0.114	0.174	0.237	0.303	0.372	0.442	0.552	0.663	0.839	0.990	1.303	1.386	1.402
	*ds*1	0.019	0.037	0.072	0.104	0.133	0.158	0.178	0.194	0.210	0.220	0.240	0.290	0.730	1.138	1.544
1.50	*ds*0	0.023	0.046	0.094	0.143	0.194	0.246	0.299	0.353	0.436	0.520	0.654	0.777	1.088	1.208	1.260
	*ds*1	0.014	0.027	0.053	0.076	0.097	0.115	0.130	0.142	0.156	0.166	0.181	0.206	0.479	0.823	1.222
1.60	*ds*0	0.019	0.039	0.079	0.120	0.162	0.204	0.247	0.290	0.356	0.421	0.528	0.628	0.913	1.050	1.130
	*ds*1	0.011	0.021	0.040	0.057	0.073	0.086	0.098	0.108	0.119	0.129	0.142	0.159	0.334	0.604	0.969
1.80	*ds*0	0.014	0.029	0.058	0.088	0.117	0.147	0.177	0.207	0.252	0.296	0.369	0.438	0.661	0.799	0.908
	*ds*1	0.006	0.013	0.024	0.035	0.044	0.053	0.060	0.067	0.075	0.083	0.094	0.105	0.195	0.355	0.628
2.00	*ds*0	0.011	0.022	0.044	0.067	0.089	0.111	0.134	0.156	0.189	0.221	0.274	0.325	0.497	0.620	0.733
	*ds*1	0.004	0.008	0.016	0.023	0.029	0.035	0.040	0.045	0.052	0.058	0.067	0.077	0.136	0.238	0.434
2.50	*ds*0	0.006	0.013	0.026	0.038	0.051	0.064	0.076	0.088	0.106	0.124	0.153	0.181	0.281	0.361	0.453
	*ds*1	0.002	0.004	0.007	0.010	0.014	0.017	0.020	0.022	0.026	0.031	0.037	0.044	0.080	0.130	0.230
3.00	*ds*0	0.004	0.008	0.017	0.025	0.033	0.041	0.049	0.057	0.068	0.080	0.098	0.116	0.181	0.236	0.303
	*ds*1	0.001	0.002	0.004	0.006	0.008	0.010	0.012	0.014	0.017	0.020	0.026	0.031	0.058	0.093	0.158
3.50	*ds*0	0.003	0.006	0.012	0.017	0.023	0.029	0.034	0.040	0.048	0.056	0.068	0.081	0.126	0.166	0.216
	*ds*1	0.001	0.001	0.003	0.004	0.006	0.007	0.009	0.010	0.013	0.015	0.019	0.024	0.046	0.073	0.122
4.00	*ds*0	0.002	0.004	0.009	0.013	0.017	0.021	0.025	0.029	0.035	0.041	0.050	0.059	0.093	0.123	0.162
	*ds*1	0.001	0.001	0.002	0.003	0.005	0.006	0.007	0.008	0.010	0.012	0.016	0.020	0.038	0.060	0.100
5.00	*ds*0	0.001	0.003	0.005	0.008	0.010	0.013	0.015	0.018	0.021	0.025	0.031	0.036	0.057	0.075	0.100
	*ds*1	0.000	0.001	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.009	0.011	0.014	0.028	0.044	0.073

Source: Calculated using Lee–Kesler equation of state, Eq. 12.65.

TABLE A.14.5 Generalized Fugacity Coefficient Table [$PI = \ln(f/P)$]: $PI = PI0 + \omega \times PI1$; Notation; Table A.14.1

T_r	P_r	0.10	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.70	2.00	2.50	3.00	5.00	7.00	10.00
0.30	*PI0*	−10.815	−11.479	−12.114	−12.462	−12.692	−12.857	−12.981	−13.078	−13.185	−13.261	−13.340	−13.378	−13.313	−13.076	−12.576
	PI1	−20.221	−20.229	−20.245	−20.261	−20.278	−20.294	−20.310	−20.326	−20.350	−20.374	−20.414	−20.455	−20.615	−20.774	−21.012
0.40	*PI0*	−5.887	−6.556	−7.202	−7.559	−7.800	−7.975	−8.110	−8.216	−8.339	−8.431	−8.535	−8.599	−8.638	−8.506	−8.164
	PI1	−11.319	−11.328	−11.348	−11.367	−11.385	−11.404	−11.423	−11.442	−11.471	−11.499	−11.546	−11.592	−11.778	−11.961	−12.231
0.50	*PI0*	−3.077	−3.749	−4.401	−4.766	−5.012	−5.194	−5.335	−5.448	−5.581	−5.682	−5.803	−5.883	−5.989	−5.923	−5.682
	PI1	−6.542	−6.551	−6.569	−6.587	−6.605	−6.623	−6.641	−6.658	−6.685	−6.711	−6.755	−6.799	−6.971	−7.139	−7.386
0.60	*PI0*	−1.304	−1.979	−2.635	−3.003	−3.254	−3.440	−3.586	−3.703	−3.842	−3.950	−4.082	−4.173	−4.323	−4.304	−4.133
	PI1	−3.790	−3.798	−3.815	−3.831	−3.847	−3.863	−3.879	−3.895	−3.919	−3.943	−3.982	−4.020	−4.172	−4.318	−4.530
0.70	*PI0*	−0.110	−0.786	−1.445	−1.816	−2.069	−2.258	−2.407	−2.527	−2.670	−2.782	−2.922	−3.021	−3.202	−3.215	−3.095
	PI1	−2.127	−2.134	−2.149	−2.164	−2.178	−2.193	−2.207	−2.221	−2.242	−2.263	−2.298	−2.331	−2.462	−2.587	−2.765
0.75	*PI0*	−0.080	−0.332	−0.991	−1.363	−1.618	−1.808	−1.957	−2.078	−2.223	−2.336	−2.478	−2.580	−2.773	−2.799	−2.699
	PI1	−0.068	−1.555	−1.569	−1.583	−1.597	−1.611	−1.624	−1.638	−1.658	−1.677	−1.709	−1.741	−1.862	−1.976	−2.138
0.80	*PI0*	−0.066	−0.137	−0.608	−0.981	−1.236	−1.426	−1.576	−1.698	−1.844	−1.959	−2.103	−2.206	−2.409	−2.445	−2.362
	PI1	−0.046	−0.099	−1.108	−1.121	−1.135	−1.148	−1.161	−1.173	−1.192	−1.210	−1.240	−1.270	−1.381	−1.485	−1.632
0.85	*PI0*	−0.055	−0.113	−0.284	−0.656	−0.911	−1.102	−1.252	−1.374	−1.521	−1.636	−1.782	−1.887	−2.097	−2.142	−2.074
	PI1	−0.030	−0.064	−0.739	−0.753	−0.765	−0.778	−0.790	−0.802	−0.820	−0.837	−0.865	−0.892	−0.994	−1.088	−1.221
0.90	*PI0*	−0.046	−0.095	−0.198	−0.382	−0.636	−0.826	−0.976	−1.098	−1.245	−1.360	−1.506	−1.613	−1.829	−1.881	−1.826
	PI1	−0.020	−0.041	−0.090	−0.458	−0.471	−0.483	−0.495	−0.507	−0.523	−0.539	−0.565	−0.590	−0.682	−0.767	−0.885
0.95	*PI0*	−0.039	−0.080	−0.166	−0.261	−0.405	−0.594	−0.742	−0.864	−1.009	−1.124	−1.270	−1.376	−1.596	−1.655	−1.610
	PI1	−0.012	−0.025	−0.053	−0.085	−0.237	−0.250	−0.261	−0.272	−0.288	−0.303	−0.326	−0.349	−0.431	−0.505	−0.609
1.00	*PI0*	−0.034	−0.068	−0.140	−0.218	−0.303	−0.406	−0.548	−0.667	−0.809	−0.923	−1.067	−1.173	−1.394	−1.457	−1.422
	PI1	−0.007	−0.014	−0.028	−0.042	−0.057	−0.072	−0.083	−0.093	−0.106	−0.119	−0.139	−0.158	−0.228	−0.293	−0.383
1.05	*PI0*	−0.029	−0.059	−0.120	−0.185	−0.254	−0.329	−0.414	−0.511	−0.644	−0.753	−0.893	−0.997	−1.217	−1.284	−1.256
	PI1	−0.003	−0.006	−0.011	−0.015	−0.017	−0.015	−0.005	0.014	0.020	0.015	0.003	−0.011	−0.067	−0.120	−0.197
1.10	*PI0*	−0.025	−0.051	−0.103	−0.158	−0.215	−0.276	−0.340	−0.410	−0.517	−0.615	−0.747	−0.847	−1.063	−1.131	−1.110
	PI1	0.000	0.000	0.002	0.004	0.009	0.016	0.028	0.047	0.077	0.094	0.101	0.097	0.061	0.019	−0.043

1.15	*PI*0	−0.022	−0.044	−0.089	−0.136	−0.184	−0.235	−0.287	−0.341	−0.425	−0.507	−0.626	−0.719	−0.929	−0.997	−0.981
	*PI*1	0.002	0.005	0.010	0.017	0.026	0.037	0.052	0.069	0.100	0.129	0.158	0.170	0.160	0.131	0.083
1.20	*PI*0	−0.019	−0.038	−0.078	−0.118	−0.159	−0.202	−0.245	−0.289	−0.357	−0.425	−0.527	−0.612	−0.811	−0.879	−0.867
	*PI*1	0.004	0.008	0.017	0.027	0.039	0.052	0.067	0.085	0.115	0.146	0.188	0.213	0.234	0.220	0.186
1.30	*PI*0	−0.015	−0.030	−0.060	−0.090	−0.121	−0.152	−0.183	−0.215	−0.262	−0.309	−0.384	−0.450	−0.619	−0.682	−0.674
	*PI*1	0.006	0.012	0.025	0.039	0.054	0.069	0.086	0.104	0.133	0.163	0.211	0.250	0.327	0.344	0.340
1.40	*PI*0	−0.012	−0.023	−0.046	−0.070	−0.093	−0.117	−0.140	−0.163	−0.198	−0.232	−0.287	−0.336	−0.472	−0.527	−0.521
	*PI*1	0.007	0.014	0.029	0.045	0.061	0.078	0.095	0.113	0.141	0.170	0.216	0.259	0.370	0.416	0.440
1.50	*PI*0	−0.009	−0.018	−0.036	−0.055	−0.073	−0.091	−0.109	−0.126	−0.152	−0.178	−0.218	−0.255	−0.361	−0.406	−0.397
	*PI*1	0.008	0.016	0.032	0.048	0.065	0.082	0.099	0.117	0.144	0.171	0.216	0.258	0.385	0.453	0.502
1.60	*PI*0	−0.007	−0.014	−0.029	−0.043	−0.057	−0.071	−0.085	−0.098	−0.118	−0.137	−0.168	−0.196	−0.277	−0.310	−0.298
	*PI*1	0.008	0.016	0.032	0.049	0.066	0.083	0.100	0.117	0.143	0.169	0.212	0.253	0.386	0.469	0.539
1.80	*PI*0	−0.005	−0.009	−0.018	−0.027	−0.035	−0.044	−0.052	−0.060	−0.072	−0.083	−0.100	−0.116	−0.159	−0.174	−0.152
	*PI*1	0.008	0.016	0.032	0.049	0.065	0.081	0.097	0.114	0.138	0.162	0.201	0.239	0.371	0.468	0.566
2.00	*PI*0	−0.003	−0.006	−0.011	−0.016	−0.022	−0.027	−0.032	−0.036	−0.043	−0.049	−0.058	−0.067	−0.086	−0.086	−0.055
	*PI*1	0.008	0.016	0.031	0.047	0.062	0.077	0.093	0.108	0.130	0.153	0.189	0.224	0.350	0.450	0.562
2.50	*PI*0	−0.001	−0.001	−0.002	−0.003	−0.004	−0.005	−0.005	−0.006	−0.006	−0.006	−0.006	−0.005	0.006	0.026	0.072
	*PI*1	0.007	0.014	0.027	0.040	0.054	0.067	0.080	0.093	0.112	0.131	0.161	0.191	0.300	0.395	0.512
3.00	*PI*0	0.000	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.009	0.011	0.016	0.020	0.042	0.070	0.121
	*PI*1	0.006	0.012	0.023	0.035	0.046	0.058	0.069	0.080	0.097	0.113	0.139	0.165	0.262	0.347	0.458
3.50	*PI*0	0.001	0.002	0.003	0.005	0.007	0.009	0.011	0.013	0.016	0.019	0.025	0.031	0.058	0.089	0.141
	*PI*1	0.005	0.010	0.021	0.031	0.041	0.051	0.061	0.070	0.085	0.099	0.123	0.146	0.232	0.309	0.412
4.00	*PI*0	0.001	0.002	0.004	0.006	0.009	0.011	0.013	0.016	0.019	0.023	0.029	0.036	0.064	0.095	0.146
	*PI*1	0.005	0.009	0.018	0.027	0.036	0.045	0.054	0.063	0.076	0.089	0.110	0.130	0.208	0.279	0.375
5.00	*PI*0	0.001	0.002	0.005	0.007	0.010	0.012	0.015	0.017	0.021	0.025	0.031	0.038	0.066	0.096	0.143
	*PI*1	0.004	0.008	0.015	0.022	0.030	0.037	0.044	0.052	0.062	0.073	0.090	0.107	0.173	0.233	0.317

Source: Calculated using Lee–Kesler equation of state, Eq. 12.65.

TABLE A.14.6 The Lee-Kesler equation of State The Lee-Kesler generalized equation of state, Eq. 12.65, is

$$Z = \frac{P_r v'_r}{T_r} = 1 + \frac{B}{v'_r} + \frac{C}{v'^2_r} + \frac{D}{v'^5_r} + \frac{c_4}{T_r^3 v'^2_r}\left(\beta + \frac{\gamma}{v'^2_r}\right)\exp\left(-\frac{\gamma}{v'^2_r}\right)$$

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3}$$

$$D = d_1 + \frac{d_2}{T_r}$$

in which

$$T_r = \frac{T}{T_c}, \qquad P_r = \frac{P}{P_c}, \qquad v'_r = \frac{v}{RT_c/P_c}$$

The two sets of constants are as follows:

Constant	*Simple Fluids*	*Reference Fluid*
b_1	0.118 119 3	0.202 657 9
b_2	0.265 728	0.331 511
b_3	0.154 790	0.027 655
b_4	0.030 323	0.203 488
c_1	0.023 674 4	0.031 338 5
c_2	0.018 698 4	0.050 361 8
c_3	0.0	0.016 901
c_4	0.042 724	0.041 577
$d_1 \times 10^4$	0.155 488	0.487 36
$d_2 \times 10^4$	0.623 689	0.074 033 6
β	0.653 92	1.226
γ	0.060 167	0.037 54

TABLE A.15SI Enthalpy of Formation, Gibbs Function of Formation, and Absolute Entropy of Various Substances at 25°C, 0.1-MPa Pressure

				$\bar{h}_f$	$\bar{g}_f$	$\bar{s}$
Substance	Formula	M	State	kJ/kmol	kJ/kmol	kJ/kmol K
Water	H_2O	18.015	gas	−241 826	−228 582	188.834
Water	H_2O	18.015	liquid	−285 830	−237 141	69.950
Carbon (graphite)	C	12.011	solid	0	0	5.740
Carbon monoxide	CO	28.011	gas	−110 527	−137 163	197.653
Carbon dioxide	CO_2	44.010	gas	−393 522	−394 389	213.795
Methane	CH_4	16.043	gas	−74 873	−50 768	186.251
Acetylene	C_2H_2	26.038	gas	+226 731	+209 200	200.958
Ethene	C_2H_4	28.054	gas	+52 467	+68 421	219.330
Ethane	C_2H_6	30.070	gas	−84 740	−32 885	229.597
Propene	C_3H_6	42.081	gas	+20 430	+62 825	267.066
Propane	C_3H_8	44.094	gas	−103 900	−23 393	269.917
Butane	C_4H_{10}	58.124	gas	−126 200	−15 970	306.647
Pentane	C_5H_{12}	72.151	gas	−146 500	−8 208	348.945
Benzene	C_6H_6	78.114	gas	+82 980	+129 765	269.562
Hexane	C_6H_{14}	86.178	gas	−167 300	+28	387.979
Heptane	C_7H_{16}	100.205	gas	−187 900	+8 227	427.805
Octane	C_8H_{18}	114.232	gas	−208 600	+16 660	466.514
Octane	C_8H_{18}	114.232	liquid	−250 105	+6 741	360.575
Methanol	CH_3OH	32.042	gas	−201 300	−162 551	239.709
Ethanol	C_2H_5OH	46.069	gas	−235 000	−168 319	282.444
Ammonia	NH_3	17.031	gas	−45 720	−16 128	192.572

Source: Consistent with thermodynamic data in *JANAF Thermochemical Tables*, third edition, Thermal Group, Dow Chemical U.S.A., Midland, MI, 1985.

TABLE A.16SI Logarithms to the Base *e* of the Equilibrium Constant *K*

For the reaction $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$, the equilibrium constant K is defined as

$$K = \frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_A} y_B^{\nu_B}} \left(\frac{P}{P^\circ}\right)^{\nu_C + \nu_D - \nu_A - \nu_B}, \quad P^\circ = 0.1 \text{ MPa}$$

Temp. K	$H_2 \rightleftharpoons 2H$	$O_2 \rightleftharpoons 2O$	$N_2 \rightleftharpoons 2N$	$2H_2O \rightleftharpoons 2H_2 + O_2$	$2H_2O \rightleftharpoons H_2 + 2OH$	$2CO_2 \rightleftharpoons 2CO + O_2$	$N_2 + O_2 \rightleftharpoons 2NO$	$N_2 + 2O_2 \rightleftharpoons 2NO_2$
298	−164.003	−186.963	−367.528	−184.420	−212.075	−207.529	−69.868	−41.355
500	−92.830	−105.623	−213.405	−105.385	−120.331	−115.234	−40.449	−30.725
1000	−39.810	−45.146	−99.146	−46.321	−51.951	−47.052	−18.709	−23.039
1200	−30.878	−35.003	−80.025	−36.363	−40.467	−35.736	−15.082	−21.752
1400	−24.467	−27.741	−66.345	−29.222	−32.244	−27.679	−12.491	−20.826
1600	−19.638	−22.282	−56.069	−23.849	−26.067	−21.656	−10.547	−20.126
1800	−15.868	−18.028	−48.066	−19.658	−21.258	−16.987	−9.035	−19.577
2000	−12.841	−14.619	−41.655	−16.299	−17.406	−13.266	−7.825	−19.136
2200	−10.356	−11.826	−36.404	−13.546	−14.253	−10.232	−6.836	−18.773
2400	−8.280	−9.495	−32.023	−11.249	−11.625	−7.715	−6.012	−18.470
2600	−6.519	−7.520	−28.313	−9.303	−9.402	−5.594	−5.316	−18.214
2800	−5.005	−5.826	−25.129	−7.633	−7.496	−3.781	−4.720	−17.994
3000	−3.690	−4.356	−22.367	−6.184	−5.845	−2.217	−4.205	−17.805
3200	−2.538	−3.069	−19.947	−4.916	−4.401	−0.853	−3.755	−17.640
3400	−1.519	−1.932	−17.810	−3.795	−3.128	0.346	−3.359	−17.496
3600	−0.611	−0.922	−15.909	−2.799	−1.996	1.408	−3.008	−17.369
3800	0.201	−0.017	−14.205	−1.906	−0.984	2.355	−2.694	−17.257
4000	0.934	0.798	−12.671	−1.101	−0.074	3.204	−2.413	−17.157
4500	2.483	2.520	−9.423	0.602	1.847	4.985	−1.824	−16.953
5000	3.724	3.898	−6.816	1.972	3.383	6.397	−1.358	−16.797
5500	4.739	5.027	−4.672	3.098	4.639	7.542	−0.980	−16.678
6000	5.587	5.969	−2.876	4.040	5.684	8.488	−0.671	−16.588

Source: Consistent with thermodynamic data in *JANAF Thermochemical Tables*, third edition, Thermal Group, Dow Chemical U.S.A., Midland, MI, 1985.

TABLE A.17 *Atomic Masses, and Melting and Boiling Points of the Elements Based on the Assigned Relative Atomic Mass of $^{12}C = 12$*

Name	Symbol	Atomic Number	Atomic Mass	Melting Point, °C	Boiling Point, °C
Actinium	Ac	89	227.028[a]	1050	3200 ± 300
Aluminum	Al	13	26.9815	660.37	2467
Americium	Am	95	(243)	994 ± 4	2607
Antimony (stibium)	Sb	51	121.75	630.74	1750
Argon	Ar	18	39.948	−189.2	−185.7
Arsenic	As	33	74.9216	817 (28 atm)	613 (sub)
Astatine	At	85	(210)	302	337
Barium	Ba	56	137.33	725	1640
Berkelium	Bk	97	(247)		
Beryllium	Be	4	9.012 18	1278 ± 5	2970 (5 mm)
Bismuth	Bi	83	208.980	271.3	1560 ± 5
Boron	B	5	10.81	2079	2550 (sub)
Bromine	Br	35	79.904	−7.2	58.78
Cadmium	Cd	48	112.41	320.9	765
Caesium (cesium)	Cs	55	132.905	28.40 ± 0.01	669.3
Calcium	Ca	20	40.08	839 ± 2	1484
Californium	Cf	98	(251)		
Carbon	C	6	12.011	3652 (sub)	t
Cerium	Ce	58	140.12	798 ± 2	3257
Cesium (caesium)	Cs	55	132.9054	28.40 ± 0.01	669.3
Chlorine	Cl	17	35.453	−100.98	−34.6
Chromium	Cr	24	51.996	1857 ± 20	2672
Cobalt	Co	27	51.9332	1495	2870
Copper (cuprum)	Cu	29	63.546	1083.4 ± 0.2	2567
Curium	Cm	96	(247)	1340 ± 40	

Dysprosium	Dy	66	162.50	1409	2335
Einsteinium	Es	99	(252)		
Erbium	Er	68	167.26	1522	2510
Europium	Eu	63	151.96	822 ± 5	1597
Fermium	Fm	100	(257)		
Fluorine	F	9	18.9984	−219.62	−188.14
Francium	Fr	87	(223)	(27)	(677)
Gadolinium	Gd	64	157.25	1311 ± 1	3233
Gallium	Ga	31	69.72	29.78	2403
Germanium	Ge	32	72.59	937.4	2830
Gold (aurum)	Au	79	196.967	1064.434	3080
Hafnium	Hf	72	178.49	2227 ± 20	4602
Helium	He	2	4.002 60	$-272.2^{26\ \text{atm}}$	−268.934
Holmium	Ho	67	164.930	1470	2720
Hydrogen	H	1	1.007 94	−259.14	−252.87
Indium	In	49	114.82	156.61	2080
Iodine	I	53	126.905	113.5	184.35
Iridium	Ir	77	192.22	2410	4130
Iron (ferrum)	Fe	26	55.847	1535	2750
Krypton	Kr	36	83.80	−156.6	-152.30 ± 0.10
Lanthanum	La	57	138.906	920 ± 5	3454
Lawrencium	Lr	103	(260)		
Lead (plumbum)	Pb	82	207.2	327.502	1740
Lithium	Li	3	6.941	180.54	1342
Lutetium	Lu	71	174.967	1656 ± 5	3315
Magnesium	Mg	12	24.305	648.8 ± 0.5	1090
Manganese	Mn	25	54.9380	1244 ± 3	1962
Mendelevium	Md	101	(258)		
Mercury (hydrargyrum)	Hg	80	200.59	−38.87	356.58
Molybdenum	Mo	42	95.94	2617	4612

[a] The values apply to elements as they exist in materials of terrestrial origin and to certain artificial elements.

Source: *Handbook of Chemistry and Physics*, sixty-seventh edition, 1986–1987, CRC Press, Boca Raton, FL, 1986.

TABLE A.17 *(Continued)* Atomic Masses, and Melting and Boiling Points of the Elements Based on the Assigned Relative Mass of $^{12}C = 12$

Name	Symbol	Atomic Number	Atomic Mass	Melting Point, °C	Boiling Point, °C
Neodymium	Nd	60	144.24	1010	3127
Neon	Ne	10	20.1179	−248.67	−246.048
Neptunium	Np	93	237.048	640 ± 1	3902
Nickel	Ni	28	58.69	1453	2732
Niobium (columbium)	Nb	41	92.9064	2468 ± 10	4742
Nitrogen	N	7	14.0067	−209.86	−195.8
Nobelium	No	102	(259)		
Osmium	Os	76	190.2	3045 ± 30	5027 ± 100
Oxygen	O	8	15.9994	−218.4	−182.962
Palladium	Pd	46	106.42	1554	3140
Phosphorus	P	15	30.9738	44.1 (white)	280 (white)
Platinum	Pt	78	195.08	1772	3827 ± 100
Plutonium	Pu	94	(244)	641	3232
Polonium	Po	84	(209)	254	962
Potassium (kalium)	K	19	39.0983	63.25	759.9
Praseodymium	Pr	59	140.908	931 ± 4	3212
Promethium	Pm	61	(145)	1080 (approx)	2460 (?)
Protoactinium	Pa	91	231.0359	1600	
Radium	Ra	88	226.025	700	1140
Radon	Rn	86	(222)	−71	−61.8
Rhenium	Re	75	186.207	3180	5627 (est.)
Rhodium	Rh	45	102.906	1965 ± 3	3727 ± 100
Rubidium	Rb	37	85.4678	38.89	686
Ruthenium	Ru	44	101.07	2310	3900

Samarium	Sm	62	150.36	1072 ± 5	1778
Scandium	Sc	21	44.9559	1539	2832
Selenium	Se	34	78.96	217	684.9 ± 1.0
Silicon	Si	14	28.0855	1410	2355
Silver (argentum)	Ag	47	107.868	961.93	2212
Sodium (natrium)	Na	11	22.9898	97.81 ± 0.03	882.9
Strontium	Sr	38	87.62	769	1384
Sulfur	S	16	32.06	112.8	444.674
Tantalum	Ta	73	180.9479	2996	5425 ± 100
Technetium	Tc	43	(98)	2172	4877
Tellurium	Te	52	127.60	449.5 ± 0.3	989.8 ± 3.8
Terbium	Tb	65	158.925	1360 ± 4	3041
Thallium	Tl	81	204.383	303.5	1457 ± 10
Thorium	Th	90	232.038	1750	4790 (approx)
Thulium	Tm	69	168.934	1545 ± 15	1727
Tin (stannum)	Sn	50	118.71	231.9681	2270
Titanium	Ti	22	47.88	1660 ± 10	3287
Tungsten (wolfram)	W	74	183.85	3410 ± 20	5660
Unnihexium	(Unh)	106	(263)		
Unnilpentium	(Unp)	105	(262)		
Unnilquadium	(Unq)	104	(261)		
Unnilseptium	(Uns)	107	(262)		
Uranium	U	92	238.029	1132 ± 0.8	3818
Vanadium	V	23	50.9415	1890 ± 10	3380
Wolfram (see tungsten)					
Xenon	Xe	54	131.29	−111.9	−107.1 ± 3
Ytterbium	Yb	70	173.04	824 ± 5	1193
Yttrium	Y	39	88.9059	1523 ± 8	3337
Zinc	Zn	30	65.39	419.58	907
Zirconium	Zr	40	91.224	1852 ± 2	4377

TABLE A.18 Series, Integrals, and Approximations

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$$

$$(x+y)^n = x^n + nx^{n-1}y + \frac{n(n-1)}{2!}x^{n-2}y^2 + \cdots \quad (y^2 < x^2)$$

n	$\int_0^\infty x^n e^{-ax^2}\,dx$	n	$\int_0^\infty x^n e^{-ax^2}\,dx$
0	$\frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$	3	$\frac{1}{2a^2}$
1	$\frac{1}{2a}$	4	$\frac{3}{8}\left(\frac{\pi}{a^5}\right)^{1/2}$
2	$\frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$	5	$\frac{1}{a^3}$

$$\int_{-\infty}^{+\infty} x^n e^{-ax^2}\,dx = 0 \qquad (n = 1, 3, 5, \ldots)$$

$$= 2\int_0^\infty x^n e^{-ax^2}\,dx \quad (n = 0, 2, 4, \ldots)$$

$$\int_0^\infty \frac{x^3}{e^x - 1}\,dx = \frac{\pi^4}{15}$$

$$\int_0^\infty x^2 \ln(1 - e^{-x})\,dx = -\frac{\pi^4}{45}$$

Error function: $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-x^2}\,dx$

x	erf (x)	x	erf (x)	x	erf (x)
0	0	0.7	0.6778	1.4	0.9523
0.1	0.1125	0.8	0.7421	1.5	0.9661
0.2	0.2227	0.9	0.7969	1.6	0.9764
0.3	0.3286	1.0	0.8427	1.7	0.9838
0.4	0.4284	1.1	0.8802	1.8	0.9891
0.5	0.5205	1.2	0.9103	1.9	0.9928
0.6	0.6039	1.3	0.9340	2.0	0.9953

TABLE A.18 *(Continued)*

Stirling's Formula:

For relatively large values of N,

$$\ln N! \cong N \ln N - N + \tfrac{1}{2} \ln 2\pi N$$

But, for very large values of N,

$$\tfrac{1}{2} \ln 2\pi N \ll N$$

and

$$\ln N! \cong N \ln N - N$$

Euler-Maclaurin Summation Formula:

Consider some function $f(j)$, where j is an integer, and the function is such that $f(j)$ changes only very slightly from j to $j+1$. If in addition the function is such that $f(j) \to 0$ for large j, then

$$\sum_{j=0}^{\infty} f(j) = \sum_{j=0}^{\infty} f(j)\Delta j \approx \int_{x=0}^{\infty} f(x)\, dx$$

If we assume also that the derivatives of $f(x) \to 0$ for large x, then it may be more accurate to represent the above summation by including the correction terms

$$\sum_{j=0}^{\infty} f(j) = \int_{0}^{\infty} f(x)\, dx + \tfrac{1}{2} f(0) - \tfrac{1}{12} f^{\mathrm{I}}(0) + \tfrac{1}{720} f^{\mathrm{III}}(0) - \tfrac{1}{30240} f^{\mathrm{V}}(0) + \cdots$$

TABLE A.19 Molecular Constants

TABLE A.19.1 Constants for Diatomic Molecules

Date	Substance	Ground Level	r_e, nm	ω_e, mm^{-1}	D_0, mm^{-1}
6/82	Br_2	$^1\Sigma_g^+$	0.2284	32.32	1597.80
6/82	Cl_2	$^1\Sigma_g^+$	0.1988	55.98	1999.70
6/82	F_2	$^1\Sigma$	0.1412	92.31	1292.00
3/77	H_2	$^1\Sigma_g^+$	0.074 17	440.53	3611.83
6/82	I_2	$^1\Sigma_g^+$	0.2666	21.45	1244.00
3/77	N_2	$^1\Sigma_g^+$	0.109 76	235.76	7871.50
3/77	O_2	$^3\Sigma_g^-$	0.120 74	158.02	4126.00
9/65	CO	$^1\Sigma^+$	0.112 81	216.95	8945.46
9/65	HBr	$^1\Sigma^+$	0.1414	264.92	2552.39
9/64	HCl	$^1\Sigma^+$	0.127 46	298.96	3573.67
6/77	HF	$^1\Sigma^+$	0.091 68	413.87	4725.63
9/61	HI	$^1\Sigma^+$	0.1604	230.91	2463.65
6/63	NO	$^2\Pi^a$	0.115 08	190.36	5233.04
6/77	OH	$^2\Pi^b$	0.097 06	373.52	3545.00

[a] Two states at 12.11 mm^{-1} above the two ground states.

[b] Two states at 13.97 mm^{-1} above the two ground states.

Source: Values from thermodynamic data in *JANAF Thermochemical Tables*, third edition. Thermal Group, Dow Chemical U.S.A., Midland, MI, 1985.

TABLE A.19.2 Constants for Linear Polyatomic Molecules

Date	Substance	Bond Distance, nm	ω_e, mm^{-1}	
9/65	O—C—O	C—O:0.1160	138.49	
			66.73	(2)
			234.93	
12/64	N—N—O	N—N:0.112 82	127.65	
		N—O:0.118 42	58.92	(2)
			222.37	
6/66	CL—C—N	CL—C:0.1631	71.45	
		C—N:0.1162	37.83	(2)
			221.55	
6/69	F—C—N	F—C:0.1262	107.7	
		C—N:0.1159	42.0	(2)
			229.0	
12/69	H—C—N	H—C:0.1066	209.63	
		C—N:0.1153	71.35	(2)
			331.15	
12/64	H—B—H	H—B:0.1200	243.0	
			84.0	(2)
			265.0	
12/70	NA—O—H	NA—O:0.193	43.1	
		O—H:0.097	33.7	(2)
			365.0	
12/70	K—O—H	K—O:0.218	40.8	
		O—H:0.097	34.0	(2)
			361.0	

Source: Values from thermodynamic in *JANAF Thermochemical Tables*, third edition, Thermal Group, Dow Chemical U.S.A., Midland, MI, 1985.

TABLE A.20 Fundamental Physical Constants

Avogadro	$N_0 = 6.022\,045 \times 10^{23}$ l/mol
Boltzmann	$k = 1.380\,662 \times 10^{-23}$ J/K
Planck	$h = 6.626\,176 \times 10^{-34}$ J s
Gas constant	$\bar{R} = N_0 k = 8.314\,41$ J/mol K
Atomic mass unit	$m_0 = 1.660\,566 \times 10^{-27}$ kg
Velocity of light	$c = 2.997\,925 \times 10^{8}$ m/s
Electron charge	$e = 1.602\,189 \times 10^{-19}$ C
Electron mass	$m_e = 9.109\,534 \times 10^{-31}$ kg
Proton mass	$m_p = 1.672\,649 \times 10^{-27}$ kg

Source: *Handbook of Chemistry and Physics*, sixty-seventh edition, 1986–1987, CRC Press, Boca Raton, FL, 1986.

TABLE A.21 English to SI Unit Conversions

To Convert from	to	Multiply by
Btu (IT)	kJ	1.055 056
Btu/lbm	kJ/kg	2.326[a]
Btu/lbm R	kJ/kg K	4.1868[a]
ft	m	0.3048[a]
ft^3	m^3	0.028 317
$in.^2$	mm^2	645.16[a]
lbf	N	4.448 222
lbm	kg	0.453 592
$lbf/in.^2$	kPa	6.894 757
ft^3/lbm	m^3/kg	0.062 428
hp	kW	0.7457
R	K	1/1.8[a]

[a] Exact relation

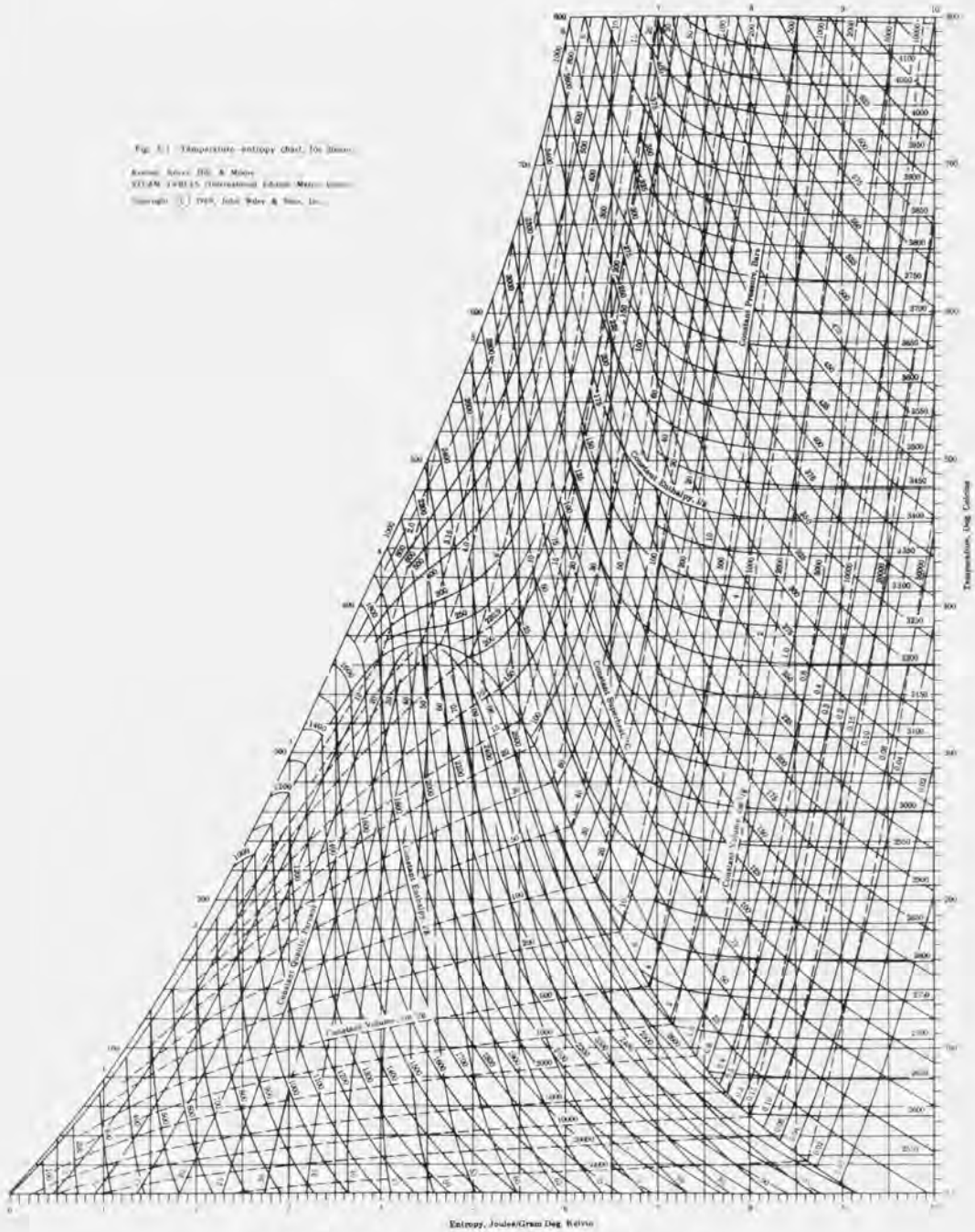


FIGURE A.1 Temperature–entropy chart for steam.

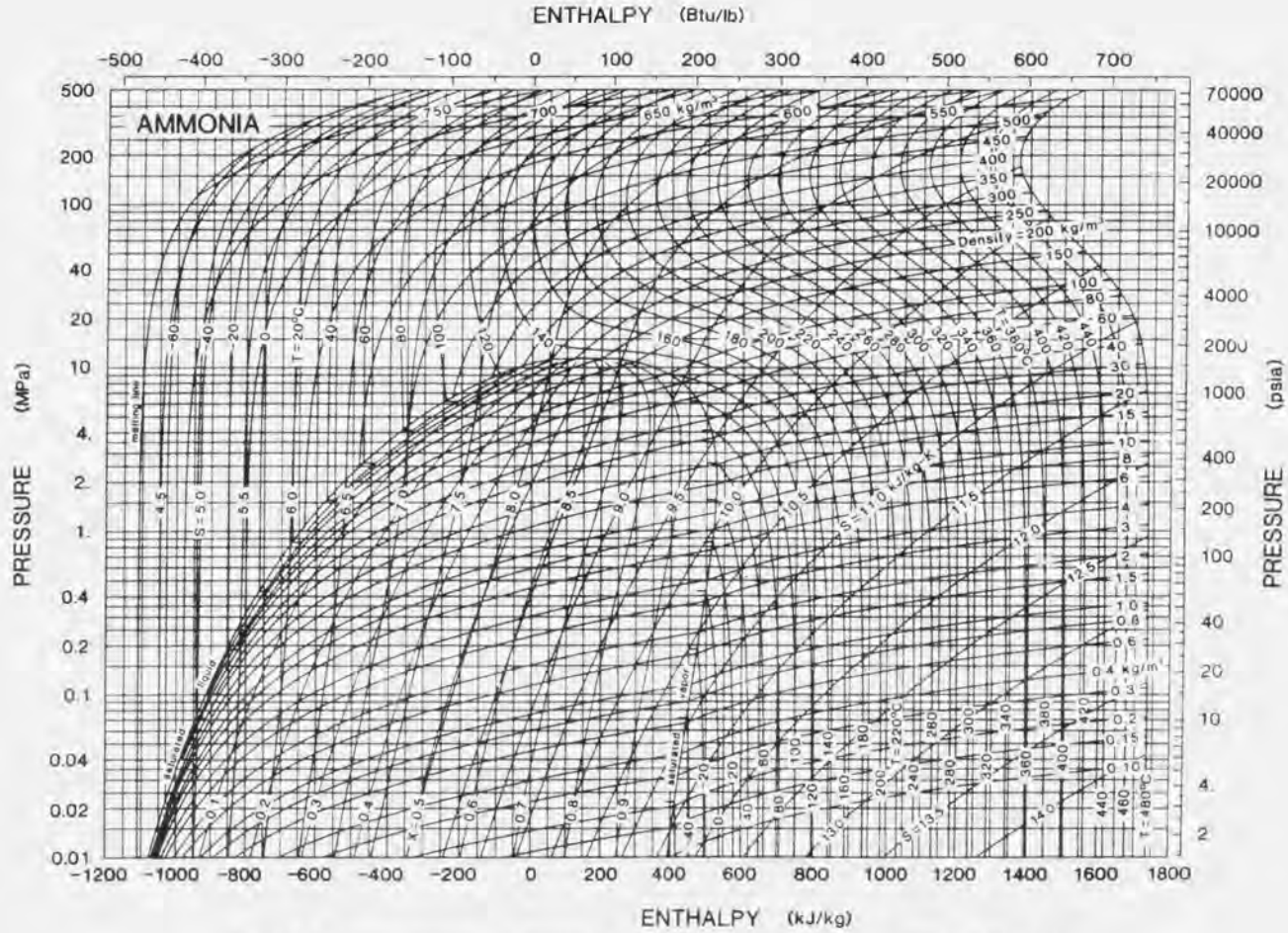


FIGURE A.2 *Pressure-enthalpy diagram for ammonia (Reprinted by permission from ASHRAE Handbook of Fundamentals 1989.)*

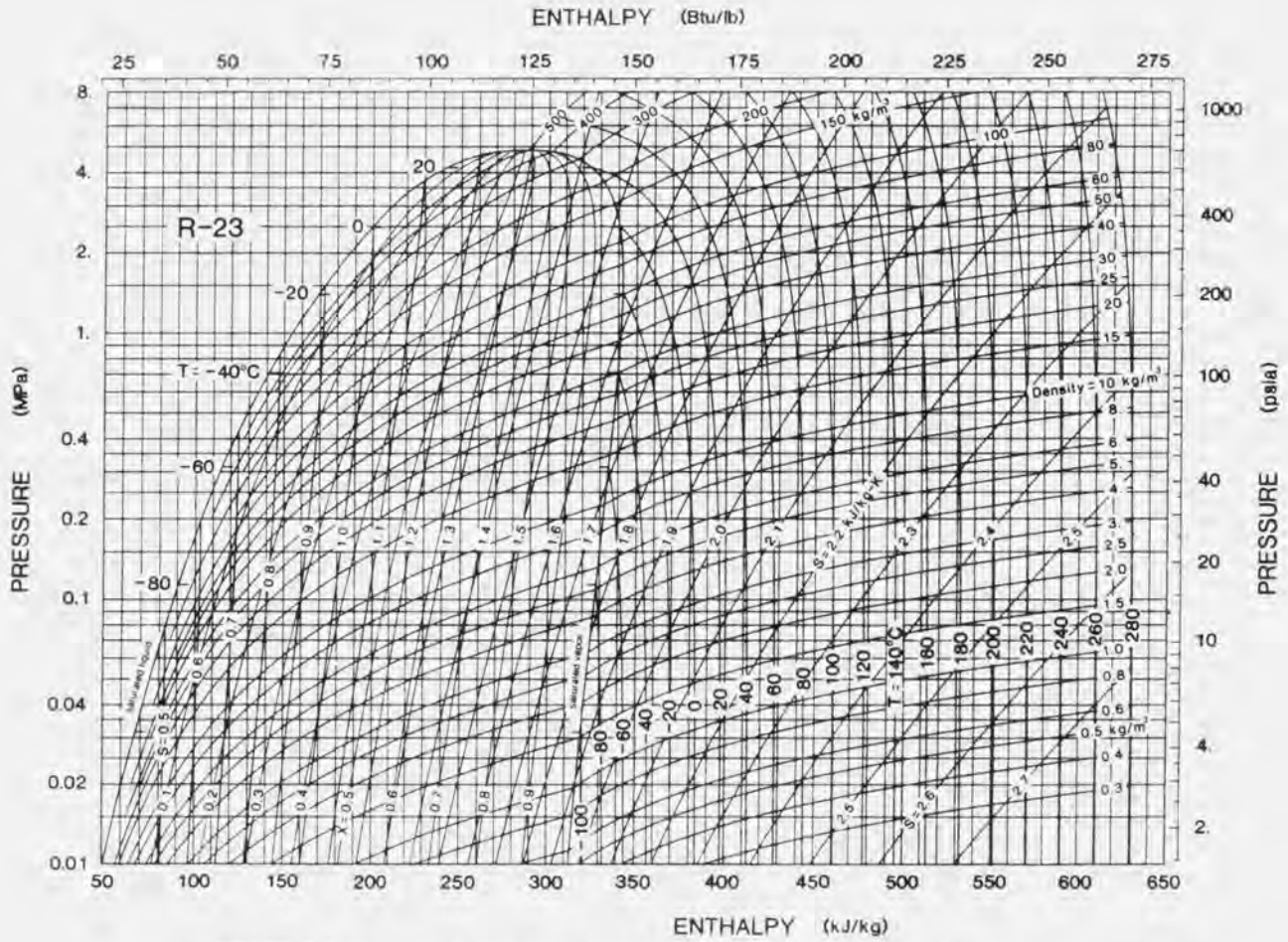


FIGURE A.3 *Pressure-enthalpy diagram for Refrig-23 (Reprinted by permission from ASHRAE Handbook of Fundamentals 1989.)*

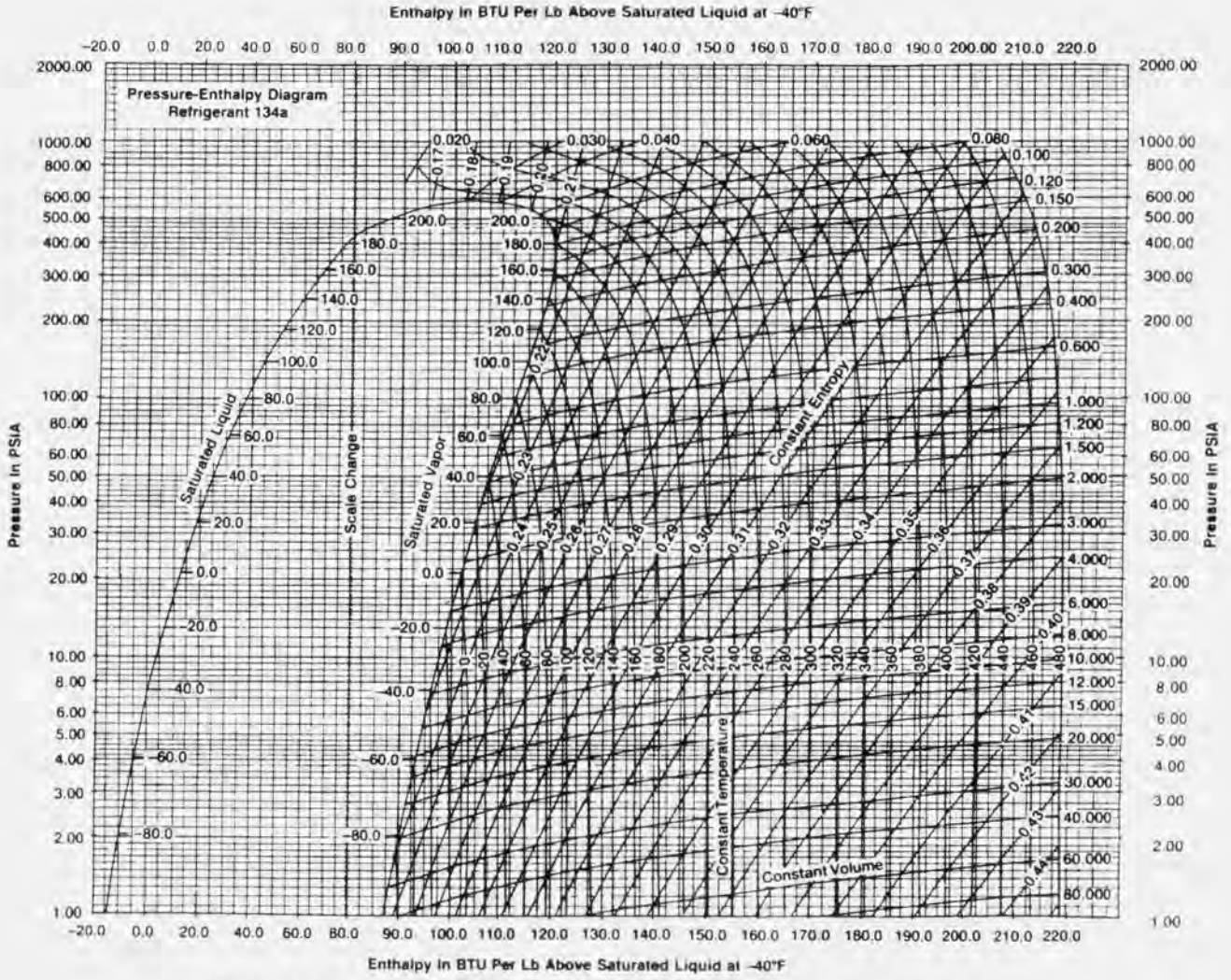


FIGURE A.4 Pressure-enthalpy diagram for Refrig-134a (Reprinted by permission from ASHRAE Handbook of Fundamentals 1989.)

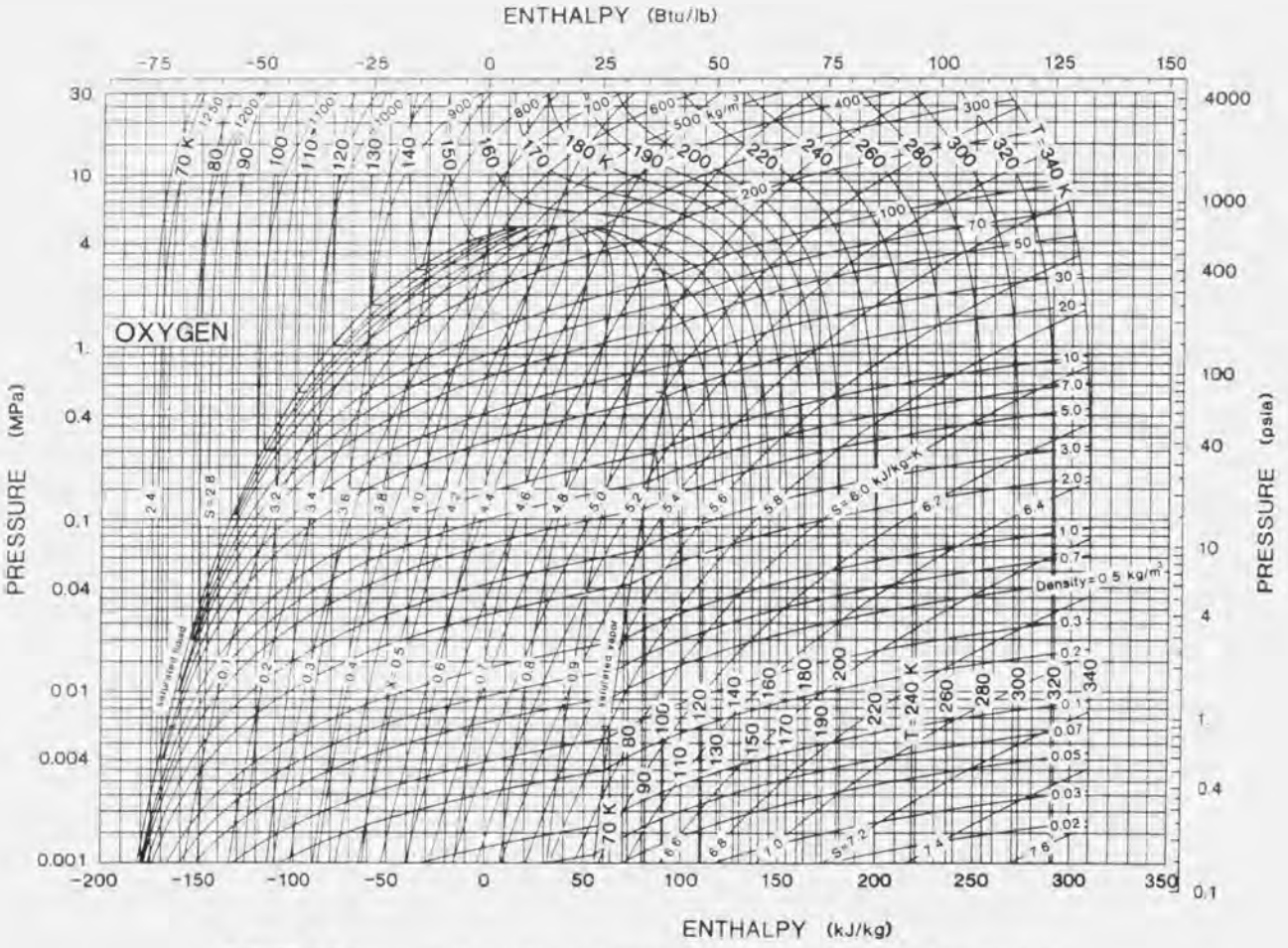


FIGURE A.5 *Pressure-enthalpy diagram for oxygen (Reprinted by permission from ASHRAE Handbook of Fundamentals 1989.)*

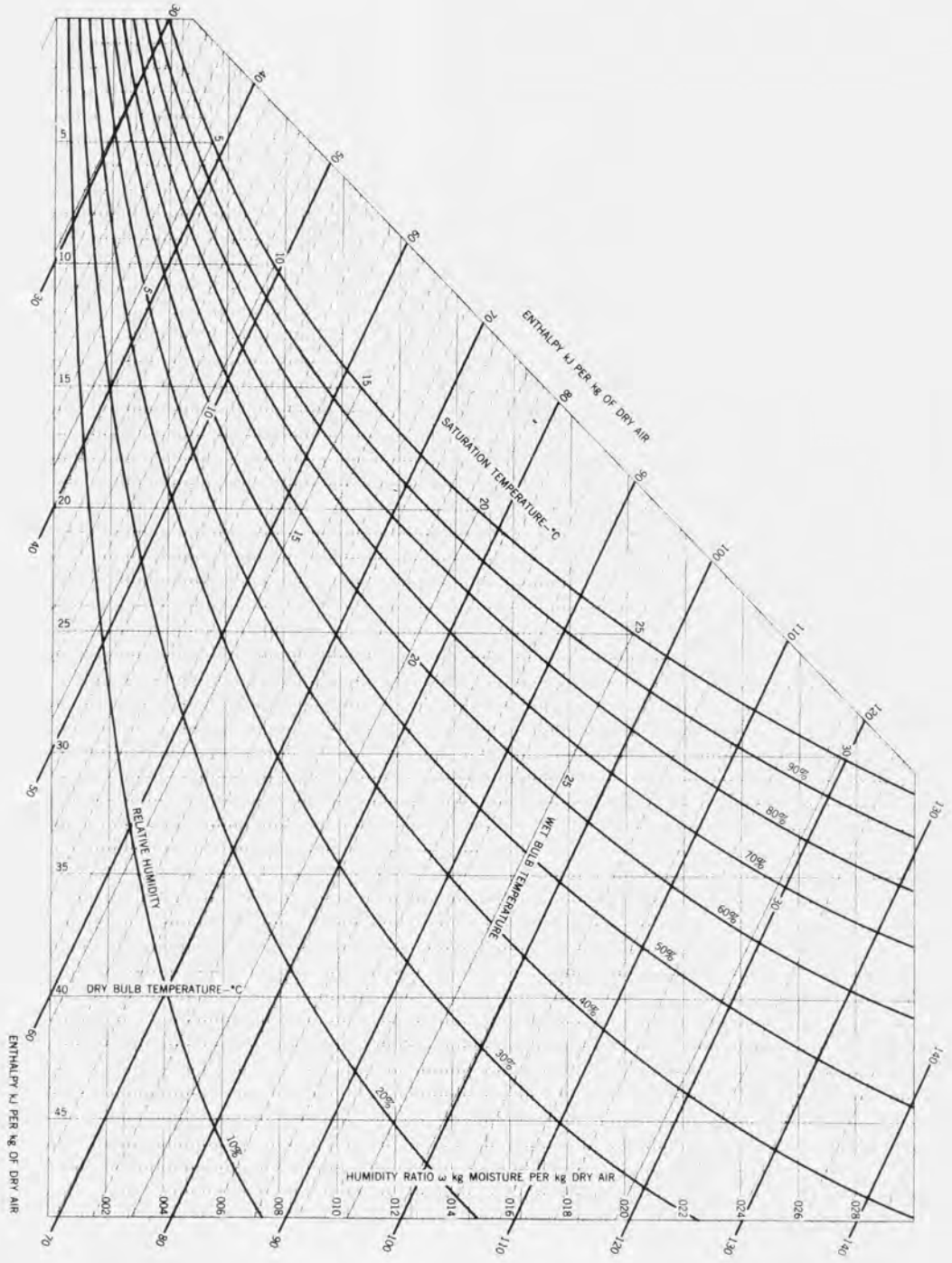


FIGURE A.6 Psychrometric chart.

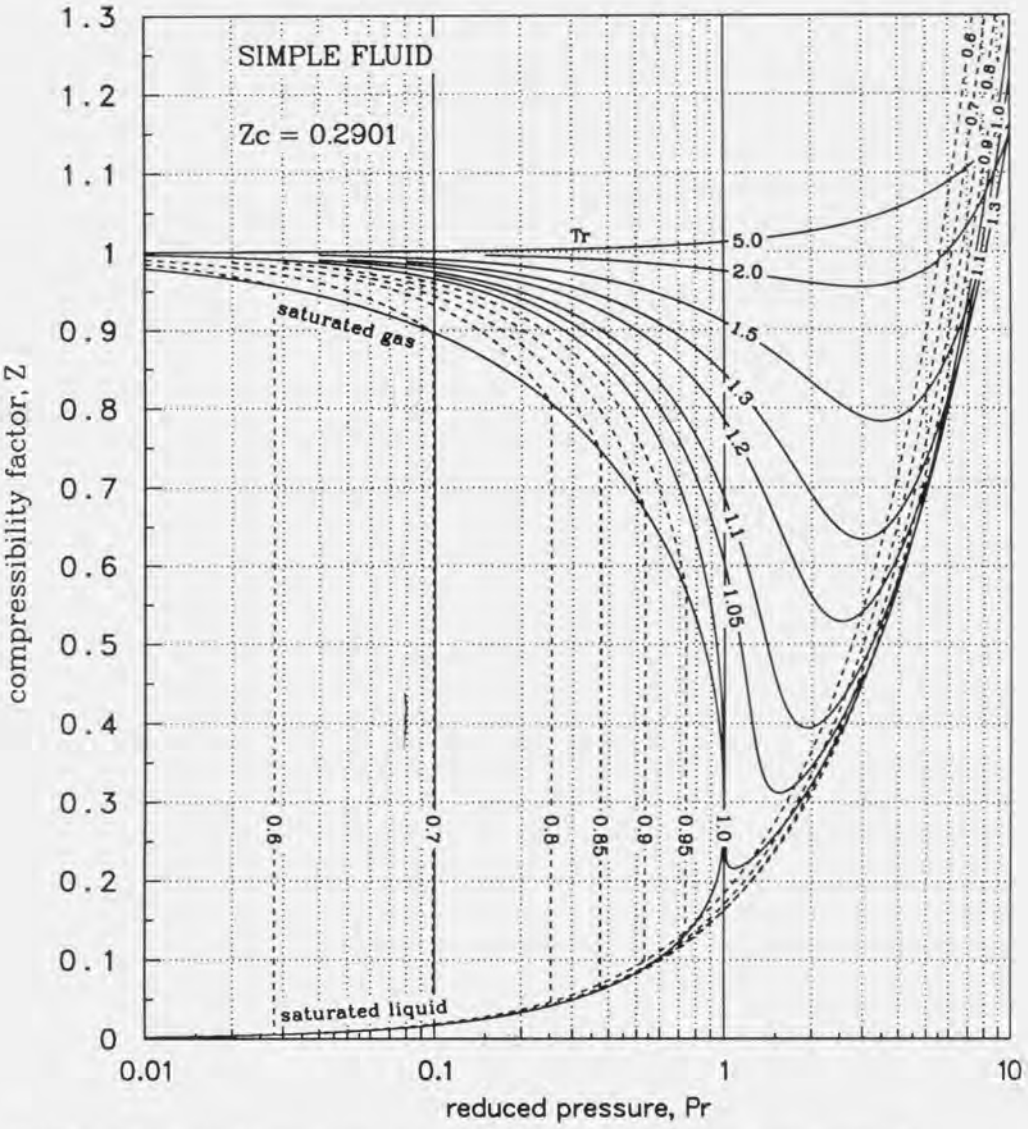


FIGURE A.7 Generalized compressibility chart, simple fluid (Calculated from Lee-Kesler equation of state. Appendix Table A.14.)

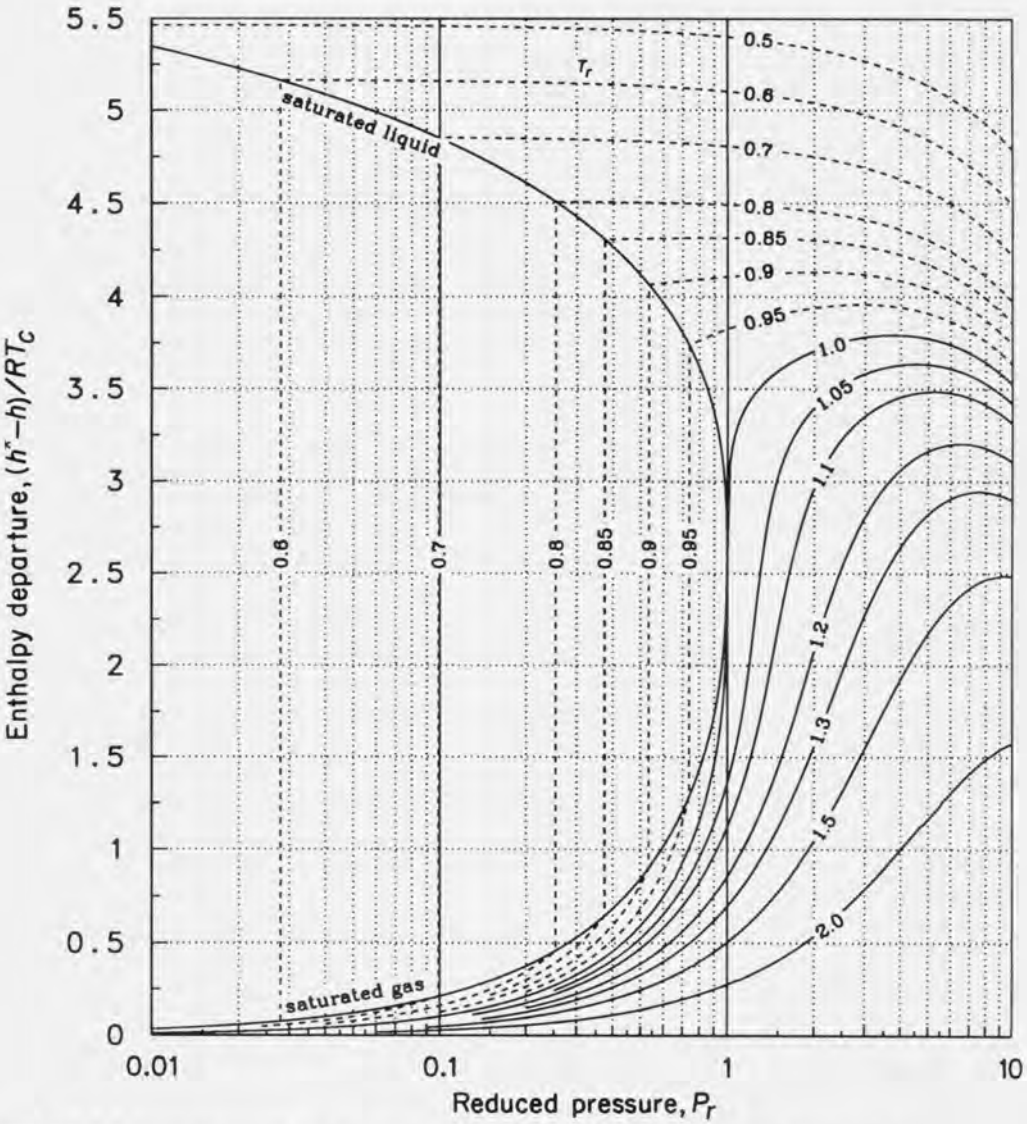


FIGURE A.8 Generalized enthalpy-departure chart, simple fluid (Calculated from Lee-Kesler equation of state, Appendix Table A.14.)

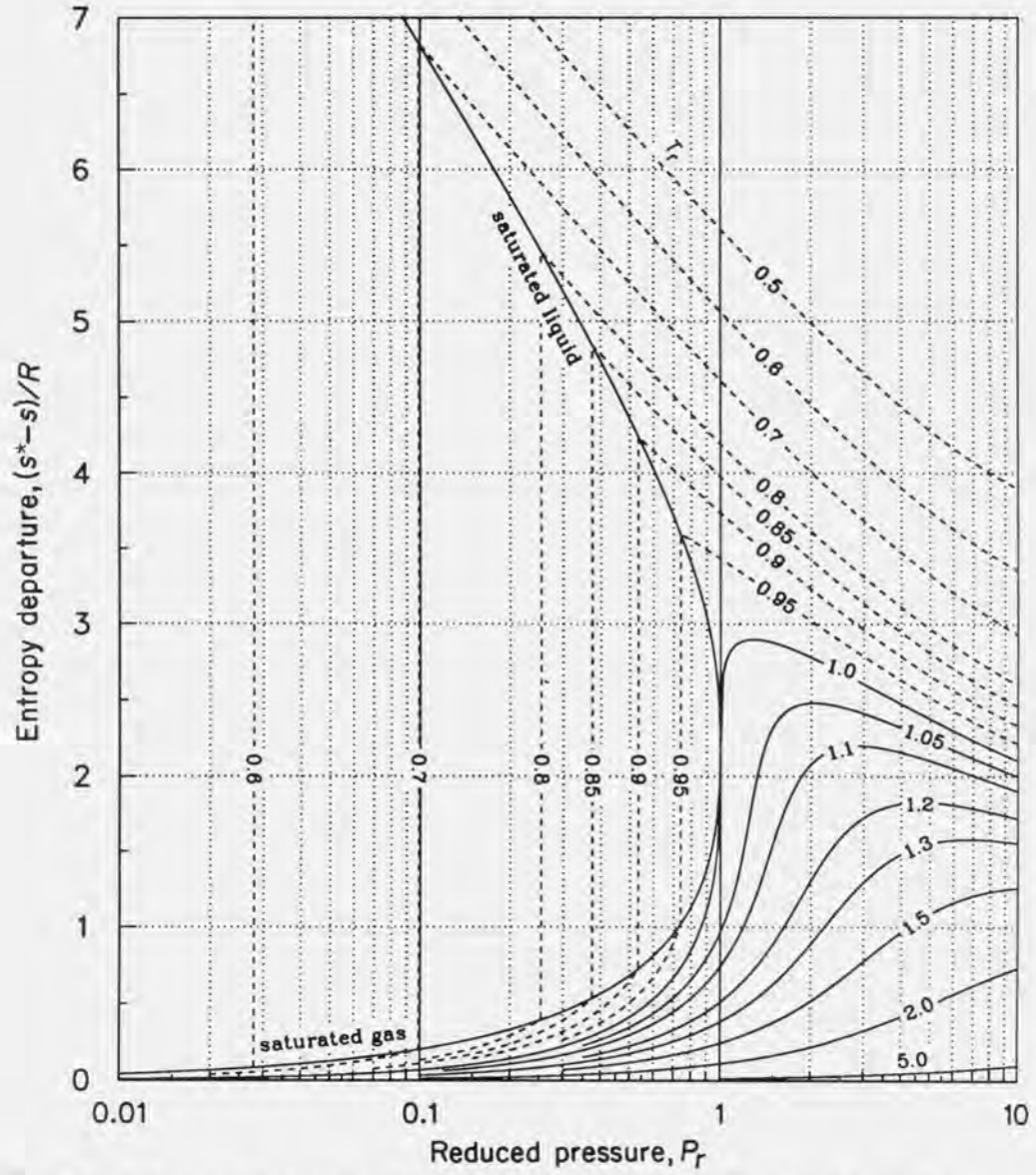


FIGURE A.9 Generalized entropy-departure chart, simple fluid (Calculated from Lee-Kesler equation of state, Appendix Table A.14.)

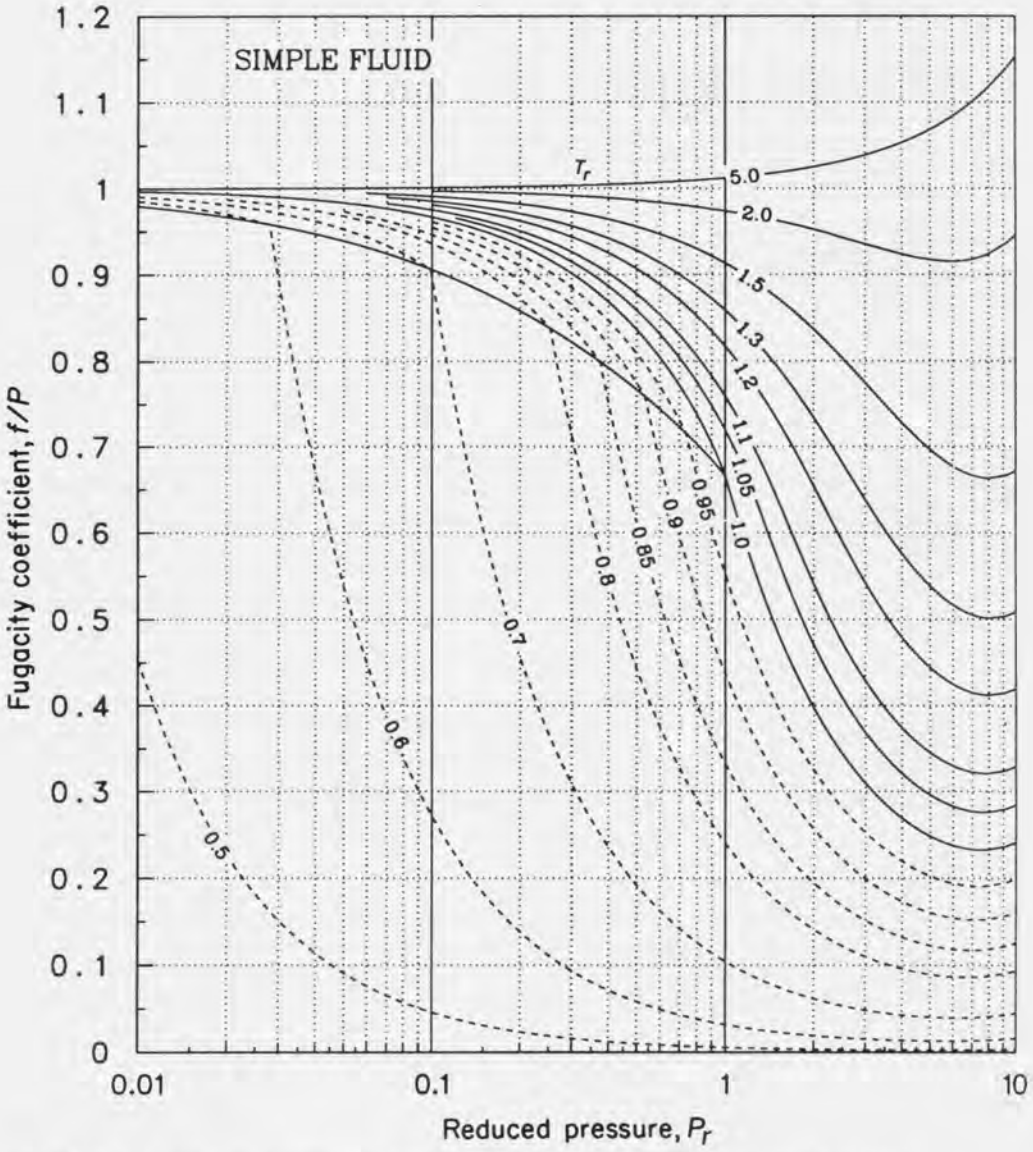


FIGURE A.10 *Generalized fugacity-coefficient chart, simple fluid (Calculated from Lee-Kesler equation of state, Appendix Table A.14.)*

APPENDIX B

COMPUTER-AIDED THERMODYNAMICS (CATH)

Two IBM PC compatible disks are enclosed with this book. The first disk contains the execution file CATH1, which includes Appendix Tables A.1 through A.6 (some additional refrigerants are also included in both Tables A.3 and A.4). This disk also contains object files, which can be linked or merged with FORTRAN programs to use these tables in solving computer problems. STEAM.OBJ is Table A.1, ANM.OBJ is Tables A.2, A.5, and A.6, and FREON.OBJ is Tables A.3 and A.4 plus other refrigerants. Each of these object files must also be linked with COMMON.OBJ, which is a subroutine for converting units. The second disk contains the execution file CATH2, which includes Appendix Tables A.7 through A.16 plus Figures A.6 through A.10. This disk also contains the object files IDEAL.OBJ, which is Tables A.11 and A.12, and LK.OBJ, which is Table A.14.

OBJECT FILES

Each binary or object file has several subroutines, function subprograms, or both, as summarized in the following table. Please do not use the same name as your subroutine name, function subprogram name, label of common statement, or block data name.

File	Subroutines or Function Subprograms							
COMMON	+ CHREAD	OPENFL	TCNVRT	TUNITS	XUNIT			
ANM	+ AAVE	AA06	ADATA	ADATA2	ADATA3	ADATA6	AINIT	AINIT2
	+ AINIT3	AINIT6	AINT3	AMELT	AMELT2	AMELT3	AMELT6	AMPT
	+ AMTPX	AMT3	AMTV	AMPH	AMPV	AMPS	ANM+	ASAT
	+ ATSAT	ATP2	APSAT	APSAT2	APSAT3	APSAT6	APVT	APVT2
	+ AVVT3	APVT6	AVPT					
FREON	+ FADATA	FCPCV	FCDATA	FGDATA	FHDATA	FLDATA	FMPH	FMPS
	+ FMPV	FMPX	FMTP	FMTS	FMTV	FMTX	FPDATA	FPSAT
	+ FPVT	FREON+	FSAT	FTDATA	FTSAT	FTPV	FUHS	FVP
	+ FVS	FVPT						
STEAM	+ SAA	SDATA	SMTP	SMTS	SMTV	SMTX	SNPH	SNPS
	+ SNPV	SNPX	SPSAT	SNVT	SRT	SSAT	STEAM+	STPV
	+ STSAT	SVPT						

IDEAL	+ AIR	BISECT	C	CO	CORRCT	CO2	EQNS	FNAIR+
	+ FNAR	FNN2	FNO2	HFS	HST	H2	H2O	HEQ
	+ MWS	N	NAMES	NO1	NO2	N2	O	OH
	+ O2	RCONST	REFS	SUBST+	TM12	TM16	XCNVRT	XH
	+ XUNITS	YCHEBY	YHHST	YSHST	YCHEBY			
LK	+ ZDATA	ZINIT	ZMAIN	ZMTP+	ZMTPX+	ZPEAK	ZPSAT	ZPVT
	+ ZTSAT	ZVPT						

+ : Can be called by user's program

EXPLANATION OF ARGUMENTS

Shown are several leading lines of subroutines that can be called by the user's own main program or subprograms. There are two types of arguments. The letter I denotes that the argument is an input variable that must have physically meaningful values and is initialized by calling the program. The letter O indicates the argument is an output variable that the subroutine returns.

It is not recommended to call subroutines by writing

```
CALL STEAM(4,1,P,V,100.D0,U,H,S,0.5D0,IPHASE).
```

This may work, but the safe way of calling the subroutine is to write

```
JOB = 4
IUNIT = 1
T = 100.D0
X = 0.5D0
CALL STEAM(JOB,IUNIT,P,V,T,U,H,S,X,IPHASE).
```

EXAMPLES

a) STEAM FILE STEAM.OBJ

```
      SUBROUTINE STEAM(JOB,IUNIT,P,V,T,U,H,S,X,IPHASE)
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
      PURPOSE
         CALCULATION OF THERMODYNAMIC PROPERTIES OF STEAM

      ARGUMENTS
         I   JOB    : JOB IDENTIFIER                    SEE NOTE 1)
         I   IUNIT  : UNIT IDENTIFIER                   SEE NOTE 2)
         I/O P      : PRESSURE                          SEE NOTE 2)
         I/O V      : SPECIFIC VOLUME                   SEE NOTE 2)
         I/O T      : TEMPERATURE                       SEE NOTE 2)
         I/O U      : SPECIFIC INTERNAL ENERGY          SEE NOTE 2)
         I/O H      : SPECIFIC ENTHALPY                 SEE NOTE 2)
         I/O S      : SPECIFIC ENTROPY                  SEE NOTE 2)
         I/O X      : QUALITY    0 (= X (= 1
         O   IPHASE : PHASE INDICATOR                   SEE NOTE 3)

      NOTE 1)

         JOB    INPUT      JOB    INPUT
          1    T AND P      5    P AND V
          2    T AND V      6    P AND H
          3    T AND S      7    P AND S
          4    T AND X      8    P AND X
```

NOTE 2)

IUNIT	T	P	V	U	H	S
1	C	MPa	m3/kg	kJ/kg	kJ/kg	kJ/kg/K
2	K	MPa	mol/dm3	kJ/kmol	kJ/kmol	kJ/kmol/K
3	F	psia	ft3/lbm	Btu/lbm	Btu/lbm	Btu/lbm/R
4	R	psia	lbmol/ft3	Btu/lbmol	Btu/lbmol	Btu/lbmol/R

NOTE 3)

IPHASE	MEANING	
0	INAPPROPRIATE DATA INPUT	
1	DENSE FLUID (T>TC)	
2	COMPRESSED LIQUID	
3	SATURATED LIQUID	
4	LIQ. VAP. MIXTURE	
5	SATURATED VAPOR	
6	SUPERHEATED VAPOR	
7	COMPRESSED SOLID	* NOT AVAILABLE
8	SATURATED SOLID	
9	SOLID VAP. MIXTURE	

b) FREON

```
        FILE FREON.OBJ
      SUBROUTINE FREON(IDR,JOB,IUNIT,P,V,T,U,H,S,X,IPHASE)
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
      PURPOSE
         CALCULATION OF THERMODYNAMIC PROPERTIES OF REFRIGERANTS

      ARGUMENTS
         I   IDR    : REFRIGERANT IDENTIFIER            SEE NOTE 1)
         I   JOB    : JOB IDENTIFIER                    SEE NOTE 2)
         I   IUNIT  : UNIT IDENTIFIER                   SEE NOTE 3)
         I/O P      : PRESSURE                          SEE NOTE 3)
         I/O V      : SPECIFIC VOLUME                   SEE NOTE 3)
         I/O T      : TEMPERATURE                       SEE NOTE 3)
         I/O U      : SPECIFIC INTERNAL ENERGY          SEE NOTE 3)
         I/O H      : SPECIFIC ENTHALPY                 SEE NOTE 3)
         I/O S      : SPECIFIC ENTROPY                  SEE NOTE 3)
         I/O X      : QUALITY    0 <= X <= 1
         O   IPHASE : PHASE INDICATOR                   SEE NOTE 4)

      NOTE 1)
          ID  SUBSTANCE  ID  SUBSTANCE  ID SUBSTANCE
          1)  R-11       2)  R-12       3) R-14
          4)  R-22       5)  R-500      6) R-502

      NOTE 2)

         JOB    INPUT    JOB    INPUT
          1    T AND P    5    P AND V
          2    T AND V    6    P AND H
          3    T AND S    7    P AND S
          4    T AND X    8    P AND X
```

NOTE 3)

IUNIT	T	P	V	U	H	S
1	C	MPa	m3/kg	kJ/kg	kJ/kg	kJ/kg/K
2	K	MPa	mol/dm3	kJ/mol	kJ/kmol	kJ/kmol/K
3	F	psia	ft3/lbm	Btu/lbm	Btu/lbm	Btu/lbm/R
4	R	psia	lbmol/ft3	Btu/lbmol	Btu/lbmol	Btu/lbmol/R

NOTE 4)

IPHASE	MEANING
0	INAPPROPRIATE DATA INPUT
1	DENSE FLUID (T)TC)
2	COMPRESSED LIQUID * NOT AVAILABLE
3	SATURATED LIQUID
4	LIQ. VAP. MIXTURE
5	SATURATED VAPOR
6	SUPERHEATED VAPOR

c) AMMONIA, NITROGEN, AND METHANE FILE ANM.OBJ

```
      SUBROUTINE ANM(ID,JOB,IUNIT,P,V,T,U,H,S,X,IPHASE)
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
      PURPOSE
         CALCULATION OF THERMODYNAMIC PROPERTIES OF AMMONIA, NITROGEN,
         AND METHANE

      ARGUMENTS
         I    ID      : SUBSTANCE IDENTIFIER              SEE NOTE 1)
         I    JOB     : JOB IDENTIFIER                    SEE NOTE 2)
         I    IUNIT   : UNIT IDENTIFIER                   SEE NOTE 3)
         I/O  P       : PRESSURE                          SEE NOTE 3)
         I/O  V       : SPECIFIC VOLUME                   SEE NOTE 3)
         I/O  T       : TEMPERATURE                       SEE NOTE 3)
         I/O  U       : SPECIFIC INTERNAL ENERGY          SEE NOTE 3)
         I/O  H       : SPECIFIC ENTHALPY                 SEE NOTE 3)
         I/O  S       : SPECIFIC ENTROPY                  SEE NOTE 3)
         I/O  X       : QUALITY     0 (= X (= 1
         O    IPHASE  : PHASE INDICATOR                   SEE NOTE 4)

      NOTE 1)
          ID  SUBSTANCE
           2  AMMONIA
           5  NITROGEN
           6  METHANE

      NOTE 2)

         JOB     INPUT     JOB     INPUT
          1     T AND P     5     P AND V
          2     T AND V     6     P AND H
          3     T AND S     7     P AND S
          4     T AND X     8     P AND X
```

NOTE 3)

IUNIT	T	P	V	U	H	S
1	C	MPa	m3/kg	kJ/kg	kJ/kg	kJ/kg/K
2	K	MPa	mol/dm3	kJ/kmol	kJ/kmol	kJ/kmol/K
3	F	psia	ft3/lbm	Btu/lbm	Btu/lbm	Btu/lbm/R
4	R	psia	lbmol/ft3	Btu/lbmol	Btu/lbmol	Btu/lbmol/R

NOTE 4)

IPHASE	MEANING
0	INAPPROPRIATE DATA INPUT
1	DENSE FLUID (T>TC)
2	COMPRESSED LIQUID
3	SATURATED LIQUID
4	LIQ. VAP. MIXTURE
5	SATURATED VAPOR
6	SUPERHEATED VAPOR

d) GENERALIZED COMPRESSIBILITY FACTOR FILE LK.OBJ

```
      SUBROUTINE ZPMT(TR,PR,W,IPHASE,Z ,DH ,DS ,FP ,
     A                Z0,DH0,DS0,FP0,Z1,DH1,DS1,FP1)
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
      PURPOSE
         CALCULATION OF THERMODYNAMIC PROPERTIES WITH GIVEN TR AND PR
      ARGUMENTS
         I   TR     : REDUCED TEMPERATURE
         I   PR     : REDUCED PRESSURE
         I   W      : ACENTRIC FACTOR
         O   Z      : COMPRESSIBILITY FACTOR
         O   FP     : FUGACITY COEFFICIENT BASED ON NATURAL LOGARITHM
                      ln( f/P )
         O   DH     : ENTHALPY DEPARTURE
         O   DS     : ENTROPY  DEPARTURE
         O   IPHASE : PHASE INDICATOR

                      0) UNDEFINED
                      1) TR ) 1
                      2) COMPRESSED LIQUID
                      3) SATURATED LIQUID
                      4) SATURATED VAPOR
                      5) SUPERHEATED VAPOR
      NOTE
         COMPRESSIBILITY                : Z = P*V/R/T
         FUGACITY COEFFICIENT           : FP = ln(f/p)
         ISOTHERMAL ENTHALPY DEPARTURE  : DH = (H-H*)/R/TC
         ISOTHERMAL ENTROPY  DEPARTURE  : DS = (S-S*)/R
```

```
 SUBROUTINE ZMTPX(IOPT,TR,PR,W,X,IPHASE,Z,DH,DS,FP,
A    ZF ,DHF ,DSF ,FPF ,ZFG,DHFG,DSFG,FPFG,ZG ,DHG ,DSG ,FPG ,
B    ZFO,DHFO,DSFO,FPFO,ZF1,DHF1,DSF1,FPF1,
C    ZGO,DHGO,DSGO,FPGO,ZG1,DHG1,DSG1,FPG1)

 IMPLICIT REAL*8 (A-H,O-Z)
```

```
PURPOSE
   CALCULATION OF THERMODYNAMIC PROPERTIES WITH GIVEN PR/TR AND X
ARGUMENTS
   I    IOPT : OPTION
     * IOPT = 1 ==) FOR A GIVEN TR FIND OTHER PROPERTIES
     * IOPT = 2 ==) FOR A GIVEN PR FIND OTHER PROPERTIES
   I/O TR    : REDUCED SATURATION TEMPERATURE
   I    X     : QUALITY   0 (= X (= 1
   I    W     : ACENTRIC FACTOR
   I/O PR    : REDUCED SATURATION PRESSURE
   O    Z     : COMPRESSIBILITY FACTOR
   O    FP    : FUGACITY COEFFICIENT BASED ON NATURAL LOGARITHM
                ln( f/p )
   O    DH    : ENTHALPY DEPARTURE
   O    DS    : ENTROPY  DEPARTURE
   O    IPHASE : PHASE INDICATOR
                 1) DENSE FLUID ( T ) TC )
                 2) COMPRESSED LIQUID
                 3) SATURATED LIQUID
                 4) LIQ. VAP. MIXTURE
                 5) SATURATED VAPOR
                 6) SUPERHEATED VAPOR
NOTE
   COMPRESSIBILITY                 : Z =  P*V/R/T
   FUGACITY COEFFICIENT            : FP = ln(f/p)
   ISOTHERMAL ENTHALPY DEPARTURE : DH = (H-H*)/R/TC
   ISOTHERMAL ENTROPY  DEPARTURE : DS = (S-S*)/R
```

---

e) PROPERTIES OF AIR FILE IDEAL.OBJ

```
      SUBROUTINE FNAIR(T,U,H,S,PR,VR)
      IMPLICIT REAL*8 (A-H,O-Z)
C-----------------------------------------------------------------------
C PURPOSE
C    CALCULATE THE IDEAL GAS PROPERTIES OF AIR
C ARGUMENTS
C    I   T : TEMPERATURE IN K
C    O   U : INTERNAL ENERGY IN kJ/kg
C    O   H : ENTHALPY        IN kJ/kg
C    O   S : ENTROPY         IN kJ/kg/K
C REFERENCE DATA
C
C    COMP.   M. WEIGHT   VOLUME (%)
C      N2      28.0134        78.03
C      O2      31.9988        20.99
C      AR      39.9480         0.98
C     AIR      28.9669
C
C    Molar Gas Constant R = 8.3144125  kJ/kmol.K
C    R of Air             = 53.348     ft.lb/R lb
C                         =  0.068556  Btu/R.lb
C                         =  0.2870315 kJ/kg K
C-----------------------------------------------------------------------
```

```
f) PROPERTIES OF GASES   FILE IDEAL.OBJ

      SUBROUTINE SUBST(ID,TEMP,H,S,ITUNIT)
      IMPLICIT REAL*8 (A-H,O-Z)
-------------------------------------------------------------------------------
      PURPOSE
         FIND H AND S FOR A GIVEN T

      ARGUMENT
         I ID     : GAS IDENTIFIER                    SEE NOTE 1)
         I TEMP   : TEMPERATURE                       SEE NOTE 2) FOR UNITS
         O H      : ENTHALPY IN kJ/kg   OR IN Btu/lbm
         O S      : ENTROPY  IN kJ/kg/K OR IN Btu/lbm/R
         I ITUNIT : UNIT OF TEMPERATURE               SEE NOTE 2)

      NOTE 1)
        ID  GAS    ID  GAS    ID  GAS    ID  GAS    ID  GAS
         1   N2     2  N       3  O2      4  O       5  CO2
         6   CO     7  H2O     8  OH      9  H2     10  H
        11   NO    12  NO2

      NOTE 2)
         ITUNIT : 1  2  3  4
         T UNIT : C  K  F  R

         IF ITUNIT = 1, 2 ==> H,S IN SI UNIT
         IF ITUNIT = 3, 4 ==> H,S IN ENGLISH UNIT
-------------------------------------------------------------------------------
```

SOME SELECTED REFERENCES

H. B. Callen, *Thermodynamics*, John Wiley & Sons, New York, 1960.

N. Davidson, *Statistical Mechanics*, McGraw-Hill Book Co., New York, 1962.

G. N. Hatsopoulos and J. H. Keenan, *Principles of General Thermodynamics*, John Wiley & Sons, New York, 1965, 1981.

J. R. Howelland R. O. Buckius, Fundamentals of Engineering Thermodynamics, McGraw-Hill Book Co., New York, 1987.

F. P. Incropera, *Introduction to Molecular Structure and Thermodynamics*, John Wiley and Sons, New York, 1974.

J. H. Keenan, *Thermodynamics* M.I.T. Press, Cambridge, MA, 1970.

J. Kestin, *A Course in Thermodynamics*, Hemisphere Publishing Corp., Washington, D.C., 1966, 1979.

J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Second Edition, John Wiley & Sons, New York, 1977.

W. C. Reynolds and H. C. Perkins, *Engineering Thermodynamics*, Second Edition, McGraw-Hill Book Co., New York, 1977.

R. E. Sonntag and G. J. Van Wylen, *Fundamentals of Statistical Thermodynamics*, John Wiley and Sons, New York, 1966.

R. E. Krieger Publishing Co., Malabar, FL, 1985.

G. J. Van Wylen and R. E. Sonntag, *Fundamentals of Classical Thermodynamics*, Third Edition, English SI Version, John Wiley & Sons, New York, 1986.

K. Wark, *Thermodynamics*, Fourth Edition, McGraw-Hill Book Co., New York, 1983.

M. W. Zemansky, M. M. Abbott, and H. C. Van Ness, *Basic Engineering Thermodynamics*, McGraw-Hill Book Co., New York, 1966, 1975.

ANSWERS TO SELECTED PROBLEMS

2.3 490.33 N
2.6 150 N
2.9 98.7 kPa
2.12 360.9 kPa
2.15 33.2 kPa

3.9 351 kPa
3.12 (a) 7.63 kg
(b) 10%
3.12E (a) 12.32 lbm
(b) 10%
3.21 95.3 kPa
3.21E 12.6 lbf/in.^{2}
3.24 2.74 h
3.27 0.123%
3.30 290 kPa_3
3.33 1.594 m^3/h

4.3 0.153 kJ
4.6 63.4 kJ
4.6E 42.8 Btu
4.9 0.222 kJ
4.12 117 kPa; 54.1 kJ
4.12E 17 lbf/in.^{2}; 47.5 Btu
4.15 117.5 kJ
4.18 −7.56 kJ
4.21 40 kJ
4.24 (a) 247 kPa; 33.6 L
(b) 5.8 kJ

5.3 1405 kJ
5.6 51 kJ
5.6E 39.6 Btu
5.9 71.4 h
5.12 −13.7°C
5.15 132.7 kPa, 403.7°C
5.18 −20°C
5.18E 6 F
5.21 −878.4 kJ
5.24 32.29 MJ
5.27 (a) 260.2 kJ/kg
(b) 460.8 kJ/kg
(c) 420.9 kJ/kg
5.30 (a) 150 kPa; −513 kJ
(b) 26.6%
5.30E (a) 24.7 lbf/in.^{2}; −130.5 Btu
(b) 30.5%
5.33 3.14 MPa; −24.2 kJ
5.36 1875 kPa; 183 kJ; 2023 kJ
5.39 (a) 17.38 MJ
(b) 441.6 kJ; −321.2 kJ

6.3 29.7 mm
6.6 0.947
6.9 7833 kW
6.9E 2.108×10^7 Btu/h
6.12 0.0794 kg/s
6.15 (a) 2673.9 kJ/kg; 0.9755
(b) 18.394 MW
(c) 22.489 MW
(d) 0.0349
(e) 126°C
(f) 120.45 MW
(g) 0.26
6.18 0.0489; 203 m/s
6.21 (a) −0.549 kW
(b) −8.654 kW
(c) 5.397 kW
6.24 8.873 kg
6.27 4.29 MPa

6.30 77.8°C
6.30E 175.3 F
6.33 318.5 kJ
6.36 (a) 0.3353
(b) 25.07 kg

7.6 0.595
7.9 2.558 kW
7.9E 2.355 kW
7.18 5886.7 kJ; 0.0142
7.12 0.687
7.12E 0.611

8.3 7.11 kJ; 59.65 kJ
8.3E 6.47 Btu; 54.46 Btu
8.6 (a) 2.048 MPa
(b) 474.3 kJ
8.6E (a) 335 lbf/in.^{2}
(b) 213.3 Btu
8.9 1.188 MPa, 476°C
8.12 (a) 7.324 kJ/K; 7.90 kJ/K; 25.856 kJ/k
8.21 1.9427 kJ/K
8.21E 0.462 Btu/R
8.24 2.3653 kJ/K
8.27 (b) 143.2 K; −623.9 kJ/kg
8.27E (b) 256.7 R; −270.7 Btu/Ibm
8.30 (a) 6.52 kg
(b) 6.61 kg
8.30E (a) 10.53 Ibm
(b) 10.72 Ibm
8.33 0.365 kJ/K
8.33E 0.2114 Btu/R
8.36 1.08 kJ; 0.28 kJ
8.42 453 kPa; 843 kJ

9.3 0.809 kg/s
9.3E 6018 1bm/h
9.6 (a) 706 K; 557.9 kJ/kg
(b) 662.1 K; 539.8 kJ/kg
9.9 6.082 MPa; 25.1°C
9.9E 951 lbf/in.^{2}; 75.2 F
9.12 365.8 kW
9.12E 414.2 hp
9.15 (a) 0.0952
(b) 0.6 kJ/kg; 328.1 kJ/kg
(c) 0.3088 kJ/K kg m_1
9.21 111.44 kJ/kg
9.21E 42.0 Btu/lbm
9.24 (a) 1.867; 0.9639
(b) 3.811; 0.9982
9.27 128.6 kPa; 313.1 K
9.30 0.0499 kW/K
9.30E 73.7 Btu/R h
9.36 92.47 kW
9.39 46.3°C; 19.8 kJ/kg
9.39E 580.3 R; 8.7 Btu/lbm
9.42 6.237 kJ/kg
9.42E 2.6 Btu/lbm
9.45 0.177 kJ/kg
9.48 60.21 kW

10.3 (a) 33 400 kW; −484 kW
(b) 142 747 kg/s; 147 324 kg/s
(c) 0.027
10.12 36.2%; 863.2 kJ/kg
10.15 (a) 6.53 kg/s
(b) 3.2 kW; 53.22 kW
(c) 304.6 kg/s
(d) 0.997 m
10.18 (a) 7.82 kg/s
(b) 47.8 kW
(c) 33.3%
10.24 2.84
10.30 (a) 0.672
(b) 1.0
10.33 (a) 8.7 kJ/kg
(b) 5.325 kW
(c) 2.219
10.36 0.147
10.39 (a) 11.12 MPa; 3623 K
(b) 0.502
(c) 1879 kPa
10.42 10.0 MPa; 3779 K; 0.595
10.42E 1557 lbf/in.^{2}; 7147 R; 0.595
10.45 (a) 2763 kPa
(b) 0.783; 0.374
10.45E (a) 402 lbf/in.^{2}
(b) 0.781; 0.374
10.48 (a) 3046 kW; 7009 kW; 0.509
(b) 221 kPa
10.51 (a) 166.33 MW; 0.399
(b) 0.53
10.51E (a) 165 600 hp; 0.396
(b) 0.53

10.54 (a) 375 kPa
(b) 442 kJ/kg; 0.339 kg/s
(c) 958.8 K; 0.687
10.60 592 kPa; 969 m/s
10.63 0.573

11.3 (a) 3.31% H_2, 65.71% CO, 30.98% CO_2
(b) 0.000 874 kg
(c) 0.072 kJ
11.6 170 kPa
11.9 1.1436 kW/K
11.9E 0.864 Btu/R s
11.12 0.5329 kg
11.12E 0.894 lbm
11.15 28.2°C; −2.77 kJ
11.15E 78 F; −1.49 Btu
11.18 (a) 0.0009 kg/s
(b) 6.23 kW
11.18E (a) 10.39 lbm/h
(b) 29 700 Btu/h
11.21 (a) −11.5 kJ
(b) 0.2023 kJ/K
11.24 (a) 1.7°C; 0.028 79 kg/kg
(b) −1.05 kW
11.24E (a) 37.1 F; 0.033 75 lbm/lbm
(b) −2370 Btu/h
11.27 811.7 kg/s; 0.0163
11.30 0.761; 5°C
11.30E 0.789; 40 F

12.3 48 Pa; 2.16×10^{-3} Pa
12.18 234 K
12.18E 422 R
12.27 2.15 kg
12.33 3970 kJ
12.33E 4770 Btu
12.36 −915 kJ
12.39 1630 kPa
12.39E 256 lbf/in.^{2}
12.42 −2137 kJ
12.45 267 K, 1200 kPa
12.48 (a) 1.0; 1.42
(b) 5.06; 8.93
12.51 0.001 442 kmol; 0.001 447 kmol
12.54 (a) 300 K, 52% A

13.3 145%
13.6 (b) 2.95
13.9 (a) 43.2°C
(b) 0.0639
13.9E (a) 110.4 F
(b) 0.069
13.12 2855 K
13.15 −673 822 kJ
13.18 (a) −859 192 kJ/kmol
(b) −778 190 kJ/kmol
13.18E (a) −369 746 Btu/lb mol
(b) −337 570 Btu/lb mol
13.21 2044 K
13.24 (a) 2909 K
(b) 7400 K
13.24E (a) 5236 R
(b) 13 320 R
13.27 (a) 410.4%
(b) 30.5°C
13.30 (a) −863 830 kJ/kmol;
−1 196 121 kJ/kmol
(b) −956 194 kJ/kmol;
−1 310 223 kJ/kmol
13.33 110 630 kJ
13.36 1839 kJ/K
13.39 (a) 2.011 MPa; 666.4 K
(b) 2907 K; 8.772 MPa
(c) 152 860 kJ
13.42 (a) 700 K
(b) 198.8 kJ/kmol K
13.45 (a) 4.078 kW
(b) 13.9%
13.45E (a) 20 910 Btu/h
(b) 13.7%
14.6E (a) 848 lbf/in.^{2}
14.3 89.6% N_2; 23.3% N_2
14.6 (a) 6137 kPa
(b) −139.53 kJ/K
14.6E (a) 848 lbf/in.^{2}
(b) −32.45 Btu/R
14.9 (a) 224.79 kJ/kmol K
(b) 0.888 kmol
14.12 exp(324.888); exp(288.855)
14.18 59.3% H_2; 26.0% CO_2; 7.35% CO;
7.35% H_2O
14.21 73.7%; 0.128% NO

14.24 (a) 1.37% C_2H_5OH; 32.42% C_2H_4; 66.21% H_2O
(b) 41 500 kJ
14.27 (a) 6.202
(b) 85.44% NH_3; 3.64% N_2; 10.92% H_2
14.30 (a) 0.002 35
14.30E (a) 0.0024
14.33 66.54% N_2; 4.65% O_2; 0.89% Ar; 22.71% O; 5.21% NO
14.39 3.885×10^{-5}

15.6 73 m/s; 10 mm/s
15.9 (a) 3.44×10^{-36} J; 3.28×10^{-33} J
(b) 9.79×10^{-38} J; 9.32×10^{-35} J

16.3 (a) 0.91
(b) 4
16.6 0.72
16.9 12 600
16.12 10/243
16.15 (a) 400; 190
(b) 400; 210
(c) 95%
16.18 18/57

17.3 1232; 536; 232
17.6 14.023 k; 15.932 k

18.9 120 824 kJ/kmol K
18.15 (b) 0.416
18.18 (b) 0.74
18.24 2.78×10^{20} $1/m^2 s$
18.36 0.9939
18.39 268.25 kJ/kmol K
18.45 −178 909 kJ/kmol
18.48 8.976×10^{-19} J; 2.162×10^{10} Pa
18.57 49.93 kPa; 99.76% He
18.60 exp(−41.635); exp(−2.826)

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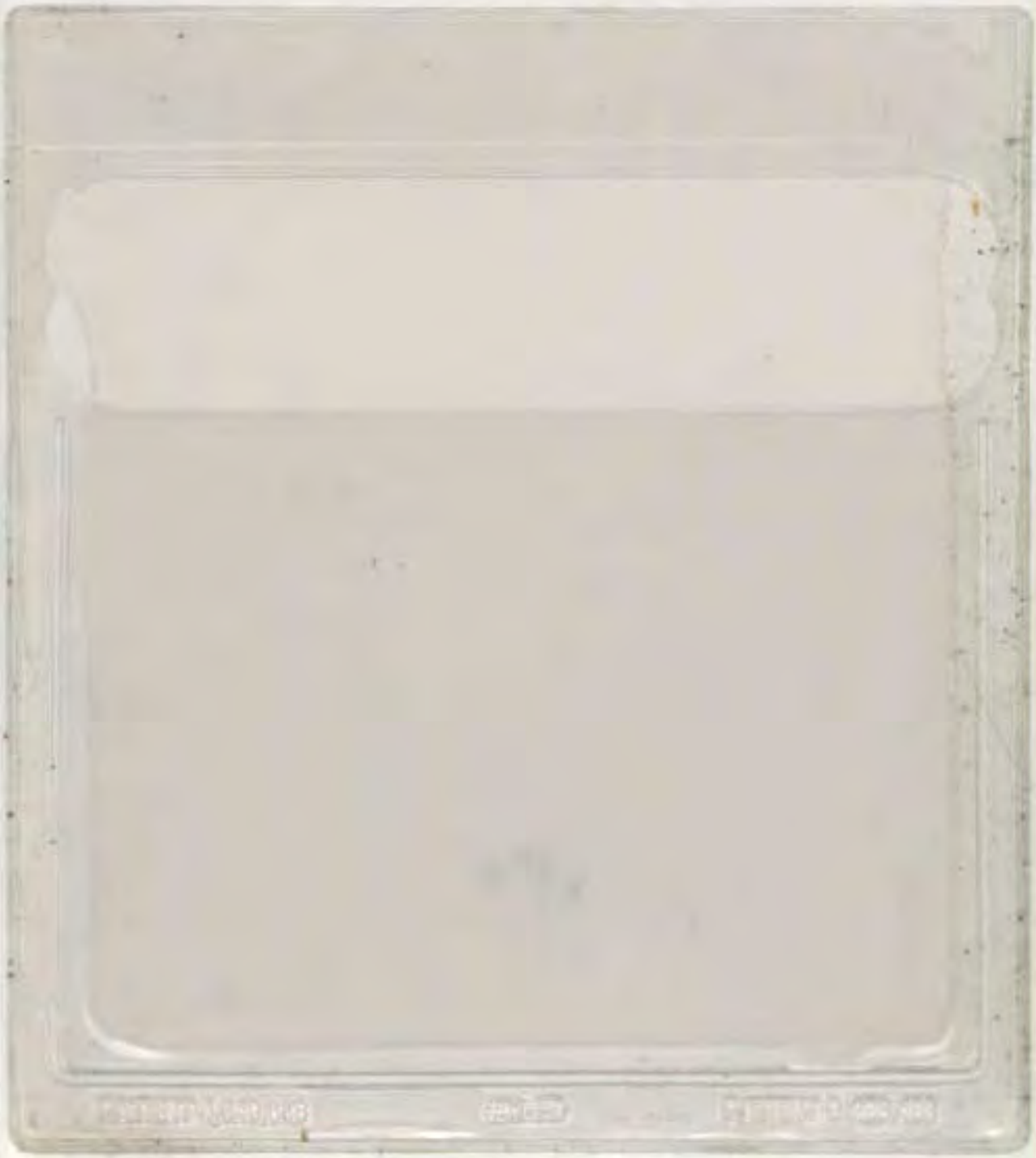
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