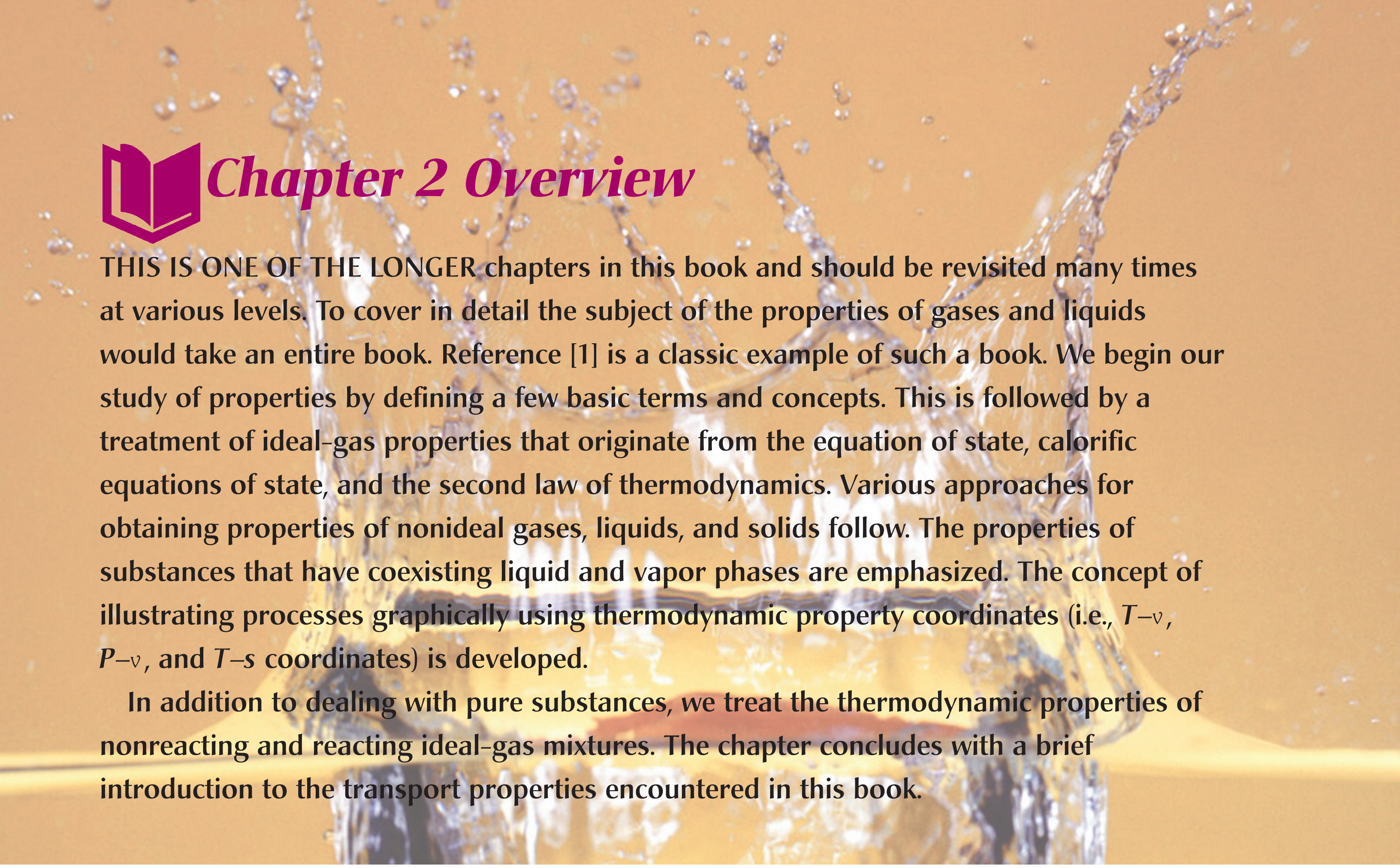
CHAPTER TWO

THERMODYNAMIC PROPERTIES, PROPERTY RELATIONSHIPS, AND PROCESSES

LEARNING OBJECTIVES

After studying Chapter 2, you should:

- *Be able to explain the meaning of the continuum limit and its importance to thermodynamics.*
- *Be familiar with the following basic thermodynamic properties: pressure, temperature, specific volume and density, specific internal energy and enthalpy, constant-pressure and constant-volume specific heats, entropy, and Gibbs free energy.*
- *Understand the relationships among absolute, gage, and vacuum pressures.*
- *Know the four common temperature scales and be proficient at conversions among all four.*
- *Know how many independent intensive properties are required to determine the thermodynamic state of a simple compressible substance.*
- *Be able to indicate what properties are involved in the following state relationships: equation of state, calorific equation of state, and the Gibbs (or T–ds) relationships.*
- *Explain the fundamental assumptions used to describe the molecular behavior of an ideal gas and under what conditions these assumptions break down.*
- *Be able to write one or more forms of the ideal gas equation of state and from this derive all other (mass, molar, mass-specific, and molar-specific) forms.*
- *Be proficient at obtaining thermodynamic properties for liquids and gases from NIST software or online databases and from printed tables.*
- *Be able to explain in words and write out mathematically the meaning of the thermodynamic property quality.*
- *Be able to draw and identify the following on T–v, P–v, and T–s diagrams: saturated liquid line, saturated vapor line, critical point, compressed liquid region, liquid–vapor region, and the superheated vapor region.*
- *Be able to draw an isobar on a T–v diagram, an isotherm on a P–v diagram, and both isobars and isotherms on a T–s diagram.*
- *Be proficient at plotting simple isobaric, isochoric, isothermal, and isentropic thermodynamic processes on T–v, P–v, and T–s coordinates.*
- *Be able to explain the approximations used to estimate properties for liquids and solids.*
- *Be able to derive all of the isentropic process relationships for an ideal gas given that $Pv^{\gamma} =$ constant.*
- *Be able to explain the meaning of a polytropic process and write the general state relationship expressing a polytropic process.*
- *Be able to explain the principle of corresponding states and the use of generalized compressibility charts.*
- *Be able to express the composition of a gas mixture using both mole and mass fractions.*
- *Be able to calculate the thermodynamic properties of an ideal-gas mixture knowing the mixture composition and the properties of the constituent gases.*
- *Understand the concept of standardized properties, in particular, standardized enthalpies, and their application to ideal-gas systems involving chemical reaction.*
- *Be able to apply the concepts and skills developed in this chapter throughout this book.*



Chapter 2 Overview

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

In addition to dealing with pure substances, we treat the thermodynamic properties of nonreacting and reacting ideal-gas mixtures. The chapter concludes with a brief introduction to the transport properties encountered in this book.

2.1 KEY DEFINITIONS

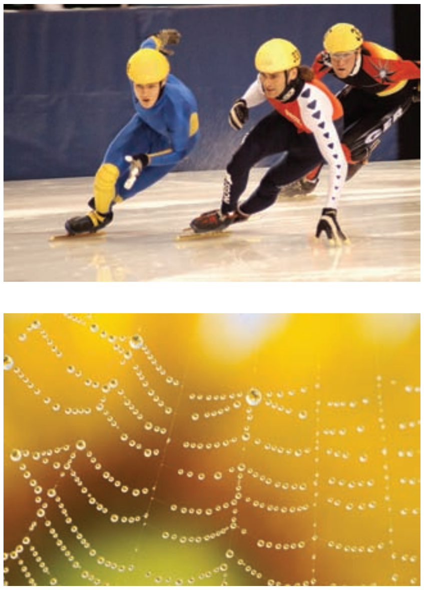
To start our study of thermodynamic properties, you should review the definitions of **properties**, **states**, and **processes** presented in Chapter 1, as these concepts are at the heart of the present chapter.

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

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

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

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



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

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

The adjectives ***simple*** and ***compressible*** greatly simplify the description of the state of a substance. Many systems of interest to engineering closely approximate simple compressible substances. Although we consider motion, fluid shear, and gravity in our study of fluid flow (Chapters 6, 9, and 10), their effects on local thermodynamic properties are quite small; thus, fluid properties are very well approximated as those of a simple compressible substance. Free surface, magnetic, and electrical effects are not considered in this book.

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

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

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

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

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

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

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

and

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

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

$$\bar{v} \equiv \mathcal{V}/N \quad [=]\ \mathrm{m^3/kmol} \tag{2.2a}$$

and

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

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[1] A more rigorous definition of a simple compressible substance is that, in a system comprising such a substance, the only reversible work mode is that associated with compression or expansion, work, that is, P–$d\mathcal{V}$ work. To appreciate this definition, however, requires an understanding of what is meant by *reversible* and by *P–$d\mathcal{V}$ work*. These concepts are developed at length in Chapters 4 and 7.

where N is the number of moles under consideration. Molar-specific properties are designated using lowercase symbols with an overbar, as shown in Eqs. 2.2. Conversions between mass-specific properties and molar-specific properties are accomplished using the following simple relationships:

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

and

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

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

2.2 FREQUENTLY USED THERMODYNAMIC PROPERTIES

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

2.2a Properties Related to the Equation of State

Mass

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

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

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

Number of Moles

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

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

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

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[2] Strictly, the atomic weight is not a weight at all but is the relative atomic mass.

Table 2.1 Common Thermodynamic Properties of Single-Phase Pure Substances

Property	Symbolic Designation		Units		Relation to Other Properties	Classification
	Extensive	Intensive*	Extensive	Intensive*		
Mass	M	—	kg	—	—	Fundamental property appearing in equation of state
Number of moles	N	—	kmol	—	—	Fundamental property appearing in equation of state
Volume and specific volume	$\mathcal{V}$	v	m^3	m^3/kg	—	Fundamental property appearing in equation of state
Pressure	—	P	—	Pa or N/m^2	—	Fundamental property appearing in equation of state
Temperature	—	T	—	K	—	Fundamental property appearing in equation of state
Density	—	ρ	—	kg/m^3	—	Fundamental property appearing in equation of state
Internal energy	U	u	J	J/kg	—	Based on first law and calculated from calorific equation of state
Enthalpy	H	h	J	J/kg	$U + P\mathcal{V}$	Based on first law and calculated from calorific equation of state
Constant-volume specific heat	—	c_v	—	J/kg·K	$(\partial u/\partial T)_v$	Appears in calorific equation of state
Constant-pressure specific heat	—	c_p	—	J/kg·K	$(\partial h/\partial T)_p$	Appears in calorific equation of state
Specific-heat ratio	—	γ	—	Dimensionless	c_p/c_v	—
Entropy	S	s	J/K	J/kg·K	—	Based on second law of thermodynamics
Gibbs free energy (or Gibbs function)	G	g	J	J/kg	$H - TS$	Based on second law of thermodynamics
Helmholtz free energy (or Helmholtz function)	A	a	J	J/kg	$U - TS$	Based on second law of thermodynamics

[*] Molar intensive properties are obtained by substituting the number of moles, N, for the mass and changing the units accordingly. For example, $s \equiv S/M$ [=] J/kg·K becomes $\bar{s} \equiv S/N$ [=] J/kmol·K.

where $\mathcal{M}$ has units of g/mol or kg/kmol. Thus, the atomic weight of carbon 12 is exactly 12. The **Avagodro constant** $\mathcal{N}_{\mathrm{AV}}$ is used to express the number of particles (atoms, molecules, etc.) in a mole:

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

For example, we can use the Avagodro constant to determine the mass of a single ^{12}C atom:

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

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

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

Volume

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

Density

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

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

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

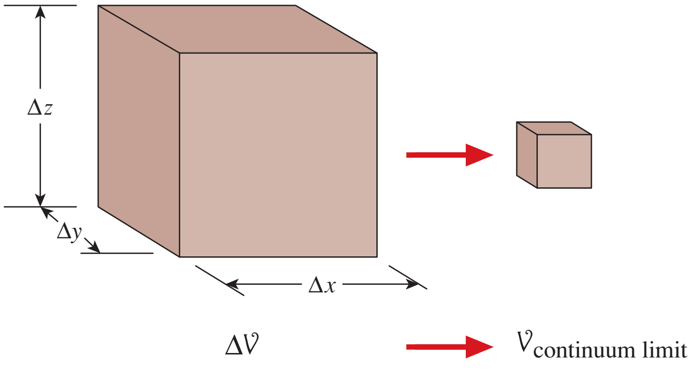

FIGURE 2.1
A finite volume element shrinks to the continuum limit to define macroscopic properties. Volumes smaller than the continuum limit experience statistical fluctuations in properties as molecules enter and exit the volume.

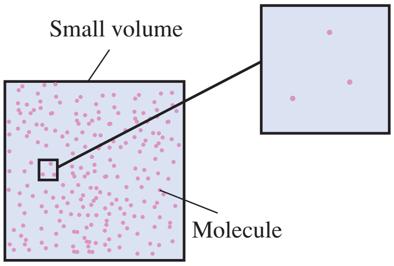

Table 2.2 Size of Gas Volume Containing *n* Molecules at 25°C and 1 atm

Number of Molecules (n)	Volume (mm^3)	Size of Equivalent Cube (mm)
10^5	4.06×10^{-12}	0.00016
10^6	4.06×10^{-11}	0.0003
10^{10}	4.06×10^{-7}	0.0074
10^{12}	4.06×10^{-5}	0.0344

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

Specific Volume

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

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

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

Pressure

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

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

This definition assumes that the fluid is in a state of equilibrium at rest. It is important to note that the pressure is a scalar quantity, having no direction associated with it. Figure 2.2 illustrates this concept showing that the pressure at a point[3] is independent of orientation. That the pressure force is always directed normal to a surface (real or imaginary) is a consequence of a fluid being unable to sustain any tangential force without movement. If a tangential force is present, the fluid layers simply slip over one another. Chapter 6 discusses pressure forces and their important role in understanding the flow of fluids.

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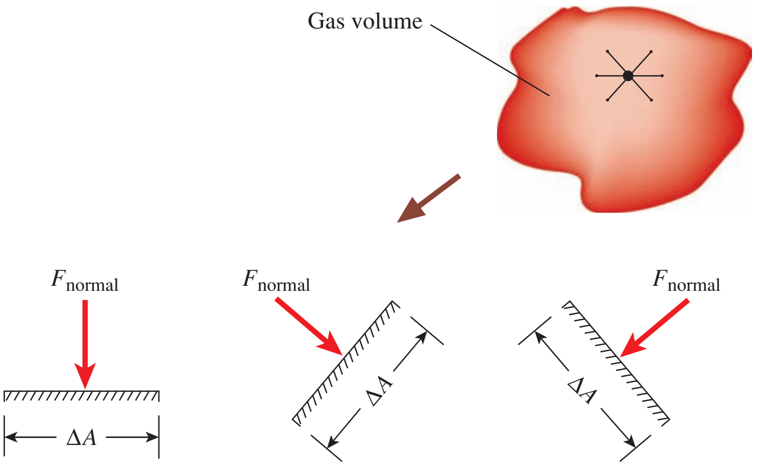
[3] Throughout this book, the idea of a *point* is interpreted in light of the continuum limit, that is, a point is of some small dimension rather than of zero dimension required by the mathematical definition of a point.

FIGURE 2.2
Pressure at a point is a scalar quantity independent of orientation. Regardless of the orientation of ΔA, application of the defining relationship (Eq. 2.10) results in the same value of the pressure.



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

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

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

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

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

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

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

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

$$\boxed{P_{\text{gage}} \equiv P_{\text{abs}} - P_{\text{atm, abs}},} \tag{2.12}$$

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

$$\boxed{P_{\text{vacuum}} = P_{\text{atm, abs}} - P_{\text{abs}}.} \tag{2.13}$$

This relationship is also illustrated in Fig. 2.3.

In addition to SI units, many other units for pressure are commonly employed. Most of these units originate from the application of a particular measurement method. For example, the use of manometers (as discussed in Chapter 6) results in pressures expressed in inches of water or millimeters of mercury. American (or British) customary units (pounds-force per square inch or *psi*) are frequently appended with a "g" or an "a" to indicate gage or absolute pressures, respectively (i.e., *psig* and *psia*). Conversion factors for common pressure units are provided at the front of this book.

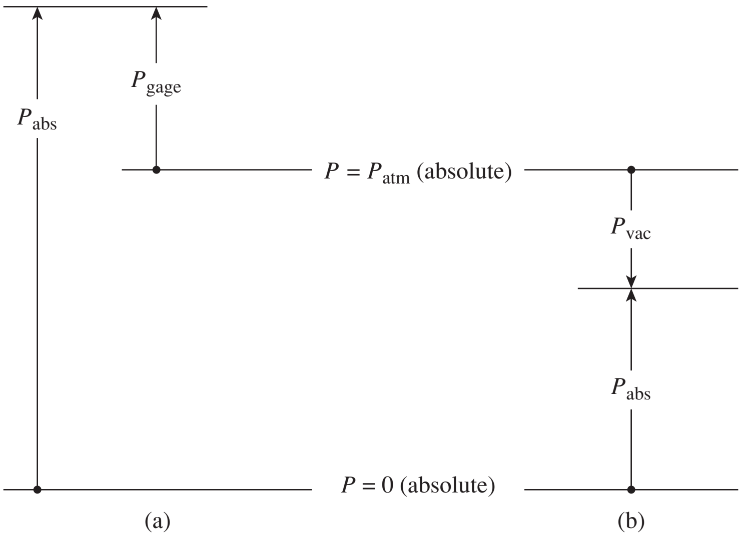


FIGURE 2.3
Absolute pressure is zero in a perfectly evacuated space; gage pressure is measured relative to the local atmospheric pressure.

Example 2.1

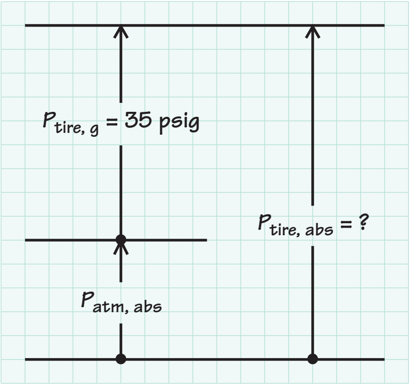
A pressure gage is used to measure the inflation pressure of a tire. The gage reads 35 psig in State College, PA, when the barometric pressure is 28.5 in of mercury. What is the absolute pressure in the tire in kPa and psia?

Solution

Known $P_{\text{tire, g}}, P_{\text{atm, abs}}$

Find $P_{\text{tire, abs}}$

Sketch



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

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

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

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

Thus,

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

Converting this result to units of kPa yields

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

Comments Note the use of three different units to express pressure: Pa (or kPa), psi (or lb_f/in^2), and in Hg. Other commonly used units are mm Hg and in H_2O. You should be comfortable working with any of these. Note also the usage *psia* and *psig* to denote *absolute* and *gage* pressures, respectively, when working with lb_f/in^2 units.

Self Test 2.1

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

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

Example 2.2 SI Engine Application

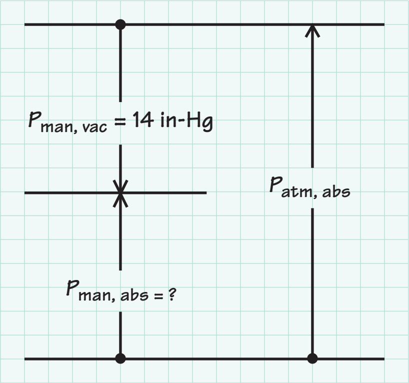
A vintage automobile has an intake manifold vacuum gage in the dashboard instrument cluster. Cruising at 20.1 m/s (45 mph), the gage reads 14 in Hg vacuum. If the local atmospheric pressure is 99.5 kPa, what is the absolute intake manifold pressure in kPa?

Solution

Given $P_{\text{man, vac}}$, $P_{\text{atm, abs}}$

Find $P_{\text{man, abs}}$

Sketch



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

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

Substituting numerical values and converting units yields

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

$$= 99.5\ \text{kPa} - 47.4\ \text{kPa} = 52.1\ \text{kPa}$$

Comments The pressure drops across the throttle plate of an SI engine (see Chapter 11). This lower pressure, in turn, results in a decreased air density and a smaller quantity of air entering the cylinder than would occur without the throttle. The throttle thus controls the power delivered by the engine.

Self Test 2.2

☑ **A technician performs a compression test on a vehicle engine and finds that the maximum pressure in one cylinder is 105 psig, while the minimum pressure in another is 85 psig. What is the absolute pressure difference between the two cylinders?**

(Answer: 20 psia)

Temperature

Like mass, length, and time, temperature is a fundamental dimension and, as such, eludes a simple and concise definition. Nevertheless, we all have some experiential notion of temperature when we say that some object is hotter than another, that is, that some object has a greater temperature than another. From a macroscopic point of view, we define temperature as that property that is shared by two systems, initially at different states, after they have been placed in thermal contact and allowed to come to thermal equilibrium. Although this definition may not be very satisfying, it is the best we can do from a macroscopic viewpoint. For the special case of an ideal gas, the microscopic (molecular) point of view may be somewhat more satisfying: Here the temperature is directly proportional to the square of the mean molecular speed. Higher temperature means faster moving molecules.

The basis for practical temperature measurement is the zeroth law of thermodynamics.[4] The **zeroth law of thermodynamics** is stated as follows:

Two systems that are each in thermal equilibrium with a third system are in thermal equilibrium with each other.

Alternatively, the zeroth law can be expressed explicitly in terms of temperature:

When two systems have equality of temperature with a third system, they in turn have equality of temperature with each other.

This law forms the basis for thermometry. A thermometer measures the same property, temperature, independent of the nature of the system subject to the measurement. A temperature of 20°C measured for a block of steel means the same thing as 20°C measured for a container of water. Putting the 20°C steel block in the 20°C water results in no temperature change to either.

As a result of the zeroth law, a *practical temperature scale* can be based on a *thermometric* substance. Such a substance expands as its temperature increases; mercury is a thermometric substance. The height of the mercury column in a glass tube can be calibrated against standard *fixed points* of reference. For example, the original Celsius scale (i.e., prior to 1954) defines

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[4] This law was established after the first and second laws of thermodynamics; however, since it expresses a concept logically preceding the other two, it has been designated the zeroth law.

Table 2.3 Temperature Scales

Temperature Scale	Units*	Relation to Other Scales
Celsius	degree Celsius (°C)	$T\,(°\mathrm{C}) = T\,(\mathrm{K}) - 273.15$ $T\,(°\mathrm{C}) = \frac{5}{9}[T\,(\mathrm{F}) - 32]$
Kelvin	kelvin (K)	$T\,(\mathrm{K}) = T\,(°\mathrm{C}) + 273.15$ $T\,(\mathrm{K}) = \frac{5}{9}T(\mathrm{R})$
Fahrenheit	degree Fahrenheit (F)	$T\,(\mathrm{F}) = T\,(\mathrm{R}) - 459.67$ $T\,(\mathrm{F}) = \frac{9}{5}T\,(°\mathrm{C}) + 32$
Rankine	degree Rankine (R)	$T\,(\mathrm{R}) = T\,(\mathrm{F}) + 459.67$ $T\,(\mathrm{R}) = \frac{9}{5}T\,(\mathrm{K})$

* Note that capital letters are used to refer to the units for each scale. The degree symbol (°), however, is used only with the Celsius unit to avoid confusion with the coulomb. Note also that the SI Kelvin scale unit is the kelvin; thus, we say that a temperature, for example, is 100 kelvins (100 K), not 100 degrees Kelvin.

0°C to be the temperature at the **ice point**[5] and 100°C to be the temperature at the **steam point**.[6] The modern Celsius scale assigns a temperature of 0.01°C to the **triple point**[7] of water and the size of a single degree equal to that from the absolute, or Kelvin, temperature scale, as discussed in Chapter 7. With the adoption of the International Temperature Scale of 1990 (ITS-90), the ice point is still 0°C, but the steam point is now 99.974°C. For practical purposes, the original and modern Celsius scales are identical.

Four temperature scales are in common use today: the Celsius scale and its absolute counterpart, the Kelvin scale, and the Fahrenheit scale and its absolute counterpart, the Rankine scale. Both absolute scales start at absolute zero, the lowest temperature possible. The conversions among these scales are shown in Table 2.3.

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[5] The **ice point** is the temperature at which an ice and water mixture is in equilibrium with water vapor–saturated air at one atmosphere.

[6] The **steam point** is the temperature at which steam and water are in equilibrium at one atmosphere.

[7] The **triple point** is the temperature at which ice, liquid water, and steam all coexist in equilibrium.

Example 2.3

On a hot day in Boston, a high of 97 degrees Fahrenheit is reported on the nightly news. What is the temperature in units of °C, K, and R?

Solution

Known $T(\mathrm{F})$

Find $T(°\mathrm{C})$, $T(\mathrm{K})$, $T(\mathrm{R})$

Analysis We apply the temperature-scale conversions provided in Table 2.3 as follows:

$$
\begin{aligned}
T(^\circ\mathrm{C}) &= \frac{5}{9}[T(\mathrm{F}) - 32] \\
&= \frac{5}{9}(97 - 32) = 36.1^\circ\mathrm{C}, \\
T(\mathrm{R}) &= T(\mathrm{F}) + 459.67 \\
&= 97 + 459.67 = 556.7\ \mathrm{R}, \\
T(\mathrm{K}) &= \frac{5}{9}T(\mathrm{R}) \\
&= \frac{5}{9}(556.7) = 309.3\ \mathrm{K}.
\end{aligned}
$$

Comments Except for the Rankine scale, you are most likely familiar with the conversions in Table 2.3. Note that the size of the temperature unit is identical for the Fahrenheit and Rankine scales. Similarly, the Celsius and Kelvin units are of identical size, and each is 9/5 (or 1.8) times the size of the Fahrenheit or Rankine unit.

Self Test 2.3

On the same hot day in Boston, the air conditioning keeps your room at 68 degrees Fahrenheit. Find the temperature difference between the inside and the outside air in (a) R, (b) °C, and (c) K.

(Answer: (a) 29 R, (b) 16.1°C, (c) 16.1 K)

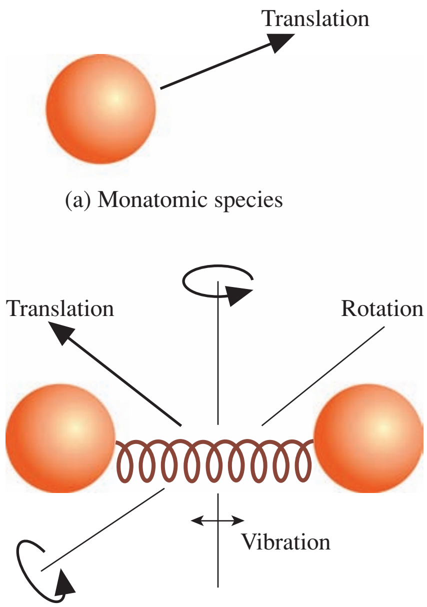


FIGURE 2.4
(a) The internal energy of a monatomic species consists only of translational (kinetic) energy.
(b) A diatomic species internal energy results from translation together with energy from vibration (potential and kinetic) and rotation (kinetic).

2.2b Properties Related to the First Law and Calorific Equation of State

Internal Energy

In this section, we introduce the thermodynamic property internal energy. Further discussion of internal energy is presented in Chapter 4, which focuses on the many ways that energy is stored and transferred.

Internal energy has its origins with the microscopic nature of matter; specifically, we define **internal energy** as the energy associated with the motions of the microscopic particles (atoms, molecules, electrons, etc.) comprising a macroscopic system. For simple monatomic gases (e.g., helium and argon) internal energy is associated only with the translational kinetic energy of the atoms (Fig. 2.4a). If we assume that a gas can be modeled as a collection of point-mass hard spheres that collide elastically, the translational kinetic energy associated with n particles is

$$U_{\mathrm{trans}} = n\frac{1}{2}M_{\mathrm{molec}}\overline{v^2}, \tag{2.14}$$

where $\overline{v^2}$ is the mean-square molecular speed. Using kinetic theory (see, for example, Ref. [2]), the translational kinetic energy can be related to temperature as

$$U_{\mathrm{trans}} = n\frac{3}{2}k_{\mathrm{B}}T, \tag{2.15}$$

where k_B is the Boltzmann constant,

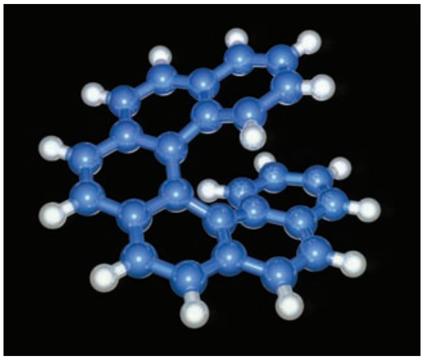
$$k_B \equiv 1.3806503 \times 10^{-23}\ \mathrm{J/K \cdot molecule},$$

and T is the absolute temperature in kelvins. [By comparing Eqs. 2.14 and 2.15, we see the previously mentioned microscopic interpretation of temperature, i.e., $T \equiv M_{\mathrm{molec}}\overline{v^2}/(3k_B)$.]

For molecules more complex than single atoms, internal energy is stored in vibrating molecular bonds and rotation of the molecule about two or more axes, in addition to the translational kinetic energy. Figure 2.4b illustrates this model of a diatomic species. In general, the internal energy is expressed

$$U = U_{\mathrm{trans}} + U_{\mathrm{vib}} + U_{\mathrm{rot}}, \tag{2.16}$$

where U_{vib} is the vibrational kinetic and potential energy, and U_{rot} is the rotational kinetic energy. The amount of energy that is stored in each mode varies with temperature and is described by quantum mechanics. One of the fundamental postulates of quantum theory is that energy is quantized; that is, energy storage is modeled by discrete bits rather than continuous functions. The translational kinetic energy states are very close together such that, for practical purposes, quantum states need not be considered and the continuum result, Eq. 2.15, is a useful model. For vibrational and rotational states, however, quantum behavior is important. We will see the effects of this later in our discussion of specific heats.



For reacting systems, chemical bonds make an important contribution to the system internal energy.

Another form of internal energy is that associated with chemical bonds and their rearrangements during chemical reaction. Similarly, internal energy is associated with nuclear bonds. We will address the topic of chemical energy storage in a later section of this chapter; nuclear energy storage, however, lies beyond our scope.

The SI unit for internal energy is the joule (J); for the mass-specific internal energy, it is joules per kilogram (J/kg); and for the molar-specific internal energy, it is joules per kilomole (J/kmol).

Enthalpy

Enthalpy is a useful property defined by the following combination of more common properties:

$$H \equiv U + P\mathcal{V}. \tag{2.17}$$

On a mass-specific basis, the enthalpy involves the specific volume or the density, that is,

$$h \equiv u + Pv \tag{2.18a}$$

or

$$h \equiv u + P/\rho. \tag{2.18b}$$

The enthalpy has the same units as internal energy (i.e., J or J/kg). Molar-specific enthalpies are obtained by the application of Eq. 2.3.

Enthalpy first appears in conservation of energy for systems in Eq. 5.12. ➤

Conservation of energy for control volumes (Eq. 5.63) uses enthalpy to replace the combination of flow work (see Chapter 4) and internal energy. ➤

The usefulness of enthalpy will become clear during our discussion of the first law of thermodynamics (the principle of energy conservation) in Chapter 5. There we will see that the combination of properties, $u + Pv$, arises naturally in analyzing systems at constant pressure and in analyzing control volumes. In the former, the P–v term results from expansion and/or compression work; for the latter, the P–v term is associated with the work needed to push the fluid into or out of the control volume, that is, flow work. Further discussion of internal energy and enthalpy is also given later in the present chapter.

Specific Heats and Specific-Heat Ratio

Here we deal with two intensive properties,

$$c_v \equiv \text{constant-volume specific heat}$$

and

$$c_p \equiv \text{constant-pressure specific heat.}$$

These properties mathematically relate to the specific internal energy and enthalpy, respectively, as follows:

$$c_v \equiv \left(\frac{\partial u}{\partial T}\right)_v \tag{2.19a}$$

and

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_p. \tag{2.19b}$$

Similar defining relationships relate molar-specific heats and molar-specific internal energy and enthalpy. Physically, the constant-volume specific heat is the slope of the internal energy-versus-temperature curve for a substance undergoing a process conducted at constant volume. Similarly, the constant-pressure specific heat is the slope of the enthalpy-versus-temperature curve for a substance undergoing a process conducted at constant pressure. These ideas are illustrated in Fig. 2.5. It is important to note that, although the definitions of these properties involve constant-volume and constant-pressure processes, c_v and c_p can be used in the description of *any* process regardless of whether or not the volume (or pressure) is held constant.

For solids and liquids, specific heats generally increase with temperature, essentially uninfluenced by pressure. A notable exception to this is mercury, which exhibits a decreasing constant-pressure specific heat with temperature. Values of specific heats for selected liquids and solids are presented in Appendices G and I.

For both real (nonideal) and ideal gases, the specific heats c_v and c_p are functions of temperature. The specific heats of nonideal gases also possess a pressure dependence. For gases, the temperature dependence of c_v and c_p is a consequence of the internal energy of a molecule consisting of three components—translational, vibrational, and rotational—and the fact that the vibrational and rotational energy storage modes become increasingly active as temperature increases, as described by quantum theory. As discussed previously, Fig. 2.4 schematically illustrates these three energy storage modes by contrasting a monatomic species, whose internal energy consists solely of translational kinetic energy, and a diatomic molecule, which stores energy in a vibrating chemical bond, represented as a spring between the two nuclei, and by rotation about two orthogonal axes, as well as possessing kinetic energy from translation. With these simple models (Fig. 2.4), we expect the specific heats of diatomic molecules to be greater than those of monatomic species, which is indeed true. In general, the more complex the molecule, the greater its molar specific heat. This can be seen clearly in Fig. 2.6, where molar-specific heats for a number of gases are shown as functions of

FIGURE 2.5

The constant-volume specific heat c_v is defined as the slope of u versus T for a constant-volume process (top). Similarly, c_p is the slope of h versus T for a constant-pressure process (bottom). Generally, both c_v and c_p are functions of temperature, as suggested by these graphs.

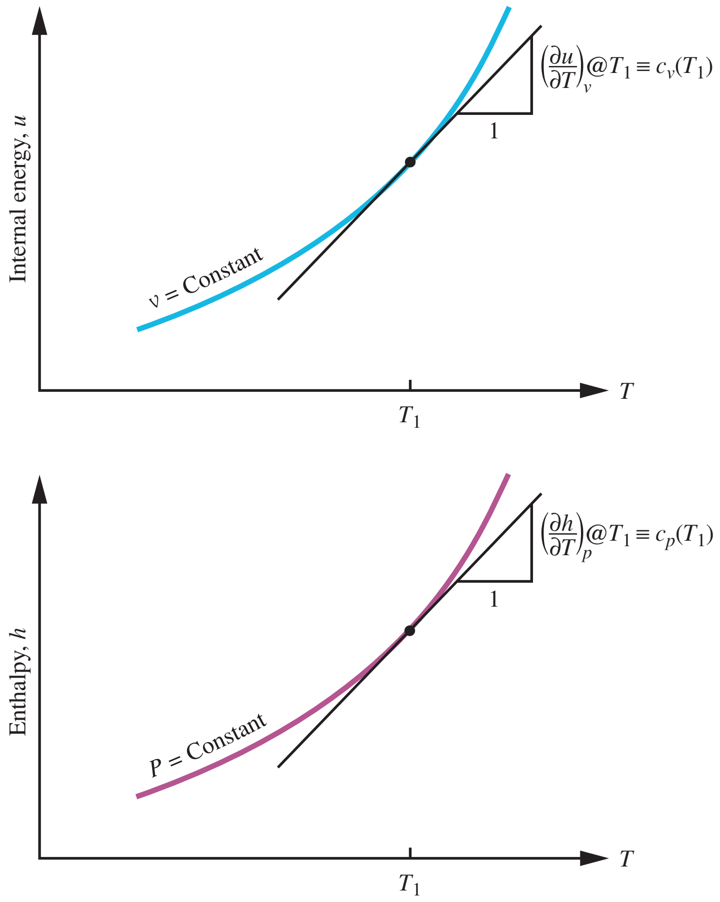
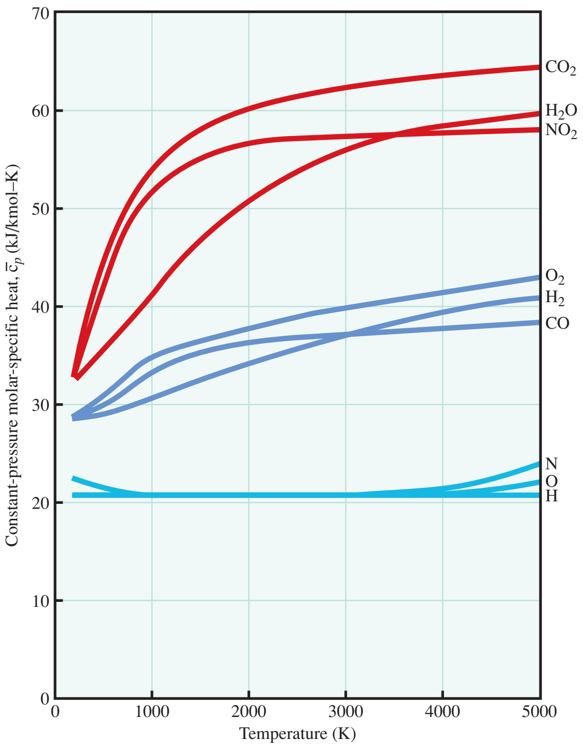


FIGURE 2.6

Molar constant-pressure specific heats as functions of temperature for monatomic (H, N, and O), diatomic (CO, H_2, and O_2), and triatomic (CO_2, H_2O, and NO_2) species. Values are from Appendix B.



temperature. As a group, the triatomics have the greatest specific heats, followed by the diatomics, and lastly, the monatomics. Note that the triatomic molecules are also more temperature dependent than the diatomics, a consequence of the greater number of vibrational and rotational modes that are available to become activated as temperature is increased. In comparison, the monatomic species have nearly constant specific heats over a wide range of temperatures; in fact, the specific heat of monatomic hydrogen is constant ($\bar{c}_p =$ 20.786 kJ/kmol·K) from 200 K to 5000 K.

Constant-pressure molar-specific heats are tabulated as a function of temperature for various ideal-gas species in Tables B.1 to B.12 in Appendix B. Also provided in Appendix B are the curve-fit coefficients, taken from the Chemkin thermodynamic database [3], which were used to generate the tables. These coefficients can be easily used with spreadsheet software to obtain $\bar{c}_p$ values at any temperature within the given temperature range.

Values of c_v and c_p for a number of substances are also available from the National Institute of Standards and Technology (NIST) online database [11] and the NIST12 software provided with this book. We discuss the use of these important resources later in this chapter.

The ratio of specific heats, γ, is another commonly used property[8] and is defined by

$$\gamma \equiv \frac{c_p}{c_v} = \frac{\bar{c}_p}{\bar{c}_v}. \tag{2.20}$$

---

[8] The specific-heat ratio is frequently denoted by k or r, as well as gamma (γ), our choice here. We will use k and r to represent the thermal conductivity and radial coordinate, respectively.

Example 2.4

Six liquid hydrogen-fueled engines power the second stage of this Saturn rocket. Courtesy of NASA.

Compare the values of the constant-pressure specific heats for hydrogen (H_2) and carbon monoxide (CO) at 3000 K using the ideal-gas molar-specific values from the tables in Appendix B. How does this comparison change if mass-specific values are used?

Solution

Known H_2 and CO at T

Find $\bar{c}_{p,H_2}$, $\bar{c}_{p,CO}$, c_{p,H_2}, $c_{p,CO}$

Assumption

Ideal-gas behavior

Analysis To answer the first question requires only a simple table look-up. Molar constant-pressure specific heats found in Table B.3 for H_2 and in Table B.1 for CO are as follows:

$$\bar{c}_{p,H_2}\ (T = 3000\ \mathrm{K}) = 37.112\ \mathrm{kJ/kmol \cdot K},$$
$$\bar{c}_{p,CO}\ (T = 3000\ \mathrm{K}) = 37.213\ \mathrm{kJ/kmol \cdot K}.$$

The difference between these values is 0.101 kJ/kmol·K, or approximately 0.3%.

Using the molecular weights of H_2 and CO found in Tables B.3 and B.1, we can calculate the mass-based constant-pressure specific heats using Eq. 2.4 as follows:

$$\begin{aligned} c_{p,\mathrm{H_2}} &= \bar{c}_{p,\mathrm{H_2}}/\mathcal{M}_{\mathrm{H_2}} \\ &= \frac{37.112\ \mathrm{kJ/kmol\cdot K}}{2.016\ \mathrm{kg/kmol}} \\ &= 18.409\ \mathrm{kJ/kg\cdot K} \end{aligned}$$

and

$$\begin{aligned} c_{p,\mathrm{CO}} &= \bar{c}_{p,\mathrm{CO}}/\mathcal{M}_{\mathrm{CO}} \\ &= \frac{37.213\ \mathrm{kJ/kmol\cdot K}}{28.010\ \mathrm{kg/kmol}} \\ &= 1.329\ \mathrm{kJ/kg\cdot K}. \end{aligned}$$

Comments We first note that, on a molar basis, the specific heats of H_2 and CO are nearly identical. This result is consistent with Fig. 2.6, where we see that the molar-specific heats are similar for the three diatomic species. On a mass basis, however, the constant-pressure specific heat of H_2 is almost 14 times greater than that of CO, which results from the molecular weight of CO being approximately 14 times that of H_2.

Self Test 2.4

☑ **Calculate the specific heat ratios for (a) H_2, (b) CO, and (c) air using the data from Table E.1 in Appendix E.**

(Answer: (a) 1.402, (b) 1.398, (c) 1.400)

2.2c Properties Related to the Second Law[9]

Entropy

As we will see in Chapter 7, a thermodynamic property called **entropy** (***S***) originates from the second law of thermodynamics.[10] This property is particularly useful in determining the spontaneous direction of a process and for establishing maximum possible efficiencies, for example.

The property entropy can be interpreted from both macroscopic and microscopic (molecular) points of view. We defer presenting a precise mathematical definition of entropy from the macroscopic viewpoint until Chapter 7; the following verbal definition, however, provides some notion of what this property is all about:

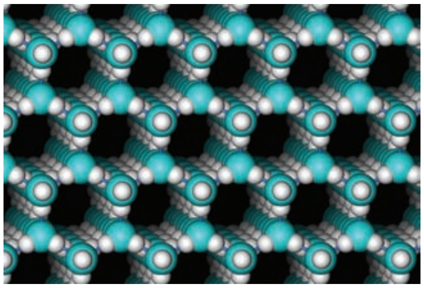
Chapter 7 revisits entropy and expands upon the discussion here. Equation 7.16 provides a formal macroscopic definition of entropy.

Entropy is a measure of the unavailability of thermal energy to do work in a closed system.

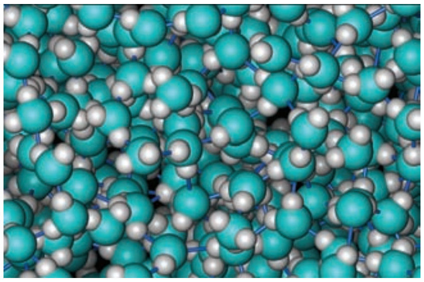
---

[9] For an introductory study of properties, this section may be skipped without any loss of continuity. This section is most useful, however, in conjunction with the study of Chapter 7.

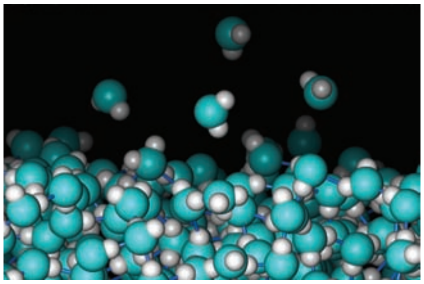
[10] Rudolf Clausius (1822–1888) chose *entropy*, a Greek word meaning transformation, because of its root meaning and because it sounded similar to *energy*, a closely related concept [4].



Hexagonal crystal structure of ice. The open structure causes ice to be less dense than liquid water.



Structure of liquid water.



Evaporating water molecules.

From this definition, we might imagine that two identical quantities of energy are not of equal value in producing useful work. Entropy is valuable in quantifying this usefulness of energy.

The following informal definition presents a microscopic (molecular) interpretation of entropy:

Entropy is a measure of the microscopic randomness associated with a closed system.

To help understand this statement, consider the physical differences between water existing as a solid (ice) and as a vapor (steam). In a piece of ice, the individual H_2O molecules are locked in relatively rigid positions, with the individual hydrogen and oxygen atoms vibrating within well-defined domains. In contrast, in steam, the individual molecules are free to move within any containing vessel. Thus, we say that the state of the steam is more disordered than that of the ice and that the steam has a greater entropy per unit mass. It is this idea, in fact, that leads to the **third law of thermodynamics**, which states that all perfect crystals have zero entropy at a temperature of absolute zero. For the case of a perfectly ordered crystal at absolute zero, there is no motion, and there are no imperfections in the lattice; thus, there is no uncertainty about the microscopic state (because there is no disorder or randomness) and the entropy is zero. A more detailed discussion of the microscopic interpretation of entropy is presented in the appendix to this chapter.

The SI units for entropy S, mass-specific entropy s, and molar-specific entropy $\bar{s}$, are J/K, J/kg·K, and J/kmol·K, respectively. Tabulated values of entropies for ideal gases, air, and H_2O are found in Appendices B, C and D, respectively. Entropies for selected substances are also available from the NIST software and online database [11].

Gibbs Free Energy or Gibbs Function

The **Gibbs free energy** or **Gibbs function, *G***, is a composite property involving enthalpy and entropy and is defined as

$$\boxed{G \equiv H - TS,} \tag{2.21a}$$

and, per unit mass,

$$\boxed{g \equiv h - Ts.} \tag{2.21b}$$

Molar-specific quantities are obtained by the application of Eq. 2.3. The Gibbs free energy is particularly useful in defining equilibrium conditions for reacting systems at constant pressure and temperature. We will revisit this property later in this chapter in the discussion of ideal-gas mixtures; in Chapter 7 this property is prominent in the discussion of chemical equilibrium.

Helmholtz Free Energy or Helmholtz Function

The **Helmholtz free energy, *A***, is also a composite property, defined similarly to the Gibbs free energy, with the internal energy replacing the enthalpy, that is,

$$A \equiv U - TS, \tag{2.22a}$$

or, per unit mass,

$$a \equiv u - Ts. \tag{2.22b}$$

Molar-specific quantities relate in the same manner as expressed by Eq. 2.22b. The Helmholtz free energy is useful in defining equilibrium conditions for reacting systems at constant volume and temperature. Although we make no use of the Helmholtz free energy in this book, you should be aware of its existence.

2.3 CONCEPT OF STATE RELATIONSHIPS

2.3a State Principle

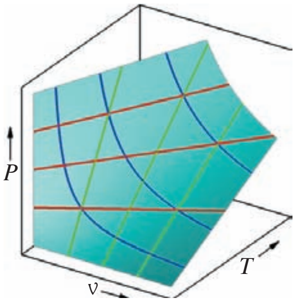
An important concept in thermodynamics is the **state principle**:

> **In dealing with a simple compressible substance, the *thermodynamic state* is completely defined by specifying two independent intensive properties.**

The state principle allows us to define **state relationships** among the various thermodynamic properties. Before developing such state relationships, we examine what is mean by *independent properties*.

The concept of independent properties is particularly important in dealing with substances when more than one phase is present. For example, temperature and pressure are not independent properties when water (liquid) and steam (vapor) coexist. As you are well aware, water at one atmosphere boils at a specific temperature (i.e., 100°C). Increasing the pressure results in an increase in the boiling point, which is the principle upon which the pressure cooker is based. One cannot change the pressure and keep the temperature constant: A fixed relationship exists between temperature and pressure; hence, they are not independent. We will examine this concept of independence in greater detail later when we study the properties of substances that exist in multiple phases.

2.3b P–v–T Equations of State



What is generally known as an **equation of state** is the mathematical relationship among the following three intensive thermodynamic properties: pressure P; specific volume v, and temperature T. The state principle allows us to determine any one of the three properties from knowledge of the other two. In its most general and abstract form, we can write the P–v–T equation of state as

$$f_1(P, v, T) = 0. \tag{2.23}$$

In the following sections, we explore the explicit functions relating P, v, and T for various substances, starting with the ideal gas, a concept with which you should already have some familiarity.

2.3c Calorific Equations of State

A second type of state relationship connects energy-related thermodynamic properties to pressure, temperature, and specific volume. The state principle also applies here; thus, for a simple compressible substance, a knowledge of any two intensive properties is sufficient to determine any of the others. The most common **calorific equations of state** relate specific internal energy u to v and T, and, similarly, enthalpy h to P and T, that is,

$$f_2\,(u, T, v) = 0, \tag{2.24a}$$

or

$$f_3\,(h, T, P) = 0. \tag{2.24b}$$

These ideas are developed in more detail for various substances in the sections that follow.

2.3d Temperature–Entropy (Gibbs) Relationships

The third and final type of state relationships we consider are those that relate entropy-based properties—that is, properties relating to the second law of thermodynamics—to pressure, specific volume, and temperature. The most common relationships are of the following general form:

$$f_4\,(s, T, P) = 0, \tag{2.25a}$$

$$f_5\,(s, T, v) = 0, \tag{2.25b}$$

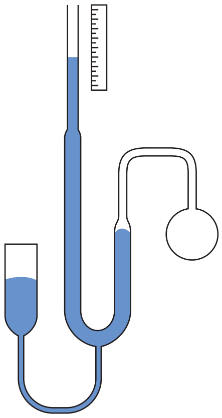
and

$$f_6\,(g, T, P) = 0. \tag{2.25c}$$

As with the other state relationships, these, too, are defined concretely in the following sections.

2.4 IDEAL GASES AS PURE SUBSTANCES

In this section, we define all of the useful state relationships for a class of pure substances known as ideal gases. We begin with the definition of an ideal gas.



An ideal-gas thermometer consists of a sensing bulb filled with an ideal gas (right), a movable closed reservoir (left), and a liquid column (center). The height of the liquid column is directly proportional to the temperature of the gas in the bulb when the reservoir position is adjusted to maintain a fixed volume for the ideal gas.

2.4a Ideal Gas Definition

The following definition of an **ideal gas** is tautological in that it uses a state relationship to define what is meant by an ideal gas:

An *ideal gas* is a gas that obeys the relationship $Pv = RT$.

In this definition P and T are the absolute pressure and absolute temperature, respectively, and R is the **particular gas constant**, a physical constant. The particular gas constant depends on the molecular weight of the gas as follows:

$$R_i \equiv R_u/\mathcal{M}_i \quad [=]\ \mathrm{J/kg\cdot K}, \tag{2.26}$$

where the subscript i denotes the species of interest, and R_u is the **universal gas constant**, defined by

$$R_u \equiv 8314.472\ (15) \quad [=]\ \mathrm{J/kmol\cdot K}. \tag{2.27}$$

This definition of an ideal gas can be made more satisfying by examining what is implied from a molecular, or microscopic, point of view. Kinetic theory predicts that $Pv = RT$, first, when the molecules comprising the system are infinitesimally small, hard, round spheres occupying negligible volume and, second, when no forces exist among these molecules except during collisions. Qualitatively, these conditions imply a gas at *low* density. What we mean by low density will be discussed in later sections.

2.4b Ideal-Gas Equation of State

Formally, the P–v–T equation of state for an ideal gas is expressed as

$$Pv = RT. \tag{2.28a}$$

Alternative forms of the ideal-gas equation of state arise in various ways. First, by recognizing that the specific volume is the reciprocal of the density ($v = 1/\rho$), we get

$$P = \rho RT. \tag{2.28b}$$

Second, expanding the definition of specific volume ($v = \mathcal{V}/M$) yields

$$P\mathcal{V} = MRT. \tag{2.28c}$$

Third, expressing the mass in terms of the number of moles and molecular weight of the particular gas of interest ($M = N\,\mathcal{M}_i$) yields

$$P\mathcal{V} = NR_uT. \tag{2.28d}$$

Finally, by employing the molar specific volume $\bar{v} = v\mathcal{M}_i$, we obtain

$$P\bar{v} = R_uT. \tag{2.28e}$$

We summarize these various forms of the ideal-gas equation of state in Table 2.4 and encourage you to become familiar with these relationships by performing the various conversions on your own (see Problem 2.36).

Table 2.4 Various Forms of the Ideal-Gas Equation of State

$Pv = RT$	Eq. 2.28a
$P = \rho RT$	Eq. 2.28b
$P\mathcal{V} = MRT$	Eq. 2.28c
$P\mathcal{V} = NR_uT$	Eq. 2.28d
$P\bar{v} = R_uT$	Eq. 2.28e

Example 2.5

A compressed-gas cylinder contains N_2 at room temperature (25°C). A gage on the pressure regulator attached to the cylinder reads 120 psig. A mercury barometer in the room in which the cylinder is located reads 750 mm Hg. What is the density of the N_2 in the tank in units of kg/m^3? Also determine the mass of the N_2 contained in the 1.54-ft^3 steel tank?

Solution

Known T_{N_2}, $P_{N_2,g}$, P_{atm}, $\mathcal{V}_{N_2}$

Find ρ_{N_2}, M_{N_2}

Assumption

Ideal-gas behavior

Analysis To find the density of nitrogen, we apply the ideal-gas equation of state (Eq. 2.28b, Table 2.4). Before doing so we must determine the particular gas constant for N_2 and perform several unit conversions of given information.

From Eqs. 2.26 and 2.27, we find the particular gas constant,

$$R_{N_2} = \frac{R_u}{\mathcal{M}_{N_2}} = \frac{8314.47 \text{ J/kmol}\cdot\text{K}}{28.013 \text{ kg/kmol}}$$

$$= 296.8 \text{ J/kg}\cdot\text{K},$$

where the molecular weight for N_2 is calculated from the atomic weights given in the front of the book (or found directly in Table B.7).

The absolute pressure in the tank is (Eq. 2.12)

$$P_{N_2} = P_{N_2,g} + P_{\text{atm,abs}},$$

where

$$P_{N_2,g} = 120 \frac{\text{lb}_f}{\text{in}^2}\left[\frac{39.370 \text{ in}}{1 \text{ m}}\right]^2 \left[\frac{1 \text{ N}}{0.224809 \text{ lb}_f}\right]$$

$$= 827{,}367 \text{ Pa (gage)}$$

and

$$P_{\text{atm,abs}} = (750 \text{ mm Hg}) \left[\frac{1 \text{ atm}}{760 \text{ mm Hg}}\right]\left[\frac{101{,}325 \text{ Pa}}{1 \text{ atm}}\right]$$

$$= 99{,}992 \text{ Pa}.$$

Thus, the absolute pressure of the N_2 is

$$P_{N_2} = 827{,}367 \text{ Pa (gage)} + 99{,}992 \text{ Pa} = 927{,}359 \text{ Pa},$$

which rounds off to

$$P_{N_2} = 927{,}000 \text{ Pa}.$$

The absolute temperature of the N_2 is

$$T_{N_2} = 25°\text{C} + 273.15 = 298.15 \text{ K}.$$

To obtain the density, we now apply the ideal-gas equation of state (Eq. 2.28b)

$$\rho_{N_2} = \frac{P_{N_2}}{R_{N_2} T_{N_2}}$$

$$= \frac{927{,}000}{296.8\,(298.15)}$$

$$= 10.5$$

$$[=] \frac{\text{Pa}\left[\frac{1 \text{ N/m}^2}{\text{Pa}}\right]}{\frac{\text{J}}{\text{kg}\cdot\text{K}}\left[\frac{1 \text{ N}\cdot\text{m}}{\text{J}}\right]\text{K}} = \text{kg/m}^3.$$

Note that we have set aside the units and unit conversions to assure their proper treatment. Unit conversion factors are always enclosed in square brackets. We obtain the mass from the definition of density (Eq. 2.8)

$$\rho_{N_2} \equiv \frac{M_{N_2}}{\mathcal{V}_{N_2}},$$

or

$$M_{N_2} = \rho_{N_2} \mathcal{V}_{N_2}.$$

The tank volume is

$$\mathcal{V}_{N_2} = 1.54\ \text{ft}^3\left[\frac{1\ \text{m}}{3.2808\ \text{ft}}\right]^3 = 0.0436\ \text{m}^3.$$

Thus,

$$M_{N_2} = 10.5\frac{\text{kg}}{\text{m}^3}0.0436\ \text{m}^3 = 0.458\ \text{kg}.$$

Comments Note that, although the application of the ideal-gas law to find the density is straightforward, unit conversions and calculations of absolute pressures and temperatures make the calculation nontrivial.

Self Test 2.5

☑ **The valve of the tank in Example 2.5 is slowly opened and 0.1 kg of N_2 escapes. Calculate the density of the remaining N_2 and find the final gage pressure in the tank assuming the temperature remains at 25°C.**

(Answer: 8.2 kg/m^3, 626.6 kPa)

Example 2.6

It is a cold, sunny day in Merrill, WI. The temperature is −10 F, the barometric pressure is 100 kPa, and the humidity is nil. Estimate the outside air density. Also estimate the molar density, $N/\mathcal{V}$, of the air.

Solution

Known T_{air}, P_{air}

Find ρ_{air}

Assumptions

i. Air can be treated as a pure substance.
ii. Air can be treated as an ideal gas.
iii. Air is dry.

Analysis With these assumptions, we use the data in Appendix C together with the ideal-gas equation of state (Eq. 2.28b) to find the air density. First, we convert the temperature to SI absolute units:

$$T_{air}\,(\text{K}) = \frac{5}{9}(-10 + 459.67) = 249.8\ \text{K}.$$

The density is thus

$$\rho_{air} = \frac{P_{air}}{R_{air}T_{air}} = \frac{100{,}000\ \text{Pa}}{287.0\ \text{J/kg}\cdot\text{K}\ (249.8\ \text{K})} = 1.395\ \text{kg/m}^3,$$

where R_{air}, the particular gas constant for air, was obtained from Table C.1 in Appendix C. The treatment of units in this calculation is the same as detailed in the previous example.

The molar density is the number of moles per unit volume. This quantity is calculated by dividing the mass density (ρ_{air}) by the apparent molecular weight of the air, that is,

$$N_{air}/\mathcal{V}_{air} = \rho_{air}/\mathcal{M}_{air} = \frac{1.395\ \text{kg/m}^3}{28.97\ \text{kg/kmol}} = 0.048\ \text{kmol/m}^3.$$

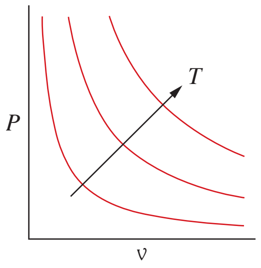
Comments The primary purpose of this example is to introduce the approximation of treating air, a mixture of gases (see Table C.1 for the composition of dry air), as a simple substance that behaves as an ideal gas. Note the introduction of the apparent molecular weight, $\mathcal{M}_{\text{air}} = 28.97$ kg/kmol, and the particular gas constant, $R_{\text{air}} = R_u/\mathcal{M}_{\text{air}} = 287.0$ J/kg·K. Ideal-gas thermodynamic properties for dry air are also tabulated in Appendix C. In our study of air conditioning (Chapter 12), we investigate the influence of moisture in air.

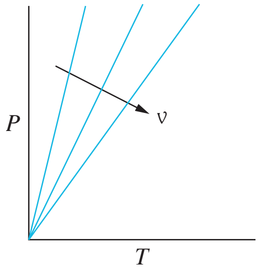
Self Test 2.6

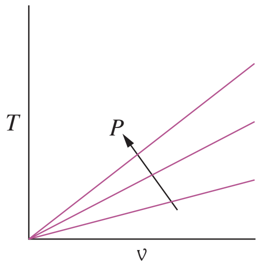
Calculate the mass of the air in an uninsulated, unheated 10 ft × 15 ft × 12 ft garage on this same cold day.

(Answer: 71.1 kg)

2.4c Processes in P–v–T Space







Plotting thermodynamic processes on P–v or other thermodynamic property coordinates is very useful in analyzing many thermal systems. In this section, we introduce this topic by illustrating common processes on P–v and T–v coordinates, restricting our attention to ideal gases. Later in this chapter, we add the complexity of a phase change.

We begin by examining P–v coordinates. Rearranging the ideal-gas equation of state (Eq. 2.28a) to a form in which P is a function of v yields the hyperbolic relationship

$$P = (RT)\frac{1}{v}. \tag{2.29}$$

By considering the temperature to be a fixed parameter, Eq. 2.29 can be used to create a family of hyperbolas for various values of T, as shown in Fig. 2.7. Increasing temperature moves the isotherms further from the origin.

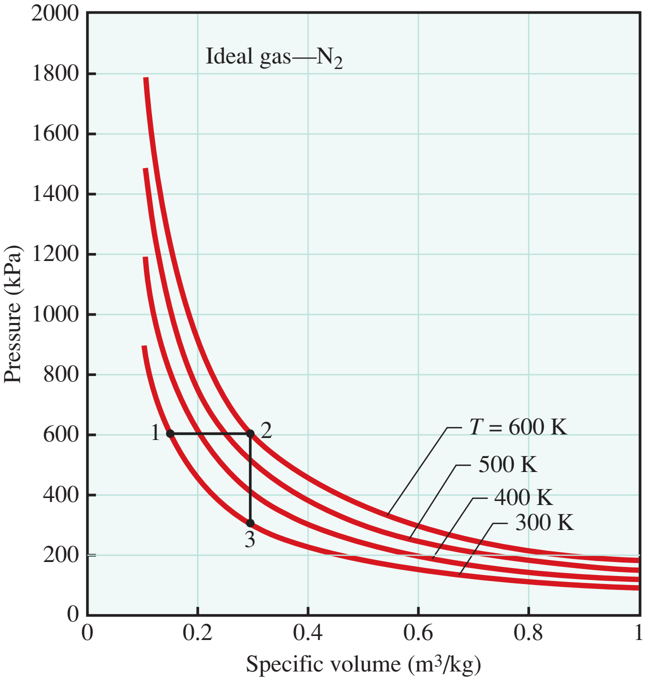
The usefulness of graphs such as Fig. 2.7 is that one can immediately visualize how properties must vary for a particular thermodynamic process. For example, consider the constant-pressure expansion process shown in Fig. 2.7, where the initial and final states are designated as points 1 and 2, respectively. Knowing the arrangement of constant-temperature lines allows us to see that the temperature must increase in the process 1–2. For the values given, the temperature increases from 300 to 600 K. The important point here, however, is not this quantitative result, but the qualitative information available from plotting processes on P–v coordinates. Also shown in Fig. 2.7 is a constant-volume process (assuming that we are dealing with a system of fixed mass). In going from state 2 to state 3 at constant volume, we immediately see that both the temperature and pressure must fall.

In choosing a pair of thermodynamic coordinates to draw a graph, one usually selects those that allow given constant-property processes to be shown as straight lines. For example, P–v coordinates are the natural choice for systems involving either constant-pressure or constant- (specific) volume processes. If, however, one is interested in a constant-temperature process, then T–v coordinates may be more useful. In this case, the ideal-gas equation of state can be rearranged to yield

$$T = \left(\frac{P}{R}\right)v. \tag{2.30}$$

FIGURE 2.7

Constant-pressure (1–2) and constant-volume (2–3) processes are shown on $P-v$ coordinates for an ideal gas (N_2). Lines of constant temperature are hyperbolic, following the ideal-gas equation of state, $P = (RT)/v$.

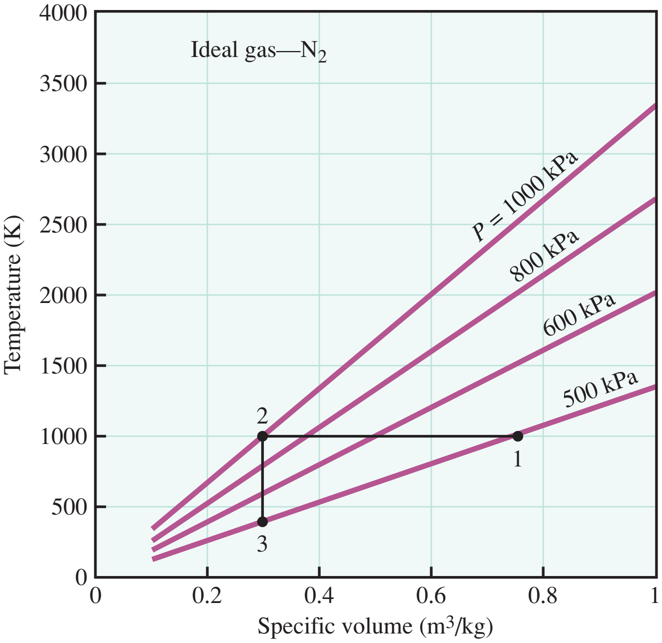


Treating pressure as a fixed parameter, this relationship yields straight lines with slopes of P/R. Higher pressures result in steeper slopes.

Figure 2.8 illustrates the ideal-gas T–v relationship. Consider a constant-temperature compression process going from state 1 to state 2. For this process, we immediately see from the graph that the pressure must increase. Also shown on Fig. 2.8 is a constant- (specific) volume process going from state 2 to state 3 for conditions of decreasing temperature. Again, we immediately see that the pressure falls during this process.

FIGURE 2.8

Constant-temperature (1–2) and constant-volume (2–3) processes are shown on $T-v$ coordinates for an ideal gas (N_2). Lines of constant pressure are straight lines, following the ideal-gas equation of state, $T = (P/R)v$.



Plotting processes on thermodynamic coordinates develops understanding and aids in problem solving. Whenever possible, we will use such diagrams in examples throughout the book. Also, many homework problems are designed to foster development of your ability to draw and use such plots.

Example 2.7

An ideal gas system undergoes a thermodynamic cycle composed of the following processes:

1–2: constant-pressure expansion,

2–3: constant-temperature expansion,

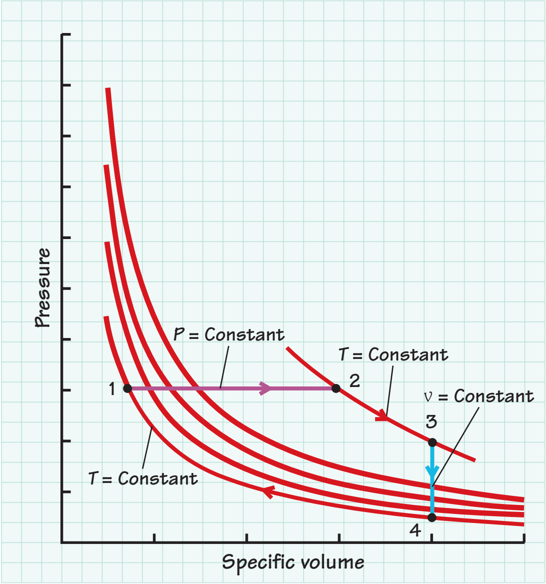
3–4: constant-volume return to the state-1 temperature, and

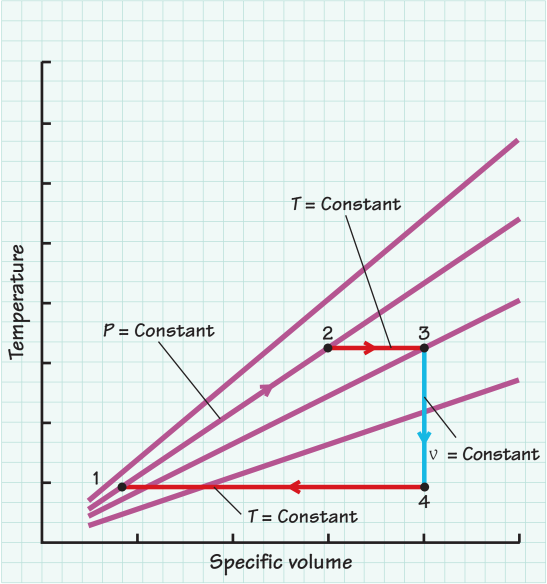
4–1: constant-temperature compression.

Sketch these processes (a) on P–ν coordinates and (b) on T–ν coordinates.

Solution

The sequences of processes are shown on the sketches.





Comments To develop skill in making such plots, the reader should redraw the requested sketches without reference to the solutions given. Note that the sequence of processes 1–2–3–4–1 constitutes a thermodynamic cycle.

Self Test 2.7

☑ **Looking at the sketches of Example 2.7, state whether the pressure P, temperature T, and specific volume ν increase, decrease, or remain the same for each of the four processes.**

(Answer: 1–2: P constant, T increases, ν increases; 2–3: P decreases, T constant, ν increases; 3–4: P decreases, T decreases, ν constant; 4–1: P increases, T constant, ν decreases)

2.4d Ideal-Gas Calorific Equations of State

From kinetic theory we predict that the internal energy of an ideal gas will be a function of temperature only. That the internal energy is independent of pressure follows from the neglect of any intermolecular forces in the model of an ideal gas. In real gases, molecules do exhibit repulsive and attractive forces that result in a pressure dependence of the internal energy. As in our discussion of the P–v–T equation of state, the ideal gas approximation, however, is quite accurate at sufficiently low densities, and the result that $u = u$ (T only) is quite useful.

Ideal-gas specific internal energies can be obtained from experimentally or theoretically determined values of the constant-volume specific heat. Starting with the general definition (Eq. 2.19a),

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v,$$

we recognize that the partial derivative becomes an ordinary derivative when $u = u$ (T only); thus

$$c_v = \frac{du}{dT}, \tag{2.31a}$$

or

$$du = c_v dT, \tag{2.31b}$$

which can be integrated to obtain $u(T)$, that is,

$$u(T) = \int_{T_{\text{ref}}}^{T} c_v dT. \tag{2.31c}$$

In Eq. 2.31c, we note that a reference-state temperature is required to evaluate the integral. We also note that, in general, the constant-volume specific heat is a function of temperature [i.e., $c_v = c_v(T)$]. From Eq. 2.31b, we can easily find the change in internal energy associated with a change from state 1 to state 2:

$$u_2 - u_1 = u(T_2) - u(T_1) = \int_{T_1}^{T_2} c_v dT. \tag{2.31d}$$

If the temperature difference between the two states is not too large, the constant-volume specific heat can be treated as a constant, $c_{v,\text{avg}}$; thus,

$$u_2 - u_1 = c_{v,\text{avg}}(T_2 - T_1). \tag{2.31e}$$

We will return to Eq. 2.31 after discussing the calorific equation of state involving enthalpy.

To obtain the h–T–P calorific equation of state for an ideal gas, we first show that the enthalpy of an ideal gas, like the internal energy, is a function only of the temperature [i.e., $h = h$ (T only)]. We start with the definition of enthalpy (Eq. 2.18),

$$h = u + P\text{v},$$

and replace the $P\text{v}$ term using the ideal-gas equation of state (Eq. 2.28a). This yields

$$h = u + RT. \tag{2.32}$$

Since $u = u$ (T only), we see from Eq. 2.32 that h, too, is a function only of temperature for an ideal gas. With $h = h$ (T only), the partial derivative becomes an ordinary derivative and so we have

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_p = \frac{dh}{dT}. \tag{2.33a}$$

From this, we can write

$$dh = c_p dT, \tag{2.33b}$$

which can be integrated to yield

$$h(T) = \int_{T_{\text{ref}}}^{T} c_p dT. \tag{2.33c}$$

The enthalpy difference for a change in state mirrors that for the internal energy, that is,

$$h_2 - h_1 = h(T_2) - h(T_1) = \int_{T_1}^{T_2} c_p dT, \tag{2.33d}$$

and if the constant-pressure specific heat does not vary much between states 1 and 2,

$$h_2 - h_1 = c_{p,\text{avg}}(T_2 - T_1). \tag{2.33e}$$

All of these relationships (Eqs. 2.31–2.33) can be expressed on a molar basis simply by substituting molar-specific properties for mass-specific properties. Note then that R becomes R_u.

Before proceeding, we obtain some useful auxiliary ideal-gas relationships by differentiating Eq. 2.32 with respect to temperature, giving

$$\frac{dh}{dT} = \frac{du}{dT} + R.$$

Recognizing the definitions of the ideal-gas specific heats (Eqs. 2.31 and 2.33a), we then have

$$c_p = c_v + R, \tag{2.34a}$$

or

$$c_p - c_v = R. \tag{2.34b}$$

Since property data sources sometimes only provide values or curve fits for c_p, one can use Eq. 2.34 to obtain values for c_v.

FIGURE 2.9

The area under the c_v-versus-T curve is the internal energy (top), and the area under the c_p-versus-T curve is the enthalpy (bottom). Note that the difference in the areas, $[h(T_1) - h(T_{ref})] - [u(T_1) - u(T_{ref})]$, is $R(T_1 - T_{ref})$.

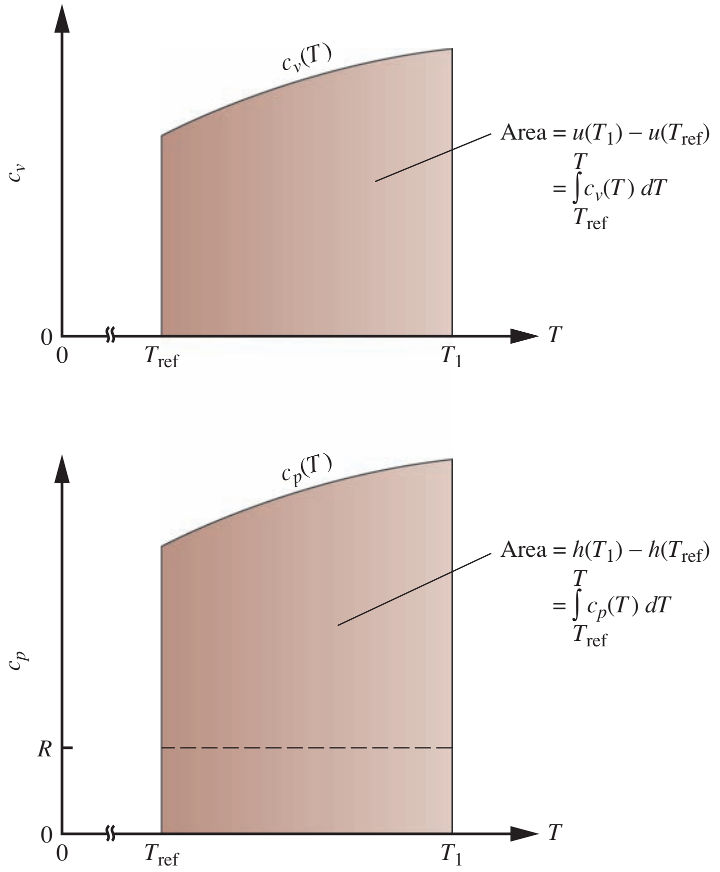


Figure 2.9 provides graphical interpretations of Eqs. 2.31c and 2.33c, our ideal-gas calorific equations of state. Here we see that the area under the c_v-versus-T curve represents the internal energy change for a temperature change from T_{ref} to T_1. A similar interpretation applies to the $c_p(T)$ curve where the area now represents the enthalpy change.

In the same spirit that we graphically illustrated the ideal-gas equation of state using P–v and T–v plots (Figs. 2.7 and 2.8, respectively), we now illustrate the ideal-gas calorific equations of state using u–T and h–T plots. Figure 2.10 illustrates these u–T and h–T relationships for N_2. Because the specific internal energy and specific enthalpy of ideal gases are functions of neither pressure nor specific volume, each relationship is expressed by a single curve.[11] This result (Fig. 2.10) contrasts with the P–v (Fig. 2.7) and T–v (Fig. 2.8) plots generated from the equation of state, where families of curves are required to express these state relationships. Being able to sketch processes on u–T and h–T coordinates, as well as on P–v and T–v coordinates, greatly aids problem solving.

Numerical values for $\bar{h}$ (and $\bar{c}_p$) are available from tables contained in Appendix B for a number of gaseous species, where ideal-gas behavior is assumed. Note the reference temperature of 298.15 K. Curve fits for $\bar{c}_p$ are also provided in Appendix B for these same gases. Although air is a mixture of gases, it can be treated practically as a pure substance (see Example 2.6). Properties of air are provided in Appendix C. Note that the reference temperature used in these air tables is 78.903 K, not 298.15 K. The following examples illustrate the use of some of the information available in the appendices.

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[11] This result shows that u and T are not independent properties for ideal gases; likewise, h and T are not independent properties. Another property is thus needed to define the state of an ideal gas.

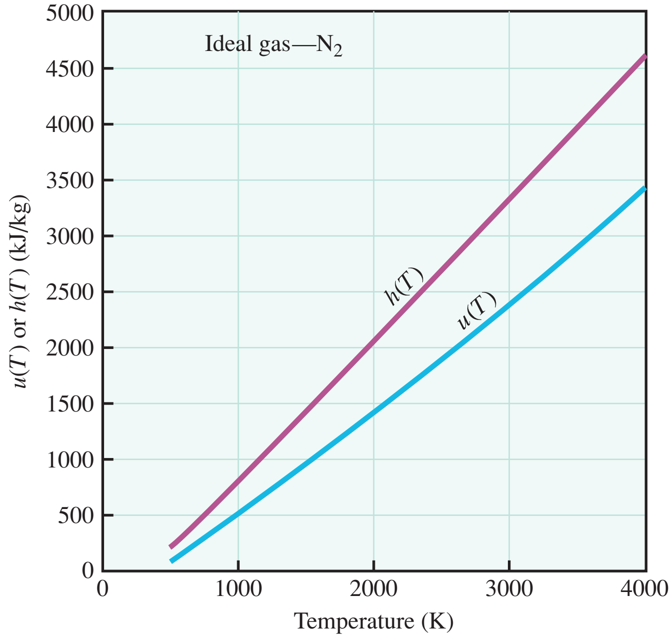
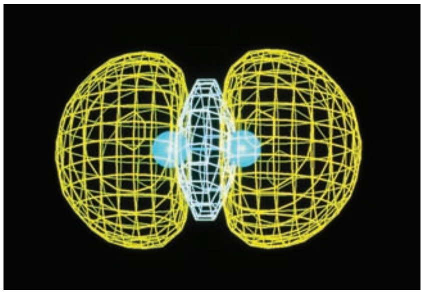


FIGURE 2.10
For ideal gases, the specific internal energy and specific enthalpy are functions of temperature only. The concave-upward curvature in these nearly straight line plots results from the fact that the specific heats (c_v and c_p) for N_2 increase with temperature.

Example 2.8



Molecular structure of nitrogen.

Determine the specific internal energy u for N_2 at 2500 K.

Solution

Known N_2, T

Find u

Assumption

Ideal-gas behavior

Analysis We use Table B.7 to determine u. Before that can be done a few preliminaries are involved. First, we note that molar-specific enthalpies, not mass-specific internal energies, are provided in the table; however, Eq. 2.32 relates u and h for ideal gases and the conversion to a mass basis is straightforward. A second issue is how to interpret the third column in Table B.7, the column containing enthalpy data. The enthalpy values listed under the complex column-three heading, $\bar{h}^{\circ}(T) - \bar{h}_{f}^{\circ}(T_{ref})$, can be interpreted in our present context[12] as simply $\bar{h}(T)$, where $\bar{h}$ is assigned a zero value at 298.15 K (i.e., $T_{ref} = 298.15$ K in Eq. 2.33c). At 2500 K, we see from Table B.7 that

$$\bar{h} = 74{,}305 \text{ kJ/kmol}.$$

We use this value to find the molar-specific internal energy from Eq. 3.32, which has been multiplied through by the molecular weight to yield

$$\begin{aligned}\bar{u} &= \bar{h} - R_u T\\ &= 74{,}305\,\frac{\text{kJ}}{\text{kmol}} - 8.31447\,\frac{\text{kJ}}{\text{kmol}\cdot\text{K}}\,2500\text{ K}\\ &= 74{,}305 \text{ kJ/mol} - 20{,}786 \text{ kJ/mol} = 53{,}519 \text{ kJ/kmol}.\end{aligned}$$

---

[12] As we will see later, the column-three heading has an enlarged meaning when dealing with reacting mixtures of ideal gases. For the present, however, this meaning need not concern us.

Converting the molar-specific internal energy to its mass-specific form (Eq. 2.4) yields

$$\begin{aligned} u &= \bar{u}/\mathcal{M}_{N_2} \\ &= \frac{53{,}519\ \text{kJ/kmol}}{28.013\ \text{kg/kmol}} \\ &= 1910.5\ \text{kJ/kg}. \end{aligned}$$

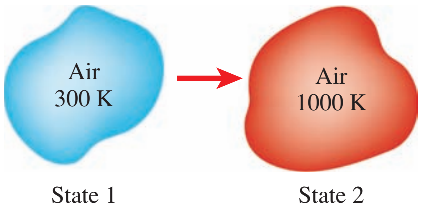
Comments Several very simple, yet very important, concepts are illustrated by this example: 1. the conversions between mass-specific and molar-specific properties, 2. the use of the enthalpy data in Tables B.1–B.12 for nonreacting ideal gases, 3. calculation of ideal-gas internal energies from enthalpies, and 4. practical recognition of the use of reference states for enthalpies (and internal energies).

Self Test 2.8

☑ **Determine the specific enthalpy h and internal energy u for air at 1500 K and 1 atm.**

(Answer: 1762.24 kJ/kg, 1331.46 kJ/kg)

Example 2.9



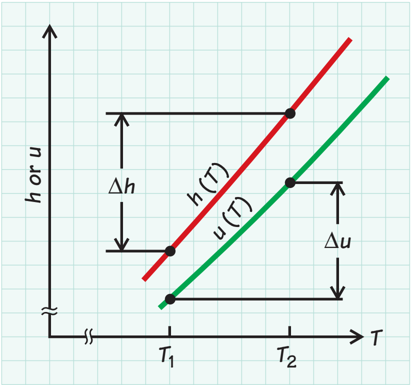
Determine the changes in the mass-specific enthalpy and the mass-specific internal energy for air for a process that starts at 300 K and ends at 1000 K. Also show that $\Delta h - \Delta u = R\Delta T$, and compare a numerical evaluation of this with tabulated data.

Solution

Known air, T_1, T_2

Find $\Delta h\ [= h(T_2) - h(T_1)]$, $\Delta u [= u(T_2) - u(T_1)]$, $\Delta h - \Delta u$

Sketch



Assumption

Air behaves as a single-component ideal gas.

Analysis From Table C.2, we obtain the following values for h and u:

T (K)	h (kJ/kg)	u (kJ/kg)
300	426.04	339.93
1000	1172.43	885.22

Using these data, we calculate

$$\begin{aligned}\Delta h &= h(T_2) - h(T_1)\\ &= h(1000) - h(300)\\ &= 1{,}172.43\ \text{kJ/kg} - 426.04\ \text{kJ/kg}\\ &= 746.39\ \text{kJ/kg}\end{aligned}$$

and

$$\begin{aligned}\Delta u &= 885.22\ \text{kJ/kg} - 339.93\ \text{kJ/kg}\\ &= 545.29\ \text{kJ/kg}.\end{aligned}$$

Applying Eq. 2.32, we can relate Δh and Δu, that is,

$$h_2 = u_2 + RT_2$$

and

$$h_1 = u_1 + RT_1.$$

Subtracting these yields

$$h_2 - h_1 = u_2 - u_1 + R(T_2 - T_1),$$

or

$$\Delta h - \Delta u = R\Delta T.$$

We evaluate this equation using the particular gas constant for air ($R = R_u/\mathcal{M}_{\text{air}}$), giving us

$$\begin{aligned}\Delta h - \Delta u &= \frac{8.31447\ \text{kJ/kmol}\cdot\text{K}}{28.97\ \text{kg/kmol}}(1000 - 300)\ \text{K}\\ &= 200.90\ \text{kJ/kg}.\end{aligned}$$

This compares to the value obtained from the Table C.1 data as follows:

$$\begin{aligned}(\Delta h - \Delta u)_{\text{tables}} &= 746.39\ \text{kJ/kg} - 545.29\ \text{kJ/kg}\\ &= 201.10\ \text{kJ/kg}.\end{aligned}$$

This result is within 0.1% of our calculation. Failure to achieve identical values is probably a result of the methods used to generate the tables (i.e., curve fitting).

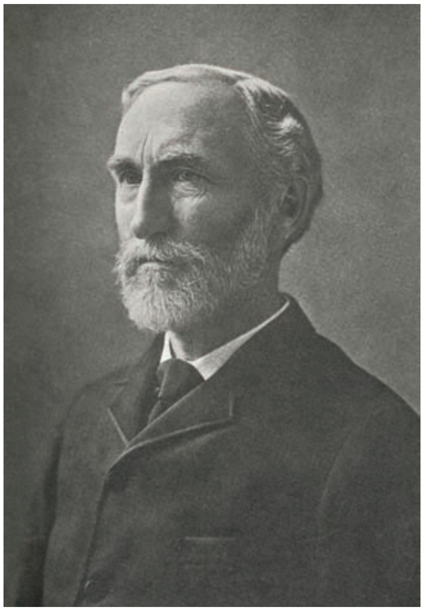
Comment This example illustrates once again the treatment of air as a single-component ideal gas and the use of Appendix C for air properties.

At this point, the reader has sufficient knowledge of properties to begin a study of Chapters 4 and 5. This is also a good entry point from Chapter 7 following Eq. 7.26.

Self Test 2.9

Recalculate the values for the change in mass-specific enthalpy and internal energy for the process in Example 2.9 using Eqs. 2.31e and 2.33e and an appropriate average value of c_v and c_p. Compare your answer with that of Example 2.9.

(Answer: 751.8 kJ/kg, 550.2 kJ/kg)



Josiah Willard Gibbs (1839–1903).

2.4e Ideal-Gas Temperature–Entropy (Gibbs) Relationships

To obtain the desired temperature–entropy relationships (Eqs. 2.25a and 2.25b) for an ideal gas, we apply concepts associated with the first and second laws of thermodynamics. These concepts are developed in Chapters 5 and 7, respectively, and the reader should be familiar with these chapters before proceeding with this section.

We begin by considering a simple compressible system that undergoes an internally reversible process that results in an incremental change in state. For such a process, the first law of thermodynamics is expressed (Eq. 5.5) as

$$\delta Q_{\text{rev}} - \delta W_{\text{rev}} = dU.$$

The incremental heat interaction δQ_{rev} is related directly to the entropy change through the formal definition of entropy from Chapter 7 (i.e., Eq. 7.16),

$$dS \equiv \left(\frac{\delta Q}{T}\right)_{\text{rev}},$$

or

$$\delta Q_{\text{rev}} = TdS.$$

For a simple compressible substance, the only reversible work mode is compression and/or expansion, that is,

$$\delta W_{\text{rev}} = Pd\mathcal{V}.$$

Substituting these expressions for δQ_{rev} and δW_{rev} into the first-law statement yields

$$TdS - Pd\mathcal{V} = dU.$$

We rearrange this result slightly and write

$$\boxed{TdS = dU + Pd\mathcal{V},} \tag{2.35a}$$

which can also be expressed on a per-unit-mass basis as

$$\boxed{Tds = du + Pdv.} \tag{2.35b}$$

Equation 2.35 is the first of the so-called Gibbs or *T–ds* equations. We obtain a second Gibbs equation by employing the definition of enthalpy (Eq. 2.17), that is,

$$U = H - P\mathcal{V},$$

which can be differentiated to yield

$$dU = dH - Pd\mathcal{V} - \mathcal{V}dP.$$

Substituting this expression for dU into Eq. 2.35a and simplifying yields

$$\boxed{TdS = dH - \mathcal{V}dP,} \tag{2.36a}$$

or on a per-unit-mass basis

$$\boxed{Tds = dh - vdP.} \tag{2.36b}$$

Note that Eqs. 2.35 and 2.36 apply to any simple compressible substance, not just an ideal gas; furthermore, these relationships apply to any incremental process, not just an internally reversible one.

We now proceed toward our objective of finding the relationships $f_4(s, T, P) = 0$ and $f_5(s, T, v) = 0$ for an ideal gas by using the ideal-gas equation of state and the ideal-gas calorific equations of state. Starting with Eq. 2.36b, we substitute $v = RT/P$ (Eq. 2.28a) and $dh = c_p dT$ to yield

$$Tds = c_p dT - \frac{RT}{P} dP,$$

which, upon dividing through by T, becomes

$$ds = c_p \frac{dT}{T} - R \frac{dP}{P}. \tag{2.37}$$

Similarly, Eq. 2.35b is transformed using the substitutions $P = RT/v$ and $du = c_v dT$ to yield

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}. \tag{2.38}$$

To evaluate the entropy change in going from state 1 to state 2 state, we integrate Eqs. 2.37 and 2.38, that is,

$$s_2 - s_1 = \int_1^2 ds = \int_1^2 c_p \frac{dT}{T} - \int_1^2 R \frac{dP}{P}$$

and

$$s_2 - s_1 = \int_1^2 ds = \int_1^2 c_v \frac{dT}{T} + \int_1^2 R \frac{dv}{v}.$$

The second term on the right-hand side of each of these expressions can be easily evaluated since R is a constant, and so

$$\boxed{s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} - R \ln \frac{P_2}{P_1}} \tag{2.39a}$$

and

$$\boxed{s_2 - s_1 = \int_1^2 c_v \frac{dT}{T} + R \ln \frac{v_2}{v_1}.} \tag{2.39b}$$

To evaluate the integrals in Eqs. 2.39a and 2.39b requires knowledge of $c_p(T)$ and $c_v(T)$. Curve-fit expressions for $c_p(T)$ are readily available for many species (e.g., Table B.13); $c_v(T)$ can be determined using the c_p curve fits and the ideal-gas relationship, $c_v(T) = c_p(T) - R$ (Eq. 2.34).

In many engineering applications, an average value of c_p (or c_v) over the temperature range of interest can be used to evaluate $s_2 - s_1$ with reasonable accuracy:

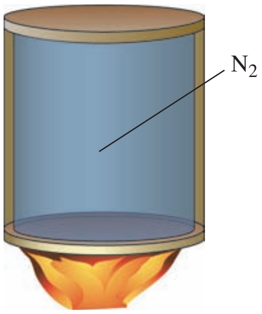
$$\boxed{s_2 - s_1 = c_{p,\text{avg}} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}} \tag{2.40a}$$

and

$$s_2 - s_1 = c_{v,\text{avg}} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}. \tag{2.40b}$$

Molar-specific forms of Eqs. 2.35–2.40 are formed by substituting molar-specific properties ($\bar{v}, \bar{u}, \bar{h}, \bar{s}, \bar{c}_p$, and $\bar{c}_v$) for their mass-specific counterparts (v, u, h, s, c_p, and c_v) and substituting R_u for R.

Example 2.10



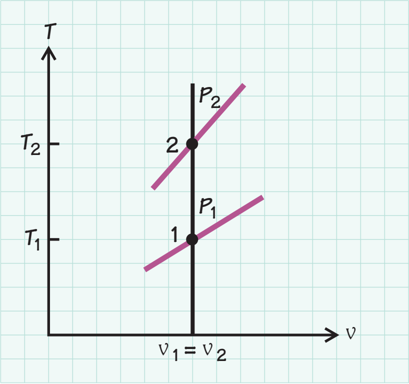
A rigid tank contains 1 kg of N_2 initially at 300 K and 1 atm. Energy is added to the gas until a final temperature of 600 K is reached. Calculate the entropy change of the N_2 associated with this heating process.

Solution

Known M_{N_2}, P_1, T_1, T_2

Find $s_2 - s_1$

Sketch



Assumptions

i. The tank is leak free and perfectly rigid; therefore, $v_2 = v_1$.
ii. The N_2 behaves like an ideal gas.

Analysis Recognizing that this is a constant-volume process (see sketch and assumptions) makes the calculation of the specific entropy change straightforward. To accomplish this, we simplify Eq. 2.40b, which applies to an ideal gas. Starting with

$$s_2 - s_1 = c_{v,\text{avg}} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1},$$

we recognize that the second term on the right-hand side is zero since $v_2 = v_1$ and $\ln v_2/v_1 = \ln(1) = 0$; thus,

$$s_2 - s_1 = c_{v,\text{avg}} \ln \frac{T_2}{T_1}.$$

To evaluate $c_{v,\mathrm{avg}}$, we use data from Table B.7 together with Eq. 2.34 as follows:

$$\begin{aligned}\bar{c}_{p,\mathrm{avg}} &= \frac{\bar{c}_p(300) + \bar{c}_p(600)}{2} \\ &= \frac{29.075 + 30.086}{2}\ \mathrm{kJ/kmol \cdot K} = 29.581\ \mathrm{kJ/kmol \cdot K}.\end{aligned}$$

Converting to a mass basis,

$$\begin{aligned}c_{p,\mathrm{avg}} &= \bar{c}_{p,\mathrm{avg}}/\mathcal{M}_{N_2} \\ &= \frac{29.581\ \mathrm{kJ/kmol \cdot K}}{28.013\ \mathrm{kg/kmol}} = 1.0560\ \mathrm{kJ/kg \cdot K},\end{aligned}$$

and calculating the specific gas constant for N_2,

$$\begin{aligned}R &= R_u/\mathcal{M}_{N_2} \\ &= \frac{8.31447\ \mathrm{kJ/kmol \cdot K}}{28.013\ \mathrm{kg/kmol}} = 0.2968\ \mathrm{kJ/kg \cdot K},\end{aligned}$$

we obtain $c_{v,\mathrm{avg}}$ from Eq. 2.34, that is,

$$\begin{aligned}c_{v,\mathrm{avg}} &= c_{p,\mathrm{avg}} - R \\ &= 1.0560\ \mathrm{kJ/kg \cdot K} - 0.2968\ \mathrm{kJ/kg \cdot K} \\ &= 0.7592\ \mathrm{kJ/kg \cdot K}.\end{aligned}$$

We now calculate the entropy change from the simplified Eq. 2.40b we just derived:

$$\begin{aligned}s_2 - s_1 &= 0.7592\ \ln\left(\frac{600\ \mathrm{K}}{300\ \mathrm{K}}\right)\ \mathrm{kJ/kg \cdot K} \\ &= 0.5262\ \mathrm{kJ/kg \cdot K}.\end{aligned}$$

Comments First, we note the importance of recognizing that the volume is constant for the given process. Discovering that a property is constant is frequently the key to solving problems. Second, we note that, because both the initial and final temperatures were given, finding an average value for the specific heat is accomplished without any iteration.

Self Test 2.10

☑ **Redo Example 2.10 using Equation 2.40a. Do you expect that your answer will be the same as in Example 2.10? Why or why not?**

(Answer: 0.5262 kJ/kg·K. Yes, because entropy is a property of the system and is defined by the states)

2.4f Ideal-Gas Isentropic Process Relationships

For an **isentropic process**, a process in which the initial and final entropies are identical, Eqs. 2.40a and 2.40b can be used to develop some useful engineering relationships. Setting $s_2 - s_1$ equal to zero in Eq. 2.40a gives

$$0 = c_{p,\mathrm{avg}} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}.$$

Dividing by R and rearranging yields

$$\ln\frac{P_2}{P_1} = \frac{c_{p,\text{avg}}}{R}\ln\frac{T_2}{T_1},$$

and removing the logarithm by exponentiation, we obtain

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\frac{c_{p,\text{avg}}}{R}},$$

This equation can be simplified by introducing the specific heat ratio γ and the fact that $c_p - c_v = R$ (Eq. 2.34b), and so

$$\frac{c_{p,\text{avg}}}{R} = \frac{c_{p,\text{avg}}}{c_{p,\text{avg}} - c_{v,\text{avg}}} = \frac{\gamma}{\gamma - 1};$$

thus,

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}}, \tag{2.41a}$$

or, more generally,

$$T^{\gamma}P^{1-\gamma} = \text{constant.} \tag{2.41b}$$

Equation 2.40b can be similarly manipulated to yield

$$\frac{v_2}{v_1} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{1-\gamma}}, \tag{2.42a}$$

or

$$Tv^{\gamma-1} = \text{constant.} \tag{2.42b}$$

Applying the ideal-gas equation of state to either Eq. 2.41 or Eq. 2.42, we obtain a third and final ideal-gas isentropic-process relationship:

$$\frac{P_2}{P_1} = \left(\frac{v_2}{v_1}\right)^{-\gamma}, \tag{2.43a}$$

or

$$Pv^{\gamma} = \text{constant.} \tag{2.43b}$$

Natural gas compressor station in Wyoming.

This last relationship (Eq. 2.43b) is easy to remember. All of the other isentropic relationships are easily derived from this by applying the ideal-gas equation of state.

The ideal-gas isentropic-process relationships are summarized in Table 2.5 for convenient future reference. One use of these relationships is to model ideal compression and expansion processes in internal combustion engines, air compressors, and gas-turbine engines, for example. Example 2.11 illustrates this use in this chapter; other examples are found throughout the book.

2.4g Processes in T–s and P–v Space

With the addition of entropy, we now have four properties (P, v, T, and s) to define states and describe processes. We now investigate T–s and P–v space

Table 2.5 Ideal-Gas Isentropic-Process Relationships

General Form	State 1 to State 2	Equation Reference
$Pv^{\gamma} = \text{constant}$	$\dfrac{P_2}{P_1} = \left(\dfrac{v_2}{v_1}\right)^{-\gamma}$	Eq. 2.43
$Tv^{\gamma-1} = \text{constant}$	$\dfrac{T_2}{T_1} = \left(\dfrac{v_2}{v_1}\right)^{1-\gamma}$	Eq. 2.42
$T^{\gamma}P^{1-\gamma} = \text{constant}$	$\dfrac{P_2}{P_1} = \left(\dfrac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}}$	Eq. 2.41

to see how various fixed-property processes appear on these coordinates. In T–s space, isothermal and isentropic processes are by definition horizontal and vertical lines, respectively. Less obvious are the lines of constant pressure and specific volume shown in Fig. 2.11. Here we see that, through any given state point, lines of constant specific volume have steeper slopes than those of constant pressure. In P–v space, constant-pressure and constant-volume processes are, again by definition, horizontal and vertical lines, whereas constant-entropy and constant-temperature processes follow curved paths as shown in Fig. 2.12. Here we see that lines of constant entropy are steeper (i.e., have greater negative slope) than those of constant temperature. You should become familiar with these characteristics of T–s and P–v diagrams.

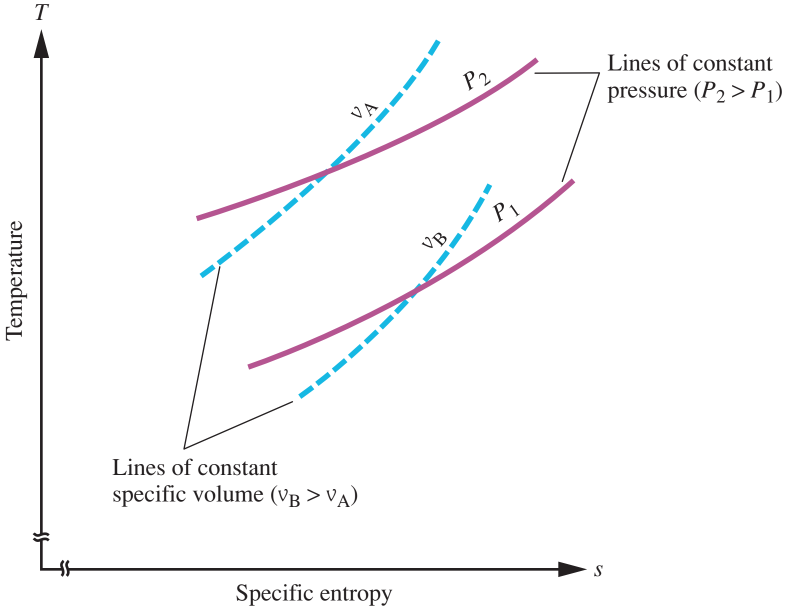
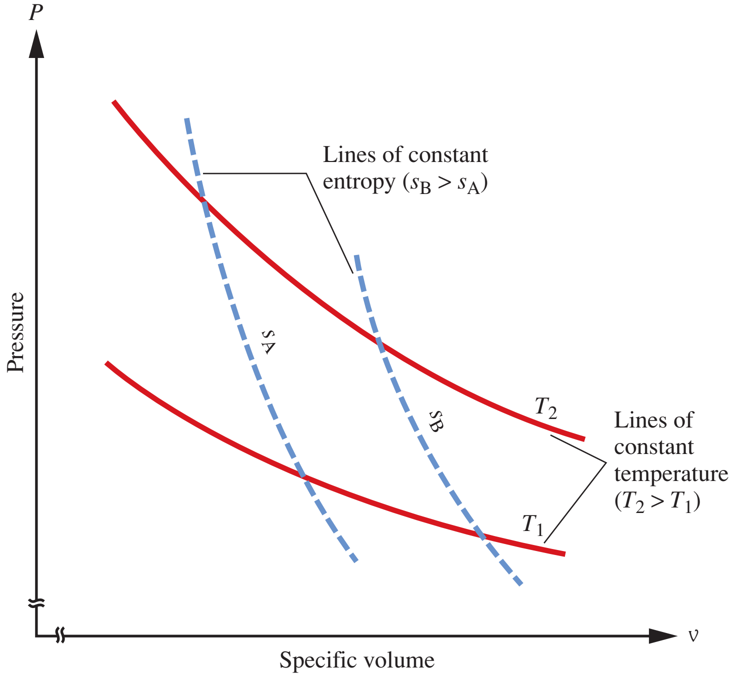


FIGURE 2.11
On a T—s diagram, lines of constant pressure (isobars) and lines of constant specific volume (isochors) both exhibit positive slopes. At a particular state, a constant-volume line has a greater slope than a constant-pressure line.

FIGURE 2.12
On a P—v diagram, lines of constant temperature (isotherms) and lines of constant entropy (isentropes) have negative slopes. At a particular state, an isentrope is steeper (has a greater negative slope) than an isotherm.



Example 2.11

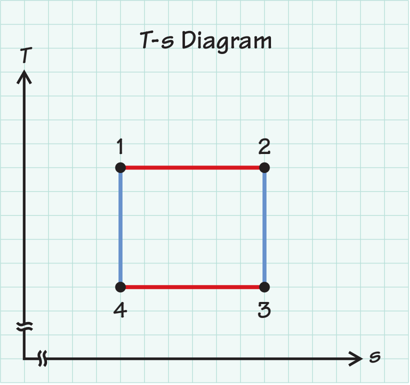
Sketch the following set of processes on T–s and P–v diagrams:

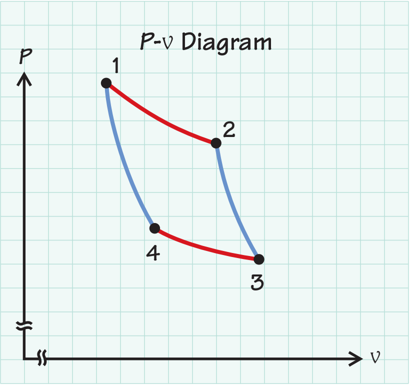
1–2: isothermal expansion,

2–3: isentropic expansion,

3–4: isothermal compression, and

4–1: isentropic compression.





Solution

We begin with the T–s diagram since the temperature is fixed for two of the four processes whereas the entropy is fixed for the remaining two. Recognizing that in an expansion process v_2 is greater than v_1 and, therefore, from Fig. 2.11 that state 2 must lie to the right of state 1, we draw process 1–2 as a horizontal line from left to right. Because the volume is continuing to increase in process 2–3, our isentrope is a vertical line downward from state 2 to state 3. In the compression process from state 3 to state 4, the volume decreases; thus, we draw the state-3 to state-4 isotherm from right to left, stopping when s_4 is equal to s_1. An upward vertical line concludes the cycle and completes a rectangle on T–s coordinates.

To draw the P–v plot, we refer to Fig. 2.12, which shows lines of constant temperature and lines of constant entropy. Because the volume increases in the process 1–2, we draw an isotherm directed downward and to the right. The expansion continues from state 2 to state 3, but the process line now follows the steeper isentrope to the lower isotherm. The cycle is completed following this lower isotherm upward and to the left until it intercepts the upper isentrope at the initial state 1.

Comments This sequence of processes is the famous Carnot cycle, which is discussed at length in Chapter 7.

Self Test 2.11

Referring to Example 2.11, for which process(es) are the equations in Table 2.5 valid? Why or why not?

(Answer: 2–3 and 4–1 only. Equations in Table 2.5 are for isentropic processes only.)

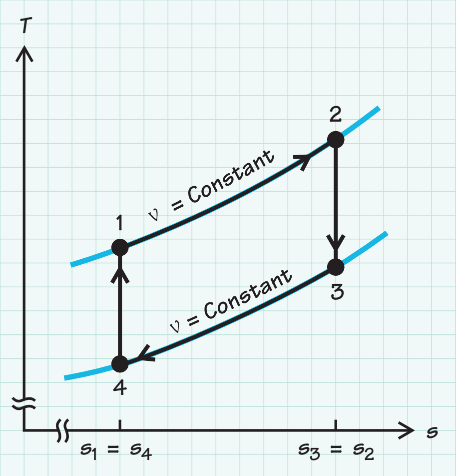
Example 2.12 SI Engine Application

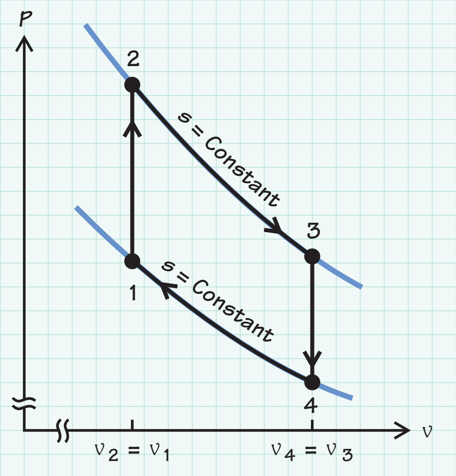
The following processes constitute the *air-standard Otto cycle*. Plot these processes on P–v and T–s coordinates:

1–2: constant-volume energy addition,
2–3: isentropic expansion,
3–4: constant-volume energy removal, and
4–1: isentropic compression.

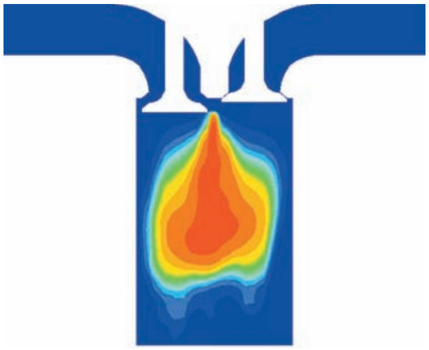
Solution

Since there are two constant-volume processes and two constant-entropy processes, we begin by drawing two isentropes on P–v coordinates and two isochors on T–s coordinates. These are shown in the sketches. Because we expect the pressure to increase with energy addition at constant volume, we draw a vertical line upward from state 1 to state 2 on the P–v diagram. Because process 2–3 is an expansion, with state 3 lying below state 2, we thus know that process 1–2 follows the upper constant-volume line on the T–s diagram. Having established the relative locations of states 1, 2, and 3 on each plot, completing the cycle is straightforward.





Comments The cycle illustrated in this example using air as the working fluid is often used as a starting point for understanding the thermodynamics of spark-ignition (Otto cycle) engines. In the real engine, a combustion process causes the pressure to rise from states 1 to 2, rather than energy addition from the surroundings. Furthermore, the real "cycle" is not closed because the gases exit the cylinder and are replaced by a fresh charge of air-fuel mixture each mechanical cycle. Nevertheless, this air-standard cycle does capture the effect of compression ratio on thermal efficiency and can be used to model other effects as well. Some of these are shown in examples throughout this book.



During the intake stroke of a real spark-ignition engine, fresh fuel and air enter the cylinder and mix with the residual gases. Image courtesy of Eugene Kung and Daniel Haworth.

Also see Example 4.2 in Chapter 4.

Self Test 2.12

☑ **Air undergoes an isentropic compression process from 100 to 300 kPa. If the initial temperature is 30°C, what is the final temperature?**

(Answer: 414.9 K)

2.4h Polytropic Processes

In the previous section, we saw that an isentropic process can be described by the equation

$$P\mathrm{v}^{\gamma} = \text{constant}.$$

By replacing γ, the specific heat ratio, by an arbitrary exponent n, we define a generalized process or **polytropic process** as

$$P\mathrm{v}^{n} = \text{constant}. \tag{2.44}$$

For certain values of n, we recover relationships previously developed. These are shown in Table 2.6. For example, when n is unity, a constant-temperature (isothermal) process is described, that is,

$$P\mathrm{v}^{1} = \text{constant } (= RT).$$

Figure 2.13 graphically illustrates these special-case polytropic processes on P–v and T–s coordinates.

The polytropic process is often used to simplify and model complex processes. A common use is modeling compression and expansion processes when heat-transfer effects are present, as illustrated in the following example.

Also see Example 5.9. ➤

Table 2.6 Special Cases of Polytropic Processes

Process	Constant Property	Polytropic Exponent (n)
Isobaric	P	0
Isothermal	T	1
Isentropic	s or S	γ
Isochoric	v or V	$\pm\infty$

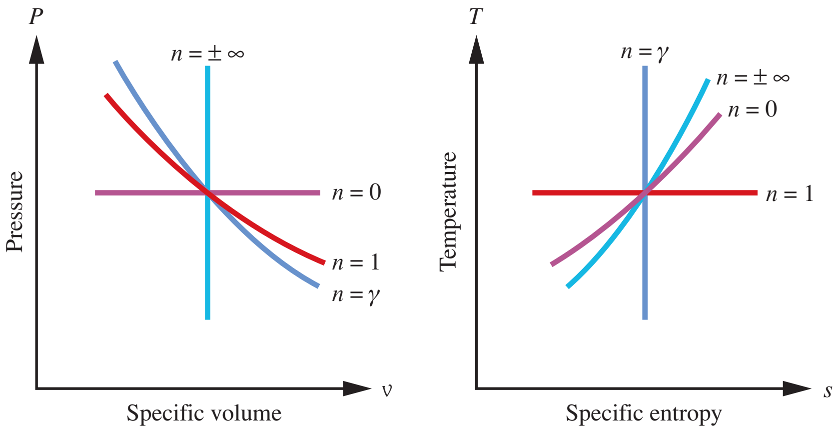
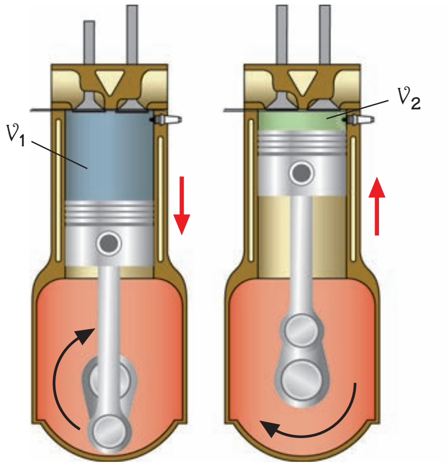


FIGURE 2.13
***P*–v and *T*–*s* diagrams illustrating polytropic process paths for special cases of constant pressure ($n = 0$), constant temperature ($n = 1$), constant entropy ($n = \gamma$), and constant volume ($n = \pm\infty$).**

Example 2.13 SI Engine Application



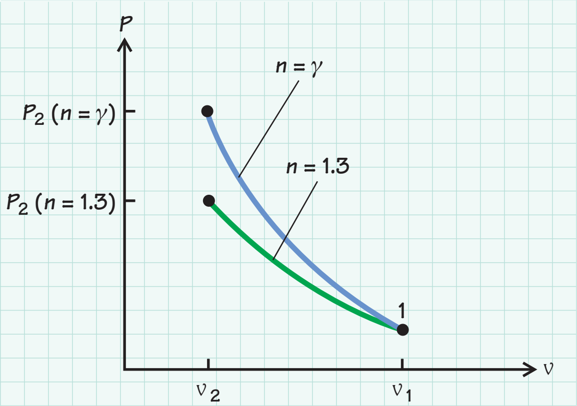
Consider a spark-ignition engine in which the effective compression ratio (CR) is 8:1. Compare the pressure at the end of the compression process for an isentropic compression ($n = \gamma = 1.4$) with that for a polytropic compression with $n = 1.3$. The initial pressure in the cylinder is 100 kPa, a wide-open-throttle condition.

Solution

Known P_1, CR, γ, n

Find $P_2(n = \gamma)$, $P_2(n = 1.3)$

Sketch



Assumption

The working fluid can be treated as air with $\gamma = 1.4$.

Analysis We apply the polytropic process relationship, Eq. 2.44, for the two processes, both starting at the same initial state. From Appendix 1A, we know that the compression ratio is defined as $\mathcal{V}_1/\mathcal{V}_2$. Since the mass is fixed, the compression ratio also equals the ratio of specific volumes, v_1/v_2. For the isentropic compression,

$$
\begin{aligned}
P_2(n = \gamma) &= P_1(v_1/v_2)^{\gamma} \\
&= 100 \text{ kPa } (8)^{1.4} \\
&= 1840 \text{ kPa.}
\end{aligned}
$$

For the polytropic compression,

$$
\begin{aligned}
P_2(n = 1.3) &= P_1(v_1/v_2)^{1.3} \\
&= 100 \text{ kPa } (8)^{1.3} \\
&= 1490 \text{ kPa.}
\end{aligned}
$$

Comments We see that the isentropic compression pressure is approximately 20% higher than the polytropic compression pressure. The ideal compression process is adiabatic and reversible, and, hence, isentropic. In an actual engine, energy is lost from the compressed gases by heat transfer through the cylinder walls, and frictional effects are also present. The combined effects result in a compression pressure lower than the ideal value. The use of a polytropic exponent is a simple way to deal with these effects.

Self Test 2.13

☑ **Given an initial temperature of 400 K, calculate the final temperature for each process in Example 2.13.**

(Answer: 920 K, 745 K)

2.5 NONIDEAL GAS PROPERTIES

2.5a State (P–v–T) Relationships

In this section, we will look at three ways to determine P–v–T state relations for gases that do not necessarily obey the ideal-gas equation of state (Eq. 2.28): 1. the use of tabular data, 2. the use of the van der Waals equation of state, and 3. the application of the concept of generalized compressibility. Before discussing these methods, however, we define the thermodynamic **critical point**, a concept important to all three.

The *critical point* is a point in P–v–T space defined by the highest possible temperature and the highest possible pressure for which distinct liquid and gas phases can be observed. (See Fig. 2.14.)

At the critical point, we designate the thermodynamic variables with the subscript c, so that

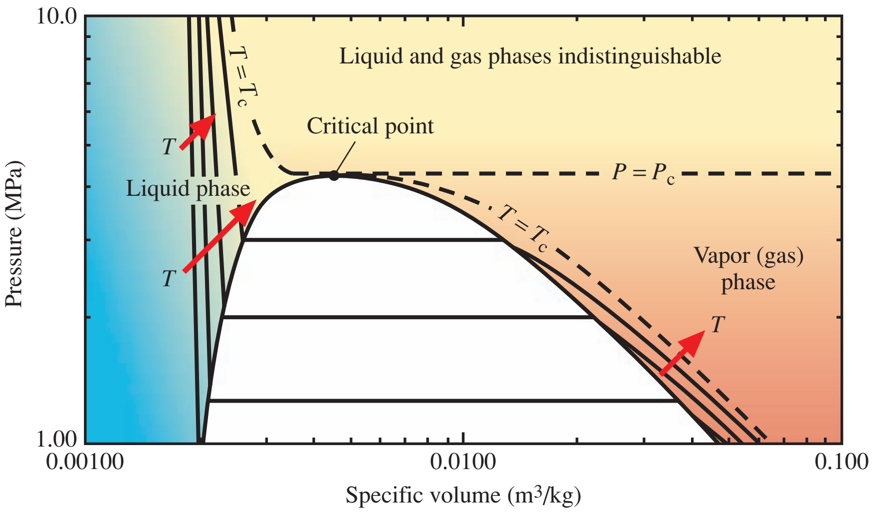
$$\text{critical temperature} \equiv T_c,$$
$$\text{critical pressure} \equiv P_c,$$

and

$$\text{critical specific volume} \equiv v_c.$$

Critical properties for a number of substances are given in Table E.1 in Appendix E. We elaborate on the significance of the critical point later in this chapter in our discussion of substances existing in multiple phases. One immediate use of critical point properties, however, is to establish a rule of thumb for determining when a gas can be considered ideal: A real gas approaches ideal-gas behavior when $P \ll P_c$. In a later section, we will see other conditions where ideal-gas behavior is approached.

FIGURE 2.14
The bold dot indicates the critical point on this P–v–T plot for propane. At temperatures and pressures above their critical values T_c and P_c, respectively, liquid and gas phases are indistinguishable.



Example 2.14

Determine if N_2 is likely to approximate ideal-gas behavior at 298 K and 1 atm.

Solution

The critical properties for N_2 from Table E.1 are

$$T_c = 126.2\ \text{K},$$
$$P_c = 3.39\ \text{MPa}.$$

Comparing the given properties with the critical properties, we have

$$\frac{T}{T_c} = \frac{298\ \text{K}}{126.2\ \text{K}} = 2.36$$

and

$$\frac{P}{P_c} = \frac{101{,}325\ \text{Pa}}{3.39 \times 10^6\ \text{Pa}} = 0.030.$$

Clearly, $P \ll P_c$; thus, the ideal-gas equation of state is likely to be a good approximation to the true state relation for N_2 at these conditions. Moreover, T is greater than T_c, which is also in the direction of ideal-gas behavior.

Comment Since P_c is quite high (33 atm) and T_c is quite low (126.2 K), ideal-gas behavior is likely to be good approximation for N_2 over a fairly wide range of conditions covering many applications. However, caution should be exercised. The methods described in the following allow us to estimate *quantitatively* the deviation of real-gas behavior from ideal-gas behavior.

Self Test 2.14

✓ **Determine if O_2 can be considered an ideal gas at 298 K and atmospheric pressure. Can air at room temperature and atmospheric pressure be considered an ideal gas?**

(Answer: $T/T_c = 1.93$ and $P/P_c = 0.020$, so ideal-gas behavior is a good approximation for O_2. Since the main constituents of air (N_2 and O_2) both behave as ideal gases, ideal-gas behavior for air is a good approximation.)

For conditions near the critical point or for applications requiring high accuracy, alternatives to the ideal-gas equation of state are needed. The following subsections present three approaches.

Tabulated Properties

Accurate P–v–T data in tabular or curve-fit form are available for a number of gases of engineering importance. Because of the importance of steam in electric power generation, a large database is available for this fluid, and tables are published in a number of sources (e.g., Refs. [7] and [8]). Particularly useful and convenient sources of thermodynamic properties are available from the NIST [9, 10]. A large portion of the NIST database is available on the CD included with this book (NIST12 v. 5.2) and from the Internet [11]. Table 2.7 lists the fluids for which properties are available from these sources. We use the NIST resources throughout this book, and the reader is encouraged to become familiar with these valuable sources of thermodynamic data. Selected tabular data are also provided in Appendix D for steam.

Table 2.7 Fluid Properties: Fluids Included in NIST12 v. 5.2 Software and NIST Online Database [11]

Fluid	NIST12 V. 5.2	NIST Online
Air	X	
Water*	X	X
Nitrogen	X	X
Hydrogen	X	X
Parahydrogen	X	X
Deuterium		X
Oxygen	X	X
Fluorine		X
Carbon monoxide	X	X
Carbon dioxide	X	X
Methane	X	X
Ethane		X
Ethene		X
Propane	X	X
Propene		X
Butane		X
Isobutane		X
Pentane		X
Hexane		X
Heptane		X
Helium	X	X
Neon		X
Argon	X	X
Krypton		X
Xenon		X
Ammonia	X	X
Nitrogen trifluoride		X
Methane, trichlorofluoro- (R-11)	X	
Methane, dichlorodifluoro- (R-12)	X	
Methane, chlorodifluoro- (R-22)	X	X
Methane, difluoro- (R-32)		X
Ethane, 2,2-dichloro-1,1,1-trifluoro- (R-123)	X	X
Ethane, pentafluoro- (R-125)		X
Ethane, 1,1,1,2-tetrafluoro- (R-134a)	X	X
Ethane, 1,1,1-trifluoro- (R-143a)		X
Ethane, 1,1-difluoro- (R-152a)		X

* See also Appendix D.

Example 2.15

Determine the deviation from ideal-gas behavior associated with the following gases and conditions:

N_2 at 200 K from 1 atm to P_c,

CO_2 at 300 K from 1 to 40 atm, and

H_2O at 600 K from 1 to 40 atm.

Solution

To quantify the deviation from ideal-gas behavior, we define the factor $Z = Pv/RT$. For an ideal gas, Z is unity for any temperature or pressure. We employ the NIST online database [11] to obtain values of specific volume for the conditions specified. These data are then used to calculate Z values. For example, the specific volume of CO_2 at 300 K and 20 atm is 0.025001 m^3/kg; thus,

$$Z = \frac{Pv}{RT} = \frac{20(101{,}325)\,0.025001}{\left(\dfrac{8314.47}{44.011}\right)300} = 0.8939$$

$$[=]\,\frac{\text{atm}\left(\dfrac{\text{Pa}}{\text{atm}}\right)\left(\dfrac{\text{m}^3}{\text{kg}}\right)}{\left(\dfrac{\text{J}}{\text{kmol}\cdot\text{K}}\right)\left(\dfrac{\text{kmol}}{\text{kg}}\right)\text{K}} \times \frac{\left[\dfrac{1\ \text{N/m}^2}{\text{Pa}}\right]}{\left[\dfrac{1\ \text{N}\cdot\text{m}}{\text{J}}\right]} = 1.$$

A few selected results are presented in the following table, and all of the results are plotted in Fig. 2.15.

	v (m^3/kg)			$Z = Pv/RT$		
P(atm)	N_2	CO_2	H_2O	N_2	CO_2	H_2O
1	0.8786	0.5566	2.7273	0.9998	0.9951	0.9980
10	0.8773	0.5309	0.2676	0.9983	0.9491	0.9792
20	0.4381	0.0250	0.1308	0.9972	0.8939	0.9572
30	0.0292	0.0155	0.0851	0.9965	0.8330	0.9341
40	—	0.0107	0.0621	—	0.7642	0.9097

Comments From the table and from Fig. 2.15, we see that N_2 behaves essentially as an ideal gas over the entire range of pressures from 1 atm to the critical pressure ($P_c = 33.46$ atm). Z values deviate less than 0.4% from the ideal-gas value of unity. Both CO_2 and water vapor, in contrast, exhibit significant departures from ideal-gas behavior, which become larger as the pressure increases. These large departures indicate the need for caution in applying the ideal-gas equation of state, $Pv = RT$.

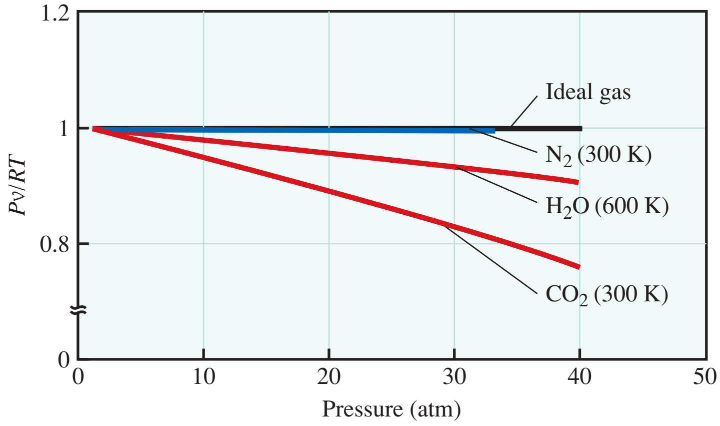


FIGURE 2.15
Deviations from ideal-gas behavior can be seen by the extent to which Z (= Pv/RT) deviates from unity. At 1 atm, CO_2, N_2, and H_2O all have Z values near unity. At higher pressures, CO_2 and H_2O deviate significantly from ideal-gas behavior, whereas N_2 still behaves essentially as an ideal gas.

Self Test 2.15

☑ **Using the ideal-gas equation of state, calculate the specific volume for H_2O at 40 atm and 600 K. Compare your answer with the value from the table in Example 2.15 and determine the calculation error.**

(Answer: 0.0683 m^3/kg, 10%)

Tutorial 1

How to Interpolate

Relationships among properties are frequently presented in tables. For example, internal energy, enthalpy, and specific volume for steam are often tabulated as functions of temperature at a fixed pressure. Table D.3 illustrates such tables and employs temperature increments of 20 K. If the temperature of interest is one of those tabulated, a simple look-up is all that is needed to retrieve the desired properties. In many cases, however, the temperature of interest will fall somewhere between the tabulated temperatures. To estimate property values for such a situation, you can apply **linear interpolation**. We illustrate this procedure with the following concrete example.

Given: Steam at 835 K and 10 MPa.
Find: Enthalpy using Table D.3P.

From the 10-MPa pressure table we see that the given temperature lies between the tabulated values:

T (K)	h (kJ/kg)
820	3494.1
835	?
840	3543.9

Linear interpolation assumes a straight-line relationship between h and T for the interval $820 \leq T \leq 840$. For the given data, we see that the desired temperature, 835 K, lies three-fourths of the way between 820 and 840 K, that is,

$$\frac{835 - 820}{840 - 820} = \frac{15}{20} = 0.75.$$

With the assumed linear relationship, the unknown h value must also lie three-fourths of the way between the two tabulated enthalpy values, that is,

$$\frac{h(835\text{ K}) - h(320\text{ K})}{h(840\text{ K}) - h(320\text{ K})} = \frac{h(835\text{ K}) - 3494.1}{3543.9 - 3494.1} = 0.75.$$

We now solve for h (835 K), obtaining

$$\begin{aligned} h(835\text{ K}) &= 0.75(3543.9 - 3494.1)\text{kJ/kg} + 3494.1\text{ kJ/kg} \\ &= 37.4\text{ kJ/kg} + 3494.1\text{ kJ/kg} = 3531.5\text{ kJ/kg}. \end{aligned}$$

To generalize, we express this procedure as follows, denoting $h(T_1)$ as h_1, $h(T_2)$ as h_2, and $h(T_3)$ as h_3:

$$\frac{h(T_3) - h(T_1)}{h(T_2) - h(T_1)} = \frac{h_3 - h_1}{h_2 - h_1} = \frac{T_3 - T_1}{T_2 - T_1},$$

or

$$h_3 = \left(\frac{T_3 - T_1}{T_2 - T_1}\right)(h_2 - h_1) + h_1.$$

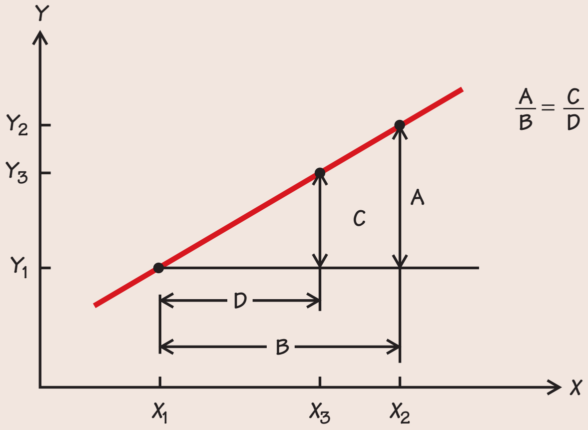
For any property pair $Y(X)$, this can be expressed

$$\frac{Y(X_3) - Y(X_1)}{Y(X_2) - Y(X_1)} = \frac{Y_3 - Y_1}{Y_2 - Y_1} = \frac{X_3 - X_1}{X_2 - X_1},$$

or

$$Y_3 = \left(\frac{X_3 - X_1}{X_2 - X_1}\right)(Y_2 - Y_1) + Y_1.$$

Rather than remembering or referring to any equations, knowing the physical interpretation of linear interpolation allows you to create the needed relationships. The following sketch provides a graphic aid for this procedure:



Although the use of computer-based property data may minimize the need to interpolate, some data may only be available in tabular form. Moreover, the ability to interpolate is a generally useful skill and should be mastered.

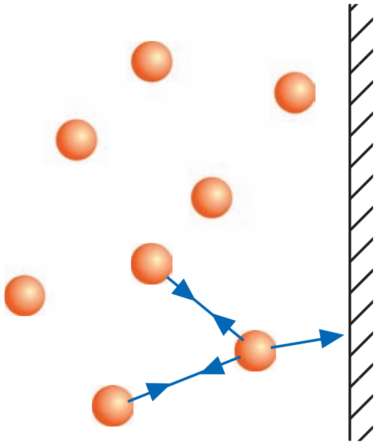


FIGURE 2.16
Intermolecular attractive forces result in a pressure less than would result from an ideal gas in which there are no long-range intermolecular forces.

Other Equations of State

The kinetic theory model of a gas that leads to the ideal-gas equation of state is based on two assumptions that break down when the density of the gas is sufficiently high. The first of these is that the molecules themselves occupy a negligible volume compared to the volume of gas under consideration. Clearly as a gas is compressed, the average spacing between molecules becomes less and the fraction of the macroscopic gas volume occupied by the microscopic molecules increases. The **van der Waals equation of state** accounts for the finite volume of the molecules by subtracting a molecular volume from the macroscopic volume; thus, the molar-specific volume $\bar{v}$ in the state equation is replaced with $\bar{v} - b$, where b is a constant for a particular gas.

The second assumption that is violated at high densities is that the long-range forces between molecules are negligible. Figure 2.16 illustrates how the existence of such forces can affect the equation of state. Since the pressure of a gas is a manifestation of the momentum transferred to the wall by molecular collisions, long-range attractive forces will "pull back" molecules as they approach the wall, thus decreasing the momentum exchange. This effect, in turn, results in a decrease in pressure. In the van der Waals equation of state, this effect of intermolecular attractive forces is accounted for by replacing the pressure P with $P + a/\bar{v}^2$, where a is a constant, again dependent upon the particular molecular species involved. The appearance of the reciprocal of $\bar{v}^2$ is a consequence of the molecular collision frequency with the wall being proportional to the density $(1/\bar{v})$ and the intermolecular attractive force also being proportional to the molar gas density $(1/\bar{v})$.

With these two corrections to the ideal-gas model, we write the van der Waals equation of state as follows:

$$\left(P + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = R_u T. \tag{2.45}$$

Values for the constants a and b for a number of gases are provided in Appendix E.

Example 2.16

Use the van der Waals equation of state to evaluate $Z\ (= P\bar{v}/R_u T)$ for CO_2 at 300 K and 30 atm. Compare this result with the value calculated using the NIST database in Example 2.15.

Solution

Known CO_2, T, P

Find Z

Sketch See Fig. 2.15.

Assumptions

van der Waals gas

Analysis We use the van der Waals equation of state (Eq. 2.45) to find the molar-specific volume $\bar{v}$. This value of $\bar{v}$ is then used to calculate Z. We rearrange Eq. 2.45,

$$\left(P + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = R_u T,$$

to the following cubic form:

$$\bar{v}^3 - \left(\frac{R_u T}{P} + b\right)\bar{v}^2 + \frac{a}{P}\bar{v} - \frac{ab}{P} = 0.$$

Before solving for $\bar{v}$, we calculate the coefficients using values for a and b from Table E.2:

$$a = 3.643 \times 10^5\ \mathrm{Pa \cdot (m^3/kmol)^2},$$
$$b = 0.0427\ \mathrm{m^3/kmol}.$$

The coefficients are thus

$$\begin{aligned}\left(\frac{R_u T}{P} + b\right) &= \frac{8314.47\ (300)}{30\ (101{,}325)} + 0.0427 \\ &= 0.863274 \\ &[=]\frac{\dfrac{\mathrm{J}}{\mathrm{kmol \cdot K}}\mathrm{K}\left[\dfrac{\mathrm{N \cdot m}}{1\ \mathrm{J}}\right]}{\mathrm{atm}\left[\dfrac{\mathrm{N/m^2}}{\mathrm{atm}}\right]} = \mathrm{m^3/kmol},\end{aligned}$$

$$\begin{aligned}\frac{a}{P} &= \frac{3.643 \times 10^5\ \mathrm{Pa \cdot (m^3/kmol)^2}}{30\ (101{,}325)\ \mathrm{Pa}} \\ &= 0.119845\ \mathrm{(m^3/kmol)^2},\end{aligned}$$

and

$$\begin{aligned}\frac{ab}{P} &= \frac{3.643 \times 10^5\ \mathrm{Pa \cdot (m^3/kmol)^2}\ (0.0427)\mathrm{(m^3/kmol)}}{30(101{,}325)\ \mathrm{Pa}} \\ &= 0.005117\ \mathrm{(m^3/kmol)^3}.\end{aligned}$$

Substituting these coefficients into the cubic van der Waals equation of state yields

$$\bar{v}^3 - 0.863274\,\bar{v}^2 + 0.119845\,\bar{v} - 0.005117 = 0.$$

Many methods exist to find the useful root of this polynomial. Using spreadsheet software to implement the iterative Newton–Raphson method with an initial guess of $\bar{v} = R_u T/P$ ($= 0.8206\ \mathrm{m^3/kmol}$) results in the following converged value for $\bar{v}$ after four interations:

$$\bar{v}\ (30\ \mathrm{atm},\ 300\ \mathrm{K}) = 0.7032\ \mathrm{m^3/kmol}.$$

With this value of $\bar{v}$, we evaluate Z:

$$\begin{aligned}Z = \frac{P\bar{v}}{R_u T} &= \frac{30\ (101{,}325)\ 0.7032}{8314.47\ (300)} \\ &= 0.8570,\end{aligned}$$

which is dimensionless.

This value of Z is only 2.9% higher than the 0.8330 calculated from the NIST database in Example 2.15.

Comments For this particular example, note that the van der Waals model did an excellent job of predicting the specific volume for conditions far from the ideal-gas regime. Although the procedure used to calculate $\bar{v}$ was straightforward, we still employed the power of a computer to solve the cubic van der Waals equation of state.

Self Test 2.16

☑ **Repeat Example 2.16 for H_2O at 40 atm and 600 K.**

(Answer: $Z = 0.930$)

Other equations of state have been developed that provide more accuracy than the van der Waals equation. Discussion of these is beyond the scope of this book. For more information, we refer the interested reader to Ref. [1].

Generalized Compressibility

As we will see later, the $T = T_c$ isotherm in P–v space exhibits an inflection point at the critical point. One can relate the constants a and b in the van der Waals equation of state to the properties at the critical state by recognizing that both slope and curvature of the $T = T_c$ isotherm are zero; thus,

$$a = \frac{27}{64}\frac{R^2T_c^2}{P_c}, \tag{2.46a}$$

$$b = \frac{RT_c}{8P_c}, \tag{2.46b}$$

$$Z = \frac{P_c v_c}{RT_c} = \frac{3}{8}. \tag{2.46c}$$

That a and b depend only on the critical pressure and critical temperature suggests that a generalized state relationship exists when actual pressures and temperatures are normalized by their respective critical values. More explicitly, defining the reduced pressure and temperature as

$$P_R \equiv \frac{P}{P_c} \tag{2.47a}$$

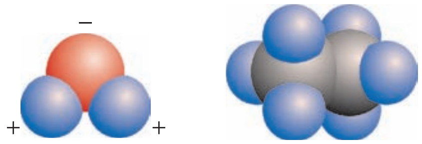
and

$$T_R \equiv \frac{T}{T_c}, \tag{2.47b}$$

respectively, we expect

$$Z = Z\,(P_R, T_R) \tag{2.47c}$$

to be a single "universal" relationship. This idea is known as the **principle of corresponding states**, and Z is called the **compressibility factor**. Figure 2.17 shows data and the best fit for this relationship, where Z is presented as a function of P_R using T_R as a parameter. For the gases chosen, individual data points are quite close to the curve fits, illustrating the "universal" nature of Eq. 2.47c. Plots such as Fig. 2.17 are known as **generalized compressibility charts**. Figure 2.18 is a working generalized compressibility chart for reduced pressures up to 10 and reduced temperatures up to 15.



Polar molecule (water) and nonpolar molecule (ethane).

In reality, Eq. 2.47c is not truly universal but rather a useful approximation. The best accuracy is obtained when gases are grouped according to shared characteristics. For example, a single plot constructed for polar compounds, such as water and alcohols, provides a tighter "universal" relationship than is obtained when nonpolar compounds are also included. Generalized compressibility charts are useful for substances for which no data are available other than critical properties.

We can also use the generalized compressibility chart to ascertain conditions where real gases deviate from ideal-gas behavior. Using Fig. 2.18 as our guide, we observe the following:

- The largest departures from ideal-gas behavior occur at conditions near the critical point. At the critical point, the ideal-gas equation of state is not at all close to reality ($Z \approx 0.3$).
- Accuracy to within 5% of ideal-gas behavior ($0.95 < Z < 1.05$) is found for the following conditions:
  - at all temperatures, provided $P_R < 0.1$, and
  - when $1.95 < T_R < 2.4$ and $T_R > 15$, both for $P_R < 7.5$.

The following example illustrates the use of generalized compressibility theory.

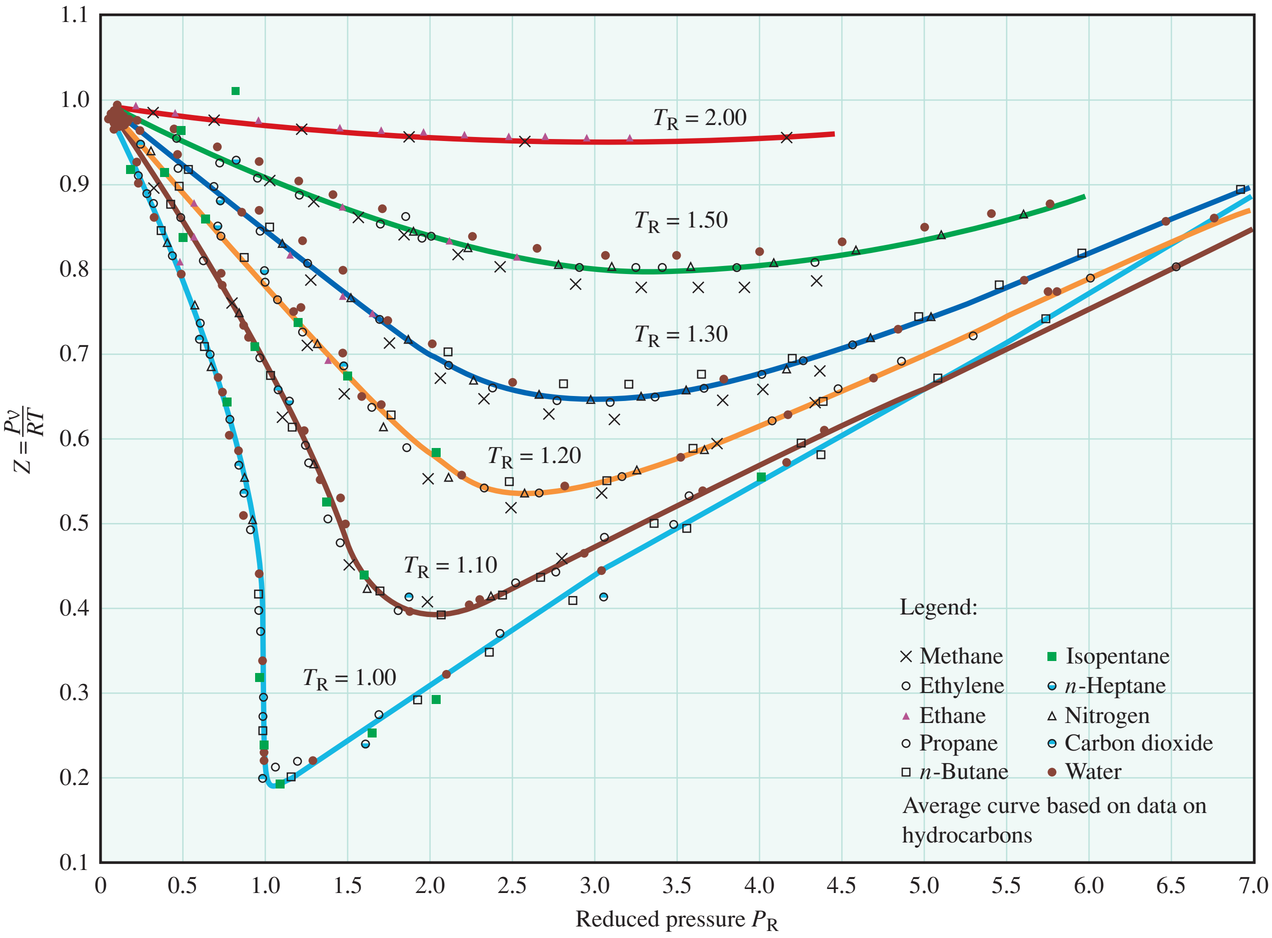


FIGURE 2.17

***The compressibility factor Z can be correlated using reduced properties (i.e., P/P_c and T/T_c). Note how the data for various substances collapse when plotted in this manner.* Adapted from Ref. [12] with permission.**

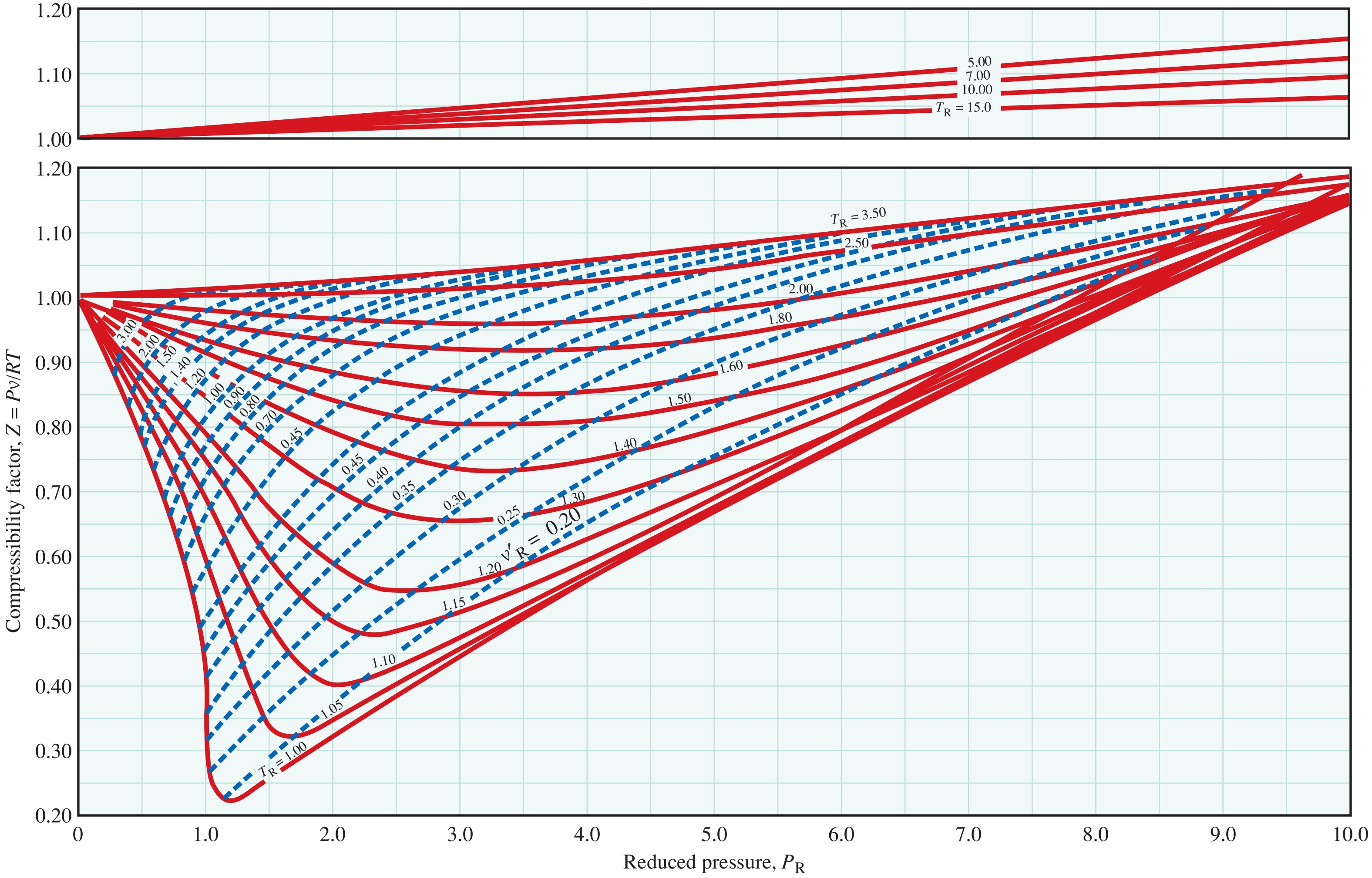


FIGURE 2.18

***Generalized compressibility chart showing extended range of reduced temperatures ($1 < T_R < 15$). The pseudo reduced specific volume ν'_R shown on the chart is defined as $\nu/(RT_c/P_c)$.* Adapted from Ref. [13] with permission.**

Example 2.17

Once again, consider CO_2 at 30 atm and 300 K. Use the generalized compressibility chart to determine the density of CO_2 at this condition. Compare this result with that obtained from the ideal-gas equation of state and with that from the NIST tables [11].

Solution

Known CO_2, P, T

Find ρ_{CO_2}

Sketch See Fig. 2.18.

Analysis To use the generalized compressibility chart requires values for the critical temperature and pressure, which we retrieve from Appendix E, Table E.1, as follows:

$$T_c = 304.2 \text{ K},$$
$$P_c = 73.9 \times 10^5 \text{ Pa}.$$

The reduced temperature and pressure are thus

$$T_R = \frac{T}{T_c} = \frac{300 \text{ K}}{304.2 \text{ K}} = 0.986,$$

$$P_R = \frac{P}{P_c} = \frac{30 \text{ atm } (101{,}325 \text{ Pa/atm})}{73.9 \times 10^5 \text{ Pa}} = 0.411.$$

Using these values, we find the compressibility factor from Fig. 2.18 to be

$$Z \approx 0.82.$$

Applying the definition of Z, we obtain the density:

$$Z \equiv \frac{Pv}{RT} = \frac{P}{\rho RT},$$

or

$$\begin{aligned}\rho &= \frac{P}{ZRT} = \frac{P\mathcal{M}_{CO_2}}{ZR_uT}\\ &= \frac{1}{0.82}\,\frac{30\,(101{,}325)\,44.01}{8314.47\,(300)}\text{kg/m}^3\\ &= \frac{53.63}{0.82}\text{ kg/m}^3 = 65 \text{ kg/m}^3.\end{aligned}$$

The reader should verify the units in this calculation. Note that the ideal-gas density is the numerator in the last line of this calculation. Using the results of Example 2.15, we make the requested comparisons:

Method	***Z***	**ρ (kg/m^3)**
Fig. 2.18	0.82	65
NIST database	0.833	64.51
Ideal gas	1.000	53.63

Comments Even though reading Z from the chart is an approximate procedure, excellent agreement is found between the density calculated from the chart and that from the NIST database.

Self Test 2.17 ☑ **Repeat Example 2.17 for H_2O at 40 atm and 600 K.**

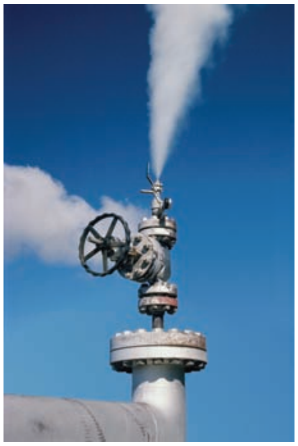
(Answer: $Z \cong 0.95$, $\rho = 15.41\ kg/m^3$)

2.5b Calorific Relationships

Use the NIST database for values of h, u, c_v, and c_p as functions of T and P for nonideal gases. For generalized corrections to ideal-gas properties, see Refs. [20, 21].

2.5c Second-Law Relationships

Use the NIST database for entropy values as functions of T and P for nonideal gases. For generalized corrections to ideal-gas properties, see Refs. [20, 21].



2.6 PURE SUBSTANCES INVOLVING LIQUID AND VAPOR PHASES

In this section, we investigate the thermodynamic properties of simple, compressible substances that frequently exist in both liquid and vapor states. Because of its engineering importance, we focus on water. When discussing water, we use the common designations, ice, water, and steam to refer to the solid, liquid, and vapor states, respectively, and use the chemical designation H_2O when we wish to be general and not designate any particular phase. The terms vapor and gas are used interchangeably in this book.[13]

2.6a State (P–v–T) Relationships

Phase Boundaries

We begin our discussion of multiphase properties by conducting a thought experiment. Consider a kilogram of H_2O enclosed in a piston–cylinder arrangement as shown in the sketch in Fig. 2.19. The weight on the piston fixes the pressure in the cylinder as we add energy to the system. At the initial state, the H_2O is liquid, and remains liquid, as we add energy by heating from A to B. You might envision that a Bunsen burner is used as the energy source, for example. The added energy results in an increase in the temperature of the water, while the water expands slightly, causing a small increase in the specific volume. The temperature and the specific volume increase until state B is reached. At this point, further addition of energy results in a portion of the water becoming vapor or steam, at a fixed temperature. At 1 atm, this phase change occurs at 373.12 K (99.97°C).[14] At

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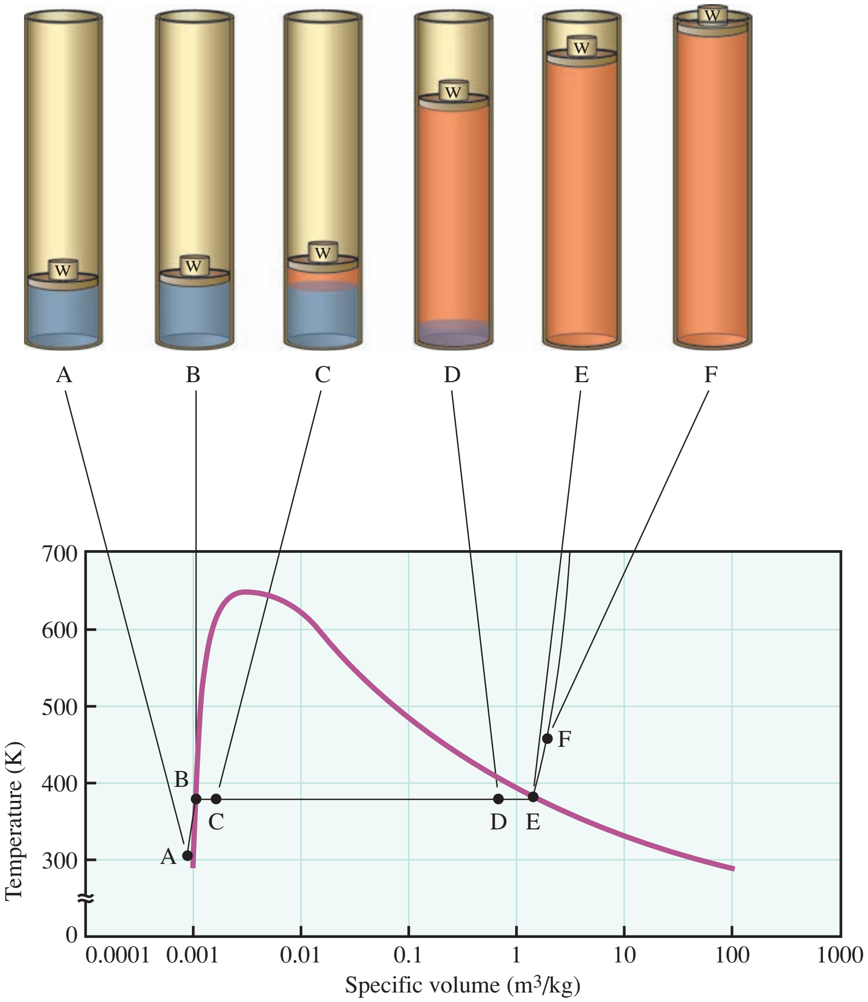
[13] Some textbooks distinguish a gas from a vapor using the critical pressure as a criterion. In this usage, gases exist above P_c, whereas vapors exist below P_c.

[14] With the adoption of the International Temperature Scale of 1990 (ITS-90), the normal boiling point of water is not exactly 100°C, but rather 99.974°C.

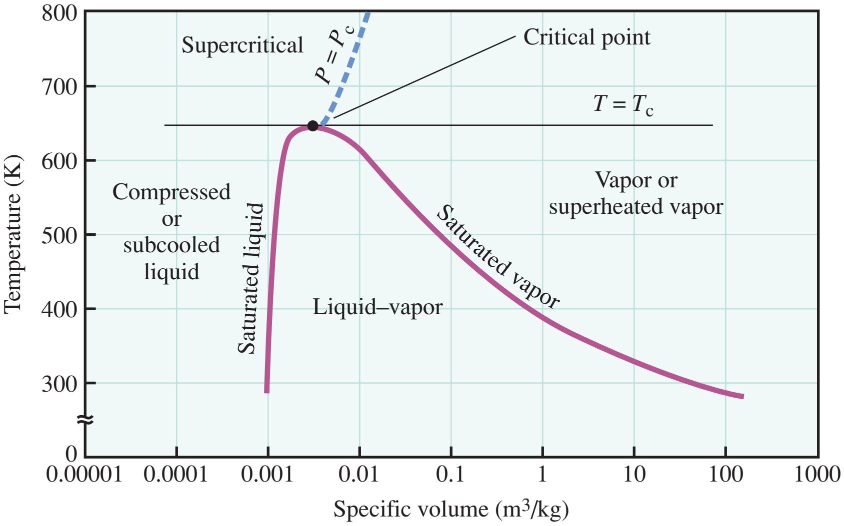
FIGURE 2.19
Heating water at constant pressure follows the path A–B–C–D–E–F on a temperature–specific volume diagram. Note the huge increase in volume in going from the liquid state (B) to the vapor state (E). The volumes shown in the piston–cylinder sketches are not to scale.



state C, we see that most of the H_2O is still in the liquid phase. With continued heating, more and more water is converted to steam. At state D, the transformation is nearly complete, and at state E, all of the liquid has turned to vapor. Adding energy beyond this point results in an increase in both the temperature and specific volume of the steam, creating what is known as superheated steam. The point at F designates a superheated state. Assuming that the heating was conducted quasi-statically, the path A–B–C–D–E–F is a collection of equilibrium states following an isobar (a line of constant pressure) in T–v space. We could repeat the experiment with lesser or greater weight on the piston (i.e., at lower or higher pressures), and map out a phase diagram showing a line where vaporization just begins (states like B) and a line where vaporization is complete (states like E). The bold line in Fig. 2.19 summarizes these thought experiments. Although we considered H_2O, similar behavior is observed for many other fluids, for example, the various fluids used as refrigerants.

Figure 2.20 presents a T–v diagram showing the designations of the various regions and lines associated with the liquid and vapor states of a fluid. Although the numerical values shown apply to H_2O, the general ideas presented in this figure and discussed in the following apply to many liquid–vapor systems.

FIGURE 2.20
On T-ν coordinates, the compressed liquid region lies to the left of the saturated liquid line, the liquid–vapor region lies between the saturated liquid and saturated vapor lines, and the vapor or superheat region lies to the right of the saturated vapor line.



Consider the region in T–ν space that lies below the critical temperature but above temperatures at which a solid phase forms. Here we have three distinct regions, corresponding to

- **Compressed** or **subcooled liquid**,
- **Liquid–vapor** or **saturation**, and
- **Vapor** or **superheated vapor**.

We also have two distinct lines, which join at the critical point:

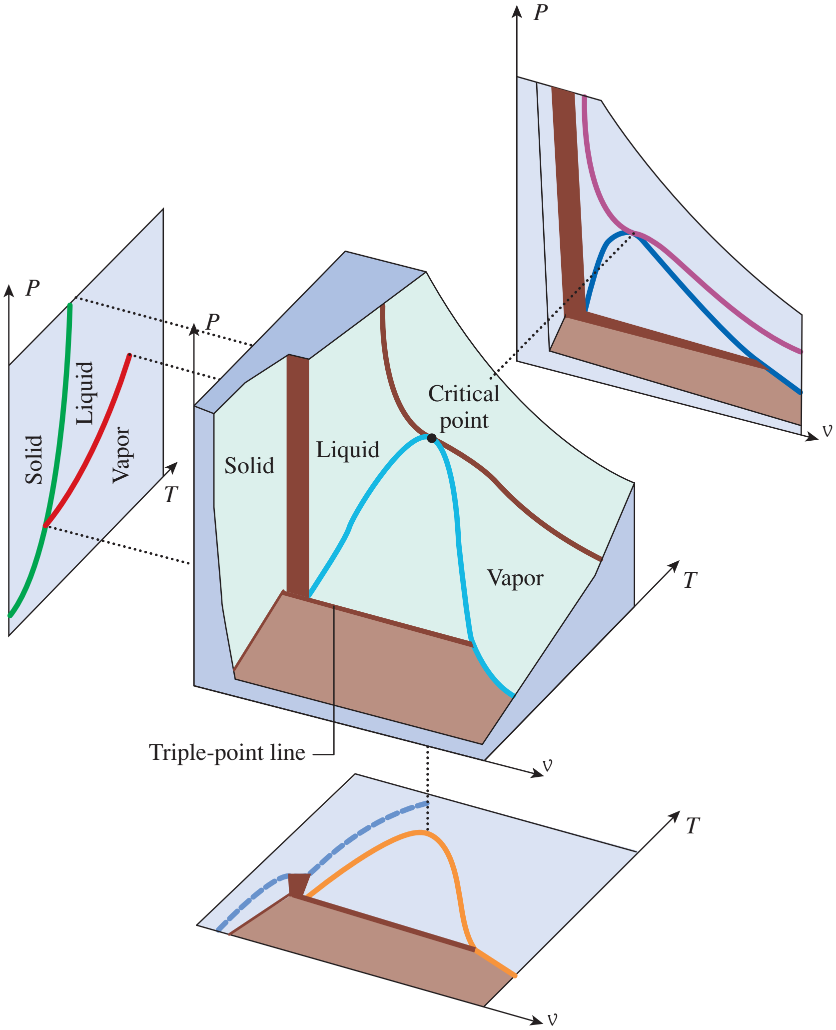
- The **saturated liquid line** and
- The **saturated vapor line**.

The saturated liquid line is the locus of states at which the addition of energy at constant pressure results in the formation of vapor (state B in Fig. 2.19). The temperature and pressure associated with states on the saturated liquid line are called the **saturation temperature** and **saturation pressure**, respectively. To the left of the saturated liquid line is the compressed liquid region, which is also known as the subcooled liquid region. These designations arise from the fact that at any given point in this region, the pressure is higher than the corresponding saturation pressure at the same temperature (thus the designation *compressed*) and, similarly, any point is at a temperature lower than the corresponding saturation temperature at the same pressure (thus the designation subcooled). The saturated liquid line terminates at the critical point with zero slope on both T–ν and P–ν coordinates.

Immediately to the right of the saturated liquid line are states that consist of a mixture of liquid and vapor. Bounding this liquid–vapor or saturation region on the right is the saturated vapor line. This line is the locus of states that consist of 100% vapor at the saturation pressure and temperature. The saturated vapor line joins the saturated liquid line at the critical point. This junction, the critical point, defines a state in which liquid and vapor properties are indistinguishable.

Figure 2.20 also shows the **supercritical region**. Within this region, the pressure and temperature exceed their respective critical values, and there is no distinction between a liquid and a gas.

FIGURE 2.21
***A P–v–T surface for a substance that contracts upon freezing.* After Ref. [22].**



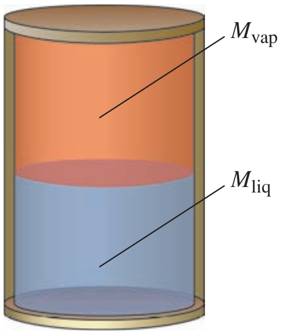
To the right of the saturated vapor line lies the vapor or superheated vapor region. The use of the word *superheated* refers to the idea that within this region the temperature at a particular pressure is greater than the corresponding saturation temperature.

The liquid–vapor or saturation region is frequently referred to as the **vapor dome** because of its shape on a T–log v plot. When dealing with water, the term *steam dome* is sometimes applied. Because two phases coexist in the saturation region, defining a thermodynamic state here is a bit more complex than in the single-phase regions. We examine this issue in the next section.

The three-dimensional P–v –T surface (Fig. 2.21) provides the most general view of a simple substance that exhibits multiple phases. From Fig. 2.21, we see that the T–v, P–v, and P–T plots are simply projections of the three-dimensional surface onto these respective planes.

A New Property–Quality

In our discussion of gases, whether ideal or real, we saw that simultaneously specifying the temperature and pressure defined the thermodynamic state. A knowledge of P and T was sufficient to define all other properties. In the liquid–vapor region, however, this situation no longer holds, although we still require two independent properties to define the thermodynamic state. In



$M_{mix} = M_{vap} + M_{liq}$

FIGURE 2.22
The property quality x defines the fraction of a liquid–vapor mixture that is vapor.

Fig. 2.19, we see that the temperature and pressure are both fixed for all states lying between point B and point E; thus, in the two-phase region, the temperature and pressure are not independent properties. If one is known, the other is a given. To define the state within the liquid–vapor mixture region thus requires another property in addition to P or T. For example, we see from Fig. 2.19 that specifying the specific volume together with the temperature can define all states along B–E.

To assist in defining states in the saturation region, a property called **quality** is used. Formally, quality (x) is defined as the mass fraction of the mixture existing in the vapor state (see Fig. 2.22); that is,

$$x \equiv \frac{M_{\text{vapor}}}{M_{\text{mix}}}. \tag{2.48a}$$

Conventional notation uses the subscript g to refer to the vapor (gas) phase and the subscript f to refer to the liquid phase.[15] Using this notation, the quality is defined as

$$x \equiv \frac{M_g}{M_g + M_f}. \tag{2.48b}$$

The quality for states lying on the saturated liquid line is zero, whereas for states lying on the saturated vapor line, the quality is unity, or 100% when expressed as a percentage. Since the actual mass in each phase is not usually known, the quality is usually derived, or related to, other intensive properties. For example, we can relate the quality to the specific volume as follows:

$$v = (1 - x)v_f + xv_g, \tag{2.49a}$$

or

$$x = \frac{v - v_f}{v_g - v_f}. \tag{2.49b}$$

That this is true is easily seen by expressing the intensive properties, v and x, in terms of their defining extensive properties, $\mathcal{V}$ and M, that is,

$$\begin{aligned} v &= \frac{M_f}{M_f + M_g}\frac{\mathcal{V}_f}{M_f} + \frac{M_g}{M_f + M_g}\frac{\mathcal{V}_g}{M_g} \\ &= \frac{\mathcal{V}_f}{M_f + M_g} + \frac{\mathcal{V}_g}{M_f + M_g} = \frac{\mathcal{V}_f + \mathcal{V}_g}{M_f + M_g} \\ &\equiv \frac{\mathcal{V}_{\text{mixture}}}{M_{\text{mixture}}}. \end{aligned}$$

The relationship expressed by Eq. 2.49a can be generalized in that any mass-specific property (e.g., u, h, and s) can be used in place of the specific volume, so that

$$\beta = (1 - x)\,\beta_f + x\beta_g, \tag{2.49c}$$

or

$$x = \frac{\beta - \beta_f}{\beta_g - \beta_f}, \tag{2.49d}$$

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[15] The subscripts f and g are actually from the German words *Flussigkeit* (liquid) and *Gaszustand* (gaseous state), respectively.

where β represents any mass-specific property. A physical interpretation of Eq. 2.49d is easy to visualize by referring to Fig. 2.19. Here we interpret the quality at state C as the length of the line B–C divided by the length of the line B–E, where a linear rather than logarithmic scale is used for v. This same interpretation applies to any mass-specific property β plotted in a similar manner.

Commonly employed rearrangements of Eqs. 2.49a and 2.49b are

$$v = v_f + x\,(v_g - v_f) \tag{2.50a}$$

and

$$\beta = \beta_f + x\,(\beta_g - \beta_f). \tag{2.50b}$$

Defining v_{fg} and β_{fg},

$$v_{fg} \equiv v_g - v_f \tag{2.50c}$$

and

$$\beta_{fg} \equiv \beta_g - \beta_f, \tag{2.50d}$$

we rewrite Eqs. 2.50a and 2.50b more compactly as

$$v = v_f + x v_{fg} \tag{2.50e}$$

and

$$\beta = \beta_f + x\beta_{fg}. \tag{2.50f}$$

Equations 2.50e and 2.50f are useful when using tables that provide values for v_{fg} and similar properties β_{fg}.

Example 2.18

A rigid tank contains 3 kg of H_2O (liquid and vapor) at a quality of 0.6. The specific volume of the liquid is 0.001041 m^3/kg and the specific volume of the vapor is 1.859 m^3/kg. Determine the mass of the vapor, the mass of the liquid, and the specific volume of the mixture.

Solution

Known M_{mix}, x, v_f, v_g

Find M_g, M_f, v_{mix}

Sketch See Fig. 2.22.

Assumptions

Equilibrium prevails.

Analysis We apply the definition of quality (Eq. 2.48b) to find the mass of H_2O in each phase:

$$\begin{aligned} M_g &= x(M_g + M_f) = xM_{mix} \\ &= 0.6(3\text{ kg}) = 1.8\text{ kg} \end{aligned}$$

and

$$\begin{aligned} M_f &= M_{mix} - M_g \\ &= 3\text{ kg} - 1.8\text{ kg} = 1.2\text{ kg}. \end{aligned}$$

Using the given quality and given values for the specific volumes of the saturated liquid and saturated vapor, we calculate the mixture specific volume (Eq. 2.49a):

$$\begin{aligned} v_{\text{mix}} &= (1 - x)\, v_{\text{f}} + x\, v_{\text{g}} \\ &= (1 - 0.6)\, 0.001041\ \text{m}^3/\text{kg} + 0.6\, (1.859\ \text{m}^3/\text{kg}) \\ &= 1.1158\ \text{m}^3/\text{kg}. \end{aligned}$$

Comments This example is a straightforward application of definitions. Knowledge of definitions can be quite important in the solution of complex problems.

Self Test 2.18

☑ **Repeat Example 2.18 with $x = 0.8$ and find the volume of the tank.**

(Answer: $M_{\text{g}} = 2.4$ kg, $M_{\text{f}} = 0.6$ kg, $v_{\text{mix}} = 1.4874\ \text{m}^3/\text{kg}$, $\mathcal{V} = 4.46\ \text{m}^3$)

Property Tables and Databases

Tabulated properties are available for H_2O and many other fluids of engineering interest (see Table 2.7). Typically, data are presented in four forms:

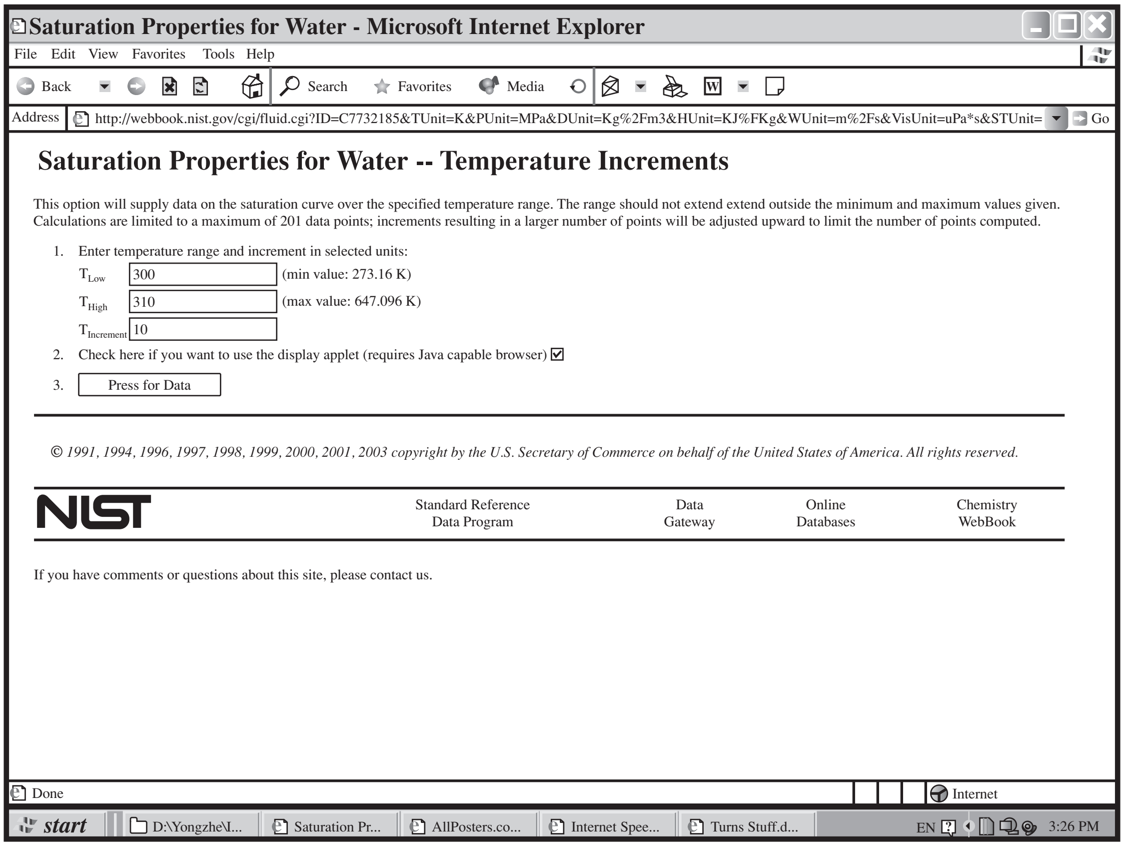
- Saturation properties for convenient temperature increments,
- Saturation properties for convenient pressure increments,
- Superheated vapor properties at various fixed pressures with convenient temperature increments, and
- Compressed (subcooled) liquid properties at various fixed pressures with convenient temperature increments.

Tables in Appendix D provide data in these forms for H_2O.

Computerized and online databases are making the use of printed tables obsolete. Using such databases also eliminates the need to interpolate, which can be tedious. Throughout this book, we illustrate the use of both tabulated data (Appendix D) and the NIST databases [9, 10]. You should develop proficiency with both sources of properties.

Figures 2.23–2.26 illustrate the use of the NIST online database. Figure 2.23 shows one of the input menus for creating your own tables and graphs. After selecting the fluid of interest and choosing the units desired (not shown), one has the choice of accessing saturation data in temperature or pressure increments (Figs. 2.24 and 2.25, respectively) or accessing data as an isotherm or as an isobar (Fig. 26). Figure 2.24 presents saturation data for temperatures from 300 to 310 K in increments of 10 K; Fig. 2.25 shows similar data but for a range of saturation pressures from 0.1 to 0.2 MPa in increments of 0.1 MPa. Figure 2.26 presents data for the 10-MPa isobar for a 800–900 K temperature range in 100-K increments. Note that the data in Fig. 2.26 all lie within the superheated vapor region as indicated in the final column of the table. Tables generated from the database can also be downloaded. Figures 2.27–2.30, for example, were generated using NIST data with spreadsheet software.

The NIST12 v. 5.2 software packaged with this book provides expanded capability to that available online. Tutorials 2 and 3 describe the use of this powerful software.



http://webbook.nist.gov/cgi/fluid.cgi?ID=C7732185&TUnit=K&PUnit=MPa&DUnit=Kg%2Fm3&HUnit=KJ%FKg&WUnit=m%2Fs&VisUnit=uPa*s&STUnit=

Saturation Properties for Water -- Temperature Increments

This option will supply data on the saturation curve over the specified temperature range. The range should not extend extend outside the minimum and maximum values given. Calculations are limited to a maximum of 201 data points; increments resulting in a larger number of points will be adjusted upward to limit the number of points computed.

1. Enter temperature range and increment in selected units:
   T_{Low} 300 (min value: 273.16 K)
   T_{High} 310 (max value: 647.096 K)
   $T_{Increment}$ 10
2. Check here if you want to use the display applet (requires Java capable browser) ☑
3. Press for Data

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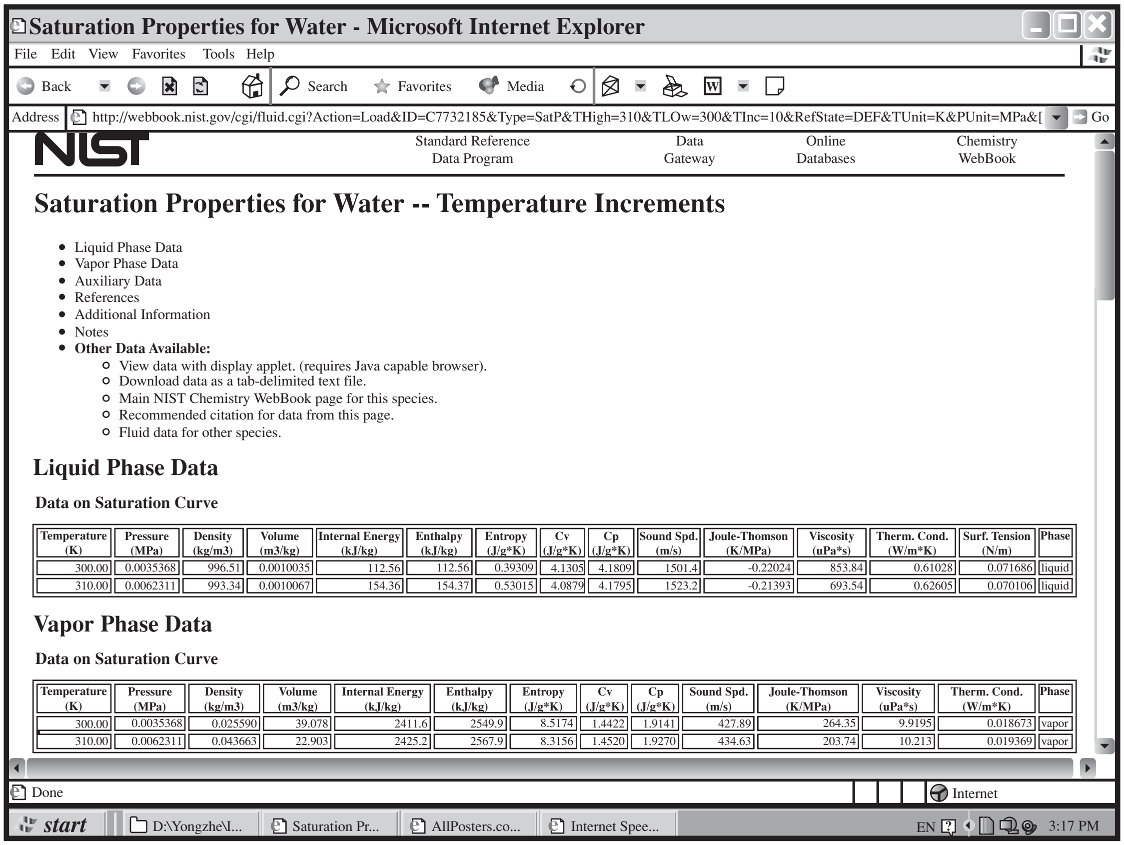
NIST Standard Reference Data Program | Data Gateway | Online Databases | Chemistry WebBook

If you have comments or questions about this site, please contact us.

FIGURE 2.23
Graphical user interface for the NIST online thermophysical property database. See Table 2.7 for fluids for which properties are provided. **From Ref. [11].**



http://webbook.nist.gov/cgi/fluid.cgi?Action=Load&ID=C7732185&Type=SatP&THigh=310&TLOw=300&TInc=10&RefState=DEF&TUnit=K&PUnit=MPa&[

NIST Standard Reference Data Program | Data Gateway | Online Databases | Chemistry WebBook

Saturation Properties for Water -- Temperature Increments

- Liquid Phase Data
- Vapor Phase Data
- Auxiliary Data
- References
- Additional Information
- Notes
- **Other Data Available:**
  - View data with display applet. (requires Java capable browser).
  - Download data as a tab-delimited text file.
  - Main NIST Chemistry WebBook page for this species.
  - Recommended citation for data from this page.
  - Fluid data for other species.

Liquid Phase Data

Data on Saturation Curve

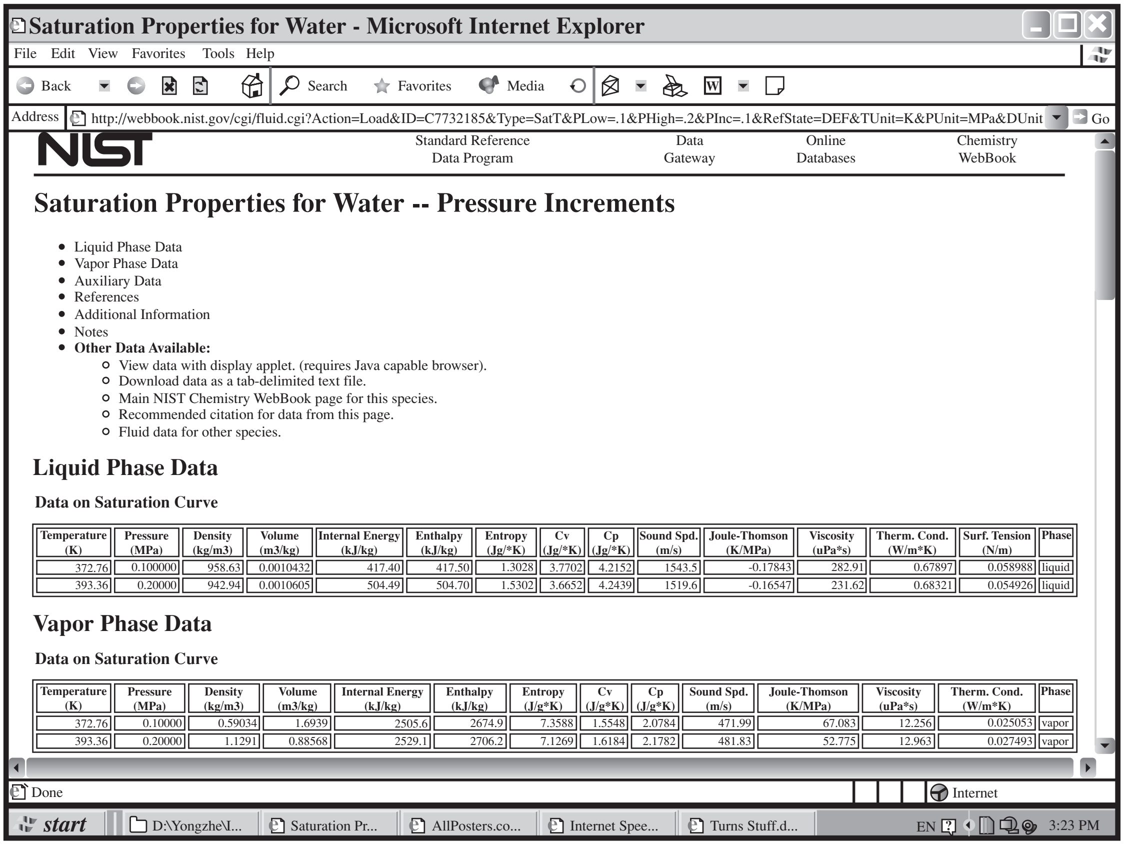
Temperature (K)	Pressure (MPa)	Density (kg/m3)	Volume (m3/kg)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (J/g*K)	Cv (J/g*K)	Cp (J/g*K)	Sound Spd. (m/s)	Joule-Thomson (K/MPa)	Viscosity (uPa*s)	Therm. Cond. (W/m*K)	Surf. Tension (N/m)	Phase
300.00	0.0035368	996.51	0.0010035	112.56	112.56	0.39309	4.1305	4.1809	1501.4	-0.22024	853.84	0.61028	0.071686	liquid
310.00	0.0062311	993.34	0.0010067	154.36	154.37	0.53015	4.0879	4.1795	1523.2	-0.21393	693.54	0.62605	0.070106	liquid

Vapor Phase Data

Data on Saturation Curve

Temperature (K)	Pressure (MPa)	Density (kg/m3)	Volume (m3/kg)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (J/g*K)	Cv (J/g*K)	Cp (J/g*K)	Sound Spd. (m/s)	Joule-Thomson (K/MPa)	Viscosity (uPa*s)	Therm. Cond. (W/m*K)	Phase
300.00	0.0035368	0.025590	39.078	2411.6	2549.9	8.5174	1.4422	1.9141	427.89	264.35	9.9195	0.018673	vapor
310.00	0.0062311	0.043663	22.903	2425.2	2567.9	8.3156	1.4520	1.9270	434.63	203.74	10.213	0.019369	vapor

FIGURE 2.24
Saturation properties for water from NIST online database: 300–310 K in 10-K increments. **From Ref. [11].**



http://webbook.nist.gov/cgi/fluid.cgi?Action=Load&ID=C7732185&Type=SatT&PLow=.1&PHigh=.2&PInc=.1&RefState=DEF&TUnit=K&PUnit=MPa&DUnit

Saturation Properties for Water -- Pressure Increments

- Liquid Phase Data
- Vapor Phase Data
- Auxiliary Data
- References
- Additional Information
- Notes
- **Other Data Available:**
    - View data with display applet. (requires Java capable browser).
    - Download data as a tab-delimited text file.
    - Main NIST Chemistry WebBook page for this species.
    - Recommended citation for data from this page.
    - Fluid data for other species.

Liquid Phase Data

Data on Saturation Curve

Temperature (K)	Pressure (MPa)	Density (kg/m3)	Volume (m3/kg)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (Jg/*K)	Cv (Jg/*K)	Cp (Jg/*K)	Sound Spd. (m/s)	Joule-Thomson (K/MPa)	Viscosity (uPa*s)	Therm. Cond. (W/m*K)	Surf. Tension (N/m)	Phase
372.76	0.100000	958.63	0.0010432	417.40	417.50	1.3028	3.7702	4.2152	1543.5	-0.17843	282.91	0.67897	0.058988	liquid
393.36	0.20000	942.94	0.0010605	504.49	504.70	1.5302	3.6652	4.2439	1519.6	-0.16547	231.62	0.68321	0.054926	liquid

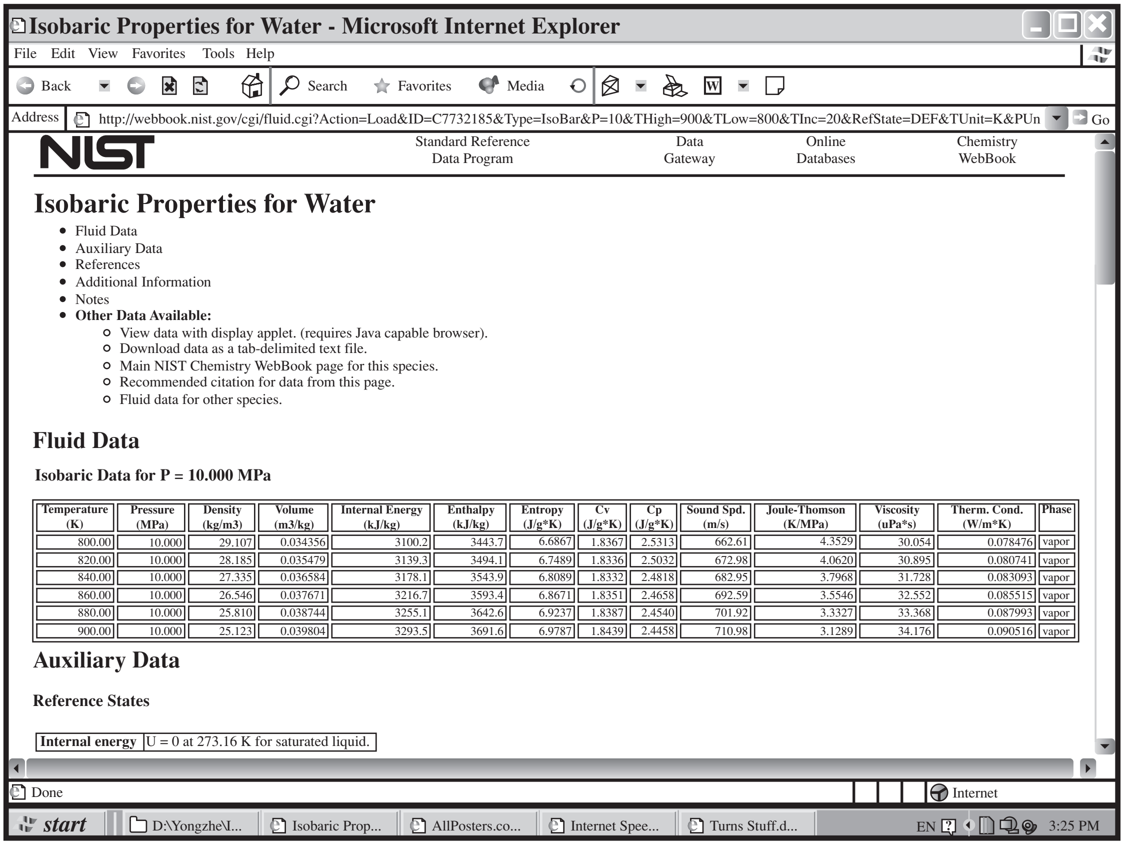
Vapor Phase Data

Data on Saturation Curve

Temperature (K)	Pressure (MPa)	Density (kg/m3)	Volume (m3/kg)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (J/g*K)	Cv (J/g*K)	Cp (J/g*K)	Sound Spd. (m/s)	Joule-Thomson (K/MPa)	Viscosity (uPa*s)	Therm. Cond. (W/m*K)	Phase
372.76	0.10000	0.59034	1.6939	2505.6	2674.9	7.3588	1.5548	2.0784	471.99	67.083	12.256	0.025053	vapor
393.36	0.20000	1.1291	0.88568	2529.1	2706.2	7.1269	1.6184	2.1782	481.83	52.775	12.963	0.027493	vapor

FIGURE 2.25

Saturation properties for water from NIST online database: 0.1–0.2 MPa in 0.1-MPa increments. **From Ref. [11].**



http://webbook.nist.gov/cgi/fluid.cgi?Action=Load&ID=C7732185&Type=IsoBar&P=10&THigh=900&TLow=800&TInc=20&RefState=DEF&TUnit=K&PUn

Isobaric Properties for Water

- Fluid Data
- Auxiliary Data
- References
- Additional Information
- Notes
- **Other Data Available:**
    - View data with display applet. (requires Java capable browser).
    - Download data as a tab-delimited text file.
    - Main NIST Chemistry WebBook page for this species.
    - Recommended citation for data from this page.
    - Fluid data for other species.

Fluid Data

Isobaric Data for P = 10.000 MPa

Temperature (K)	Pressure (MPa)	Density (kg/m3)	Volume (m3/kg)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (J/g*K)	Cv (J/g*K)	Cp (J/g*K)	Sound Spd. (m/s)	Joule-Thomson (K/MPa)	Viscosity (uPa*s)	Therm. Cond. (W/m*K)	Phase
800.00	10.000	29.107	0.034356	3100.2	3443.7	6.6867	1.8367	2.5313	662.61	4.3529	30.054	0.078476	vapor
820.00	10.000	28.185	0.035479	3139.3	3494.1	6.7489	1.8336	2.5032	672.98	4.0620	30.895	0.080741	vapor
840.00	10.000	27.335	0.036584	3178.1	3543.9	6.8089	1.8332	2.4818	682.95	3.7968	31.728	0.083093	vapor
860.00	10.000	26.546	0.037671	3216.7	3593.4	6.8671	1.8351	2.4658	692.59	3.5546	32.552	0.085515	vapor
880.00	10.000	25.810	0.038744	3255.1	3642.6	6.9237	1.8387	2.4540	701.92	3.3327	33.368	0.087993	vapor
900.00	10.000	25.123	0.039804	3293.5	3691.6	6.9787	1.8439	2.4458	710.98	3.1289	34.176	0.090516	vapor

Auxiliary Data

Reference States

Internal energy	U = 0 at 273.16 K for saturated liquid.

FIGURE 2.26

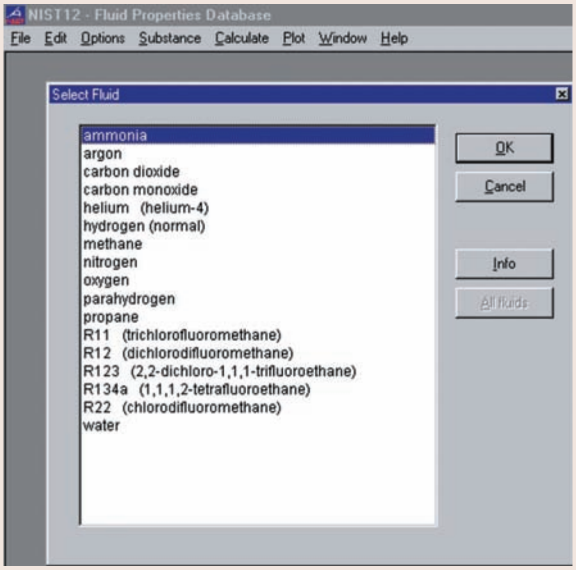
Properties of water for the 10-MPa isobar from NIST online database: 800–900 K in 20-K increments. **From Ref. [11].**

Tutorial 2 How to Use the NIST Software

Packaged with this book is a CD containing the software package NIST12 Version 5.2. This software, an invaluable resource for thermodynamic and transport properties of many pure substances and air, is very easy to use: You can learn to use it in only a few minutes and can be an expert in less than an hour. The purpose of this tutorial is to acquaint you with the basic capabilities of this powerful package and to encourage you to become an expert user.

What fluids are contained in the NIST database?

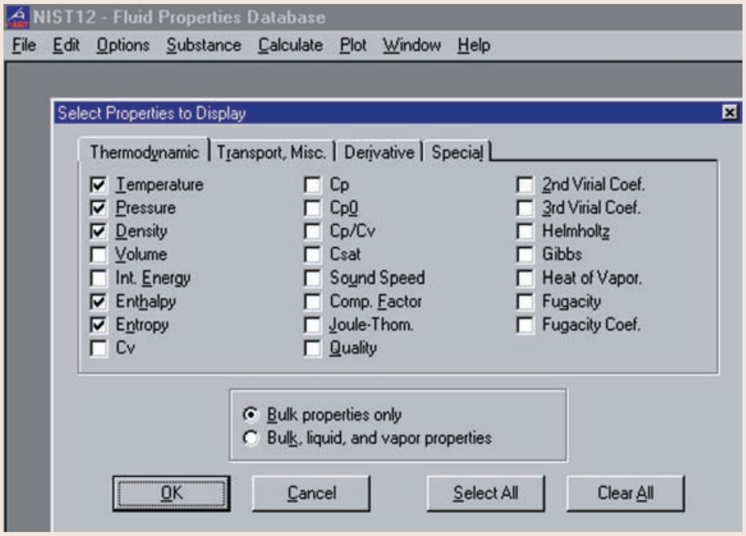
From the "Substance" menu a selection of seventeen pure fluids is available. A listing is shown in the figure. Air is also available as a pseudo-pure fluid from the substance menu.



- ammonia
- argon
- carbon dioxide
- carbon monoxide
- helium (helium-4)
- hydrogen (normal)
- methane
- nitrogen
- oxygen
- parahydrogen
- propane
- R11 (trichlorofluoromethane)
- R12 (dichlorodifluoromethane)
- R123 (2,2-dichloro-1,1,1-trifluoroethane)
- R134a (1,1,1,2-tetrafluoroethane)
- R22 (chlorodifluoromethane)
- water

What properties are available?

All of the properties used in this book and many others are provided. "Properties" can be selected from the "Options" menu as illustrated here.



☑ Temperature
☑ Pressure
☑ Density
☐ Volume
☐ Int. Energy
☑ Enthalpy
☑ Entropy
☐ Cv
☐ Cp
☐ Cp0
☐ Cp/Cv
☐ Csat
☐ Sound Speed
☐ Comp. Factor
☐ Joule-Thom.
☐ Quality
☐ 2nd Virial Coef.
☐ 3rd Virial Coef.
☐ Helmholtz
☐ Gibbs
☐ Heat of Vapor.
☐ Fugacity
☐ Fugacity Coef.

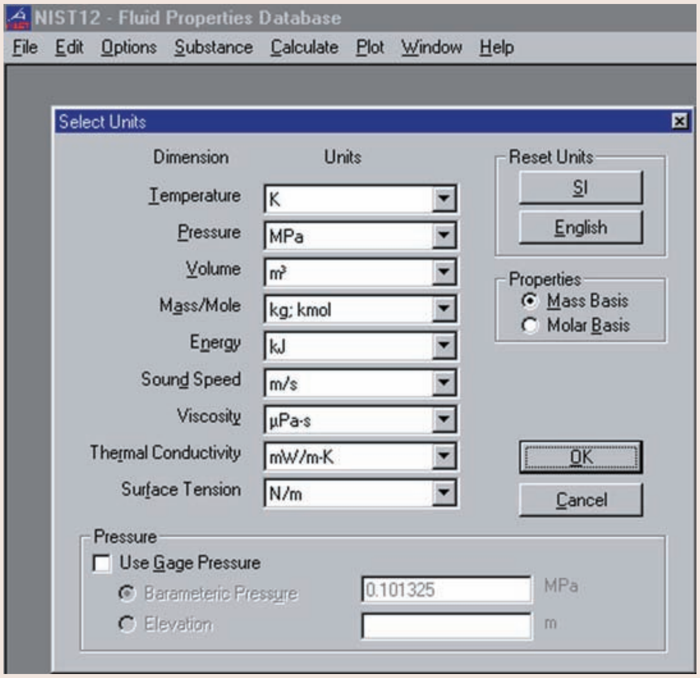
● Bulk properties only
○ Bulk, liquid, and vapor properties

(Continued on next page)

Tutorial 2 How to Use the NIST Software *(continued)*

What units can be used?

From the "Options" menu, the user can select SI, U.S. customary, and other units using pull-down selections. Mixed units can be used if desired and either mass- or molar-specific quantities can be selected.



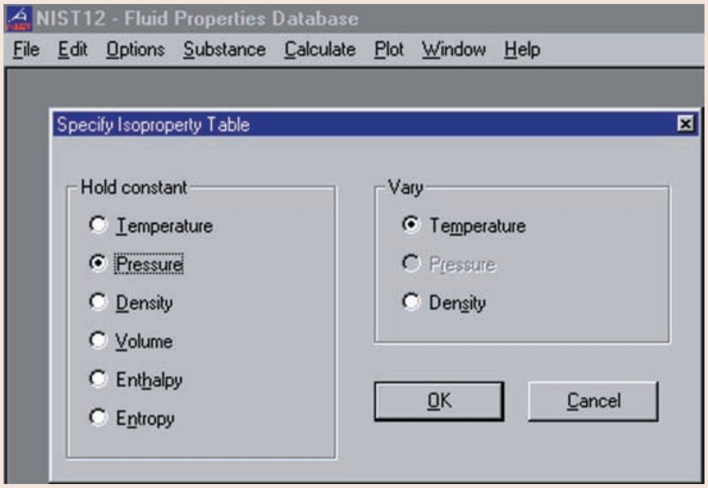
Dimension	Units
Temperature	K
Pressure	MPa
Volume	m^3
Mass/Mole	kg; kmol
Energy	kJ
Sound Speed	m/s
Viscosity	μPa-s
Thermal Conductivity	mW/m-K
Surface Tension	N/m

Properties
● Mass Basis
○ Molar Basis

Pressure
☐ Use Gage Pressure
● Barameteric Pressure 0.101325 MPa
○ Elevation m

Can tables be generated?

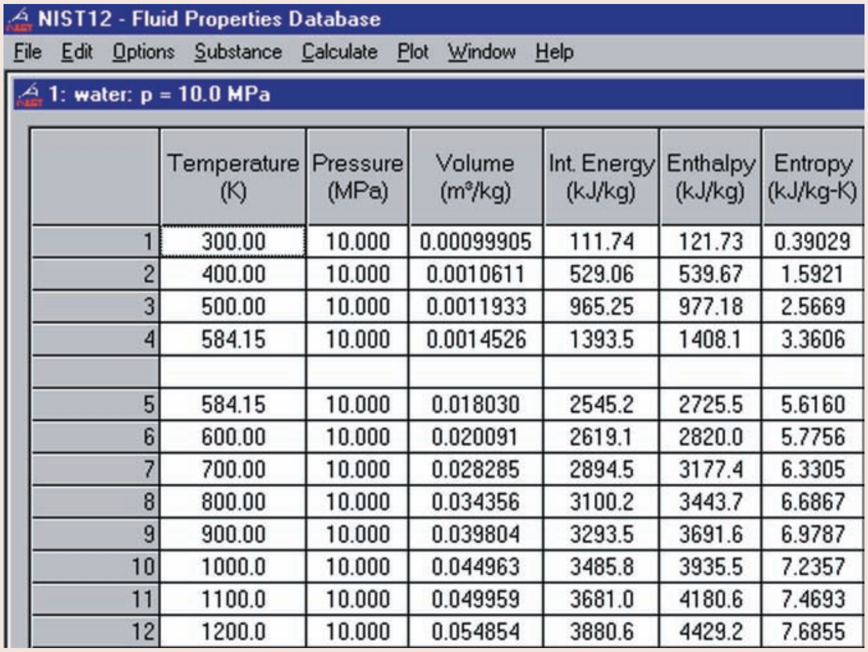
Under the "Calculate" menu, the user has the option to generate two types of tables: saturation tables and isoproperty tables. The creation of an isoproperty (P fixed) table is illustrated here.



Hold constant
○ Temperature
● Pressure
○ Density
○ Volume
○ Enthalpy
○ Entropy

Vary
● Temperature
○ Pressure
○ Density

(Continued on next page)



1: water: p = 10.0 MPa

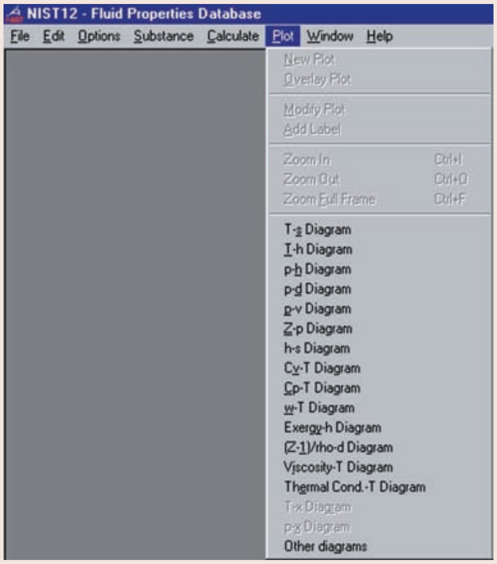
	Temperature (K)	Pressure (MPa)	Volume (m^3/kg)	Int. Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)
1	300.00	10.000	0.00099905	111.74	121.73	0.39029
2	400.00	10.000	0.0010611	529.06	539.67	1.5921
3	500.00	10.000	0.0011933	965.25	977.18	2.5669
4	584.15	10.000	0.0014526	1393.5	1408.1	3.3606
5	584.15	10.000	0.018030	2545.2	2725.5	5.6160
6	600.00	10.000	0.020091	2619.1	2820.0	5.7756
7	700.00	10.000	0.028285	2894.5	3177.4	6.3305
8	800.00	10.000	0.034356	3100.2	3443.7	6.6867
9	900.00	10.000	0.039804	3293.5	3691.6	6.9787
10	1000.0	10.000	0.044963	3485.8	3935.5	7.2357
11	1100.0	10.000	0.049959	3681.0	4180.6	7.4693
12	1200.0	10.000	0.054854	3880.6	4429.2	7.6855

What if I want properties at a single state point?

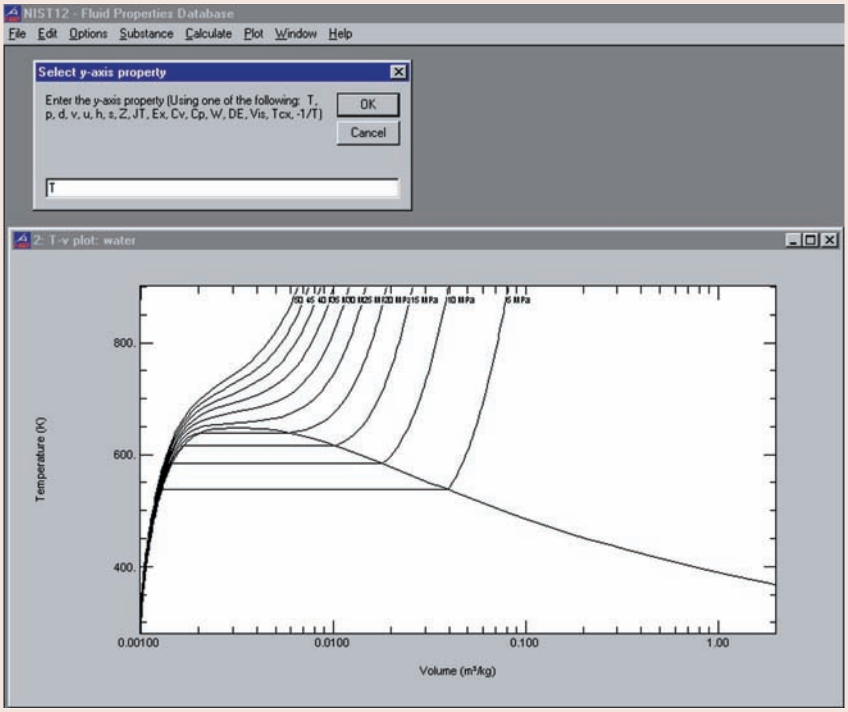
From the "Calculate" menu the user can select "Specified State Points" or "Saturation Points."

What plots can be generated with the software?

All of the standard thermodynamic coordinates (P–v, T–s, h–s, etc.) and others are available from the "Plot" menu. Plots with iso-lines, as shown in the figure, are easy to create. The option "Other Diagrams" allows the user to select any pair of thermodynamic coordinates. The T–v diagram here illustrates this option.



Tutorial 2 How to Use the NIST Software *(continued)*



Enter the y-axis property (Using one of the following: T, p, d, v, u, h, s, Z, JT, Ex, Cv, Cp, W, DE, Vis, Tcx, -1/T)

T

Is the NIST software compatible with other common software?

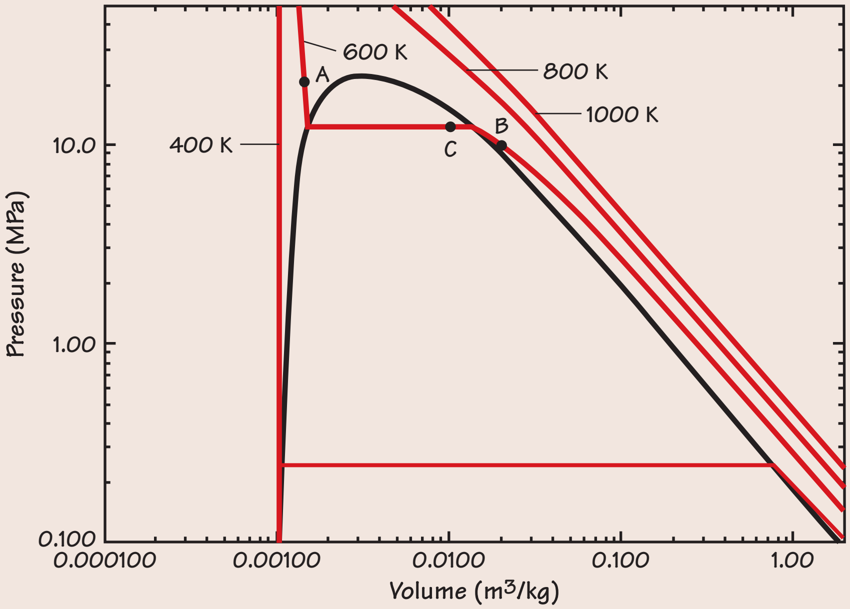
Tables generated using NIST12 Version 5.2 can be easily pasted into spreadsheets. Similarly, plots can be pasted into word-processing documents.

The reader is encouraged to use this software to solve the homework problems provided in this book.

Tutorial 3 How to Define a Thermodynamic State

Whether employing tabular data or the NIST software, one needs to become proficient at identifying and defining thermodynamic states. What we mean by that is the following: Given a pair of properties (e.g., P_1, T_1), can you determine the region, or region boundary, in or on which the state lies? Specifically, is the state of the substance a compressed liquid, saturated liquid, liquid–vapor mixture, saturated vapor, or superheated vapor? Or does the state lie at the critical point or within the supercritical region? This tutorial offers hints to help you answer such questions efficiently and with confidence.

Given an arbitrary temperature T_1 and pressure P_1, we desire to identify the state and to determine the specific volume v_1. To aid our analysis, we employ the following P–v diagram for H_2O.



We begin with a few concrete examples using H_2O, with all states having the same temperature of 600 K. The 600-K isotherm is one of the several shown on our P–v plot.

Given: $T = 600$ K, $P = 20$ MPa.
Find: Region, v.

The key to defining the region is determining the relationship of the given properties to those of (1) the critical point and (2) the saturation states. For H_2O, the critical point is 22.064 MPa and 647.1 K. Since the given pressure is less than the critical pressure, we can rule out the supercritical region, which we can easily verify by inspecting the P–v diagram. Next we determine the saturation states corresponding to the given P and T. Using Tables D.1 and D.2, respectively (or the NIST database), we find that

$$P_{sat}\ (600\ \mathrm{K}) = 12.34\ \mathrm{MPa}, \qquad \text{(Table D.1)},$$
$$T_{sat}\ (20\ \mathrm{MPa}) = 638.9\ \mathrm{K} \qquad \text{(Table D.2)}.$$

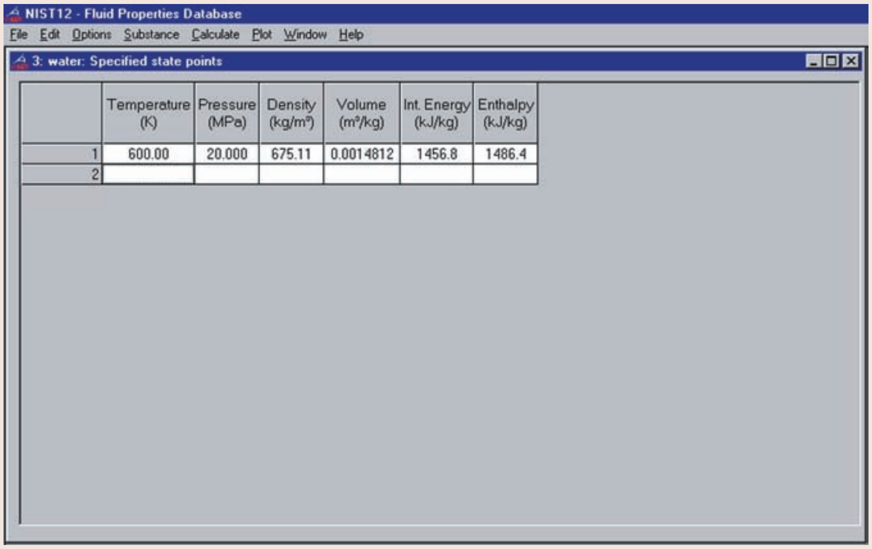
(Continued on next page)

Tutorial 3 How to Define a Thermodynamic State *(continued)*

From these values, we see that the given temperature, 600 K, is less than the saturation value, 638.9 K [i.e., $T\,(20\text{ MPa}) < T_{sat}\,(20\text{ MPa})$]. The state thus lies in the subcooled region. Alternatively, we see that the given pressure, 20 MPa, is greater than the saturation value, 12.34 MPa [i.e., $P\,(600\text{ K}) < P_{sat}\,(600\text{ K})$]; the state thus lies in the compressed-liquid region. The compressed-liquid and subcooled-liquid regions are synonymous. Point A on the P–v plot denotes this state. Now knowing the region, we turn to the compressed-liquid table, Table D.4D, to find the specific volume. No interpolation is needed and we read the value directly:

$$v\,(20\text{ MPa}, 600\text{ K}) = 0.001481\text{ m}^3/\text{kg}.$$

A simpler, but less instructive, procedure is to use the NIST software. By selecting "Specified State Points" from the "Calculate" menu, we obtain the density [$= 675.11\text{ kg/m}^3 = 1/v = 1/(0.001481\text{ m}^3/\text{kg})$].



	Temperature (K)	Pressure (MPa)	Density (kg/m³)	Volume (m³/kg)	Int. Energy (kJ/kg)	Enthalpy (kJ/kg)
1	600.00	20.000	675.11	0.0014812	1456.8	1486.4
2						

Note that finding the region in which the state lies must be a separate step because the "Specified State Point" calculation does not identify the state location. Being able to locate a state relative to the liquid, liquid–vapor mixture, and vapor boundaries is an essential skill.

Given: $T = 600$ K, $P = 10$ MPa.
Find: Region, v.

Again, we use Tables D.1 and D.2 to find the corresponding saturation values:

$$P_{sat}\,(600\text{ K}) = 12.34\text{ MPa} \qquad \text{(Table D.1)},$$
$$T_{sat}\,(10\text{ MPa}) = 584.15\text{ K} \qquad \text{(Table D.2)}.$$

Because T (10 MPa) > T_{sat} (10 MPa) (i.e., 600 K > 584.15 K), the state lies in the superheated vapor region. We come to the same conclusion by recognizing that P (600 K) < P_{sat} (600 K). Point B on the P–v plot denotes this state. To find the specific volume, we employ the superheated vapor table for 10 MPa, Table D.3P, which directly yields

$$v\,(10\text{ MPa}, 600\text{ K}) = 0.020091\text{ m}^3/\text{kg}.$$

The given values were deliberately selected to avoid any interpolation. Finding properties in the superheat region may be complicated by the need to interpolate both temperature and pressure. In such cases, use of the NIST software is recommended to avoid this tedious process.

Given: $T = 600$, $v = 0.01$ m^3/kg.
Find: Region, P.

Since the specific volume is given, we determine the relationship of this value to those of the saturated liquid and saturated vapor at the same temperature to define the region. From Table D.1, we obtain

$$v_{\text{sat liq}}\,(600\text{ K}) = 0.0015399\text{ m}^3/\text{kg},$$
$$v_{\text{sat vapor}}\,(600\text{ K}) = 0.014984\text{ m}^3/\text{kg}.$$

Because the given specific volume falls between these two values, the state must lie in the liquid–vapor mixture region. The pressure must then be the saturation value, P_{sat} (600 K) = 12.34 MPa. If the given specific volume were less than $v_{\text{sat liq}}$, we would have to conclude that the state lies in the compressed-liquid region. Similarly, if the given specific volume were greater than $v_{\text{sat vapor}}$, the state would then lie in the superheated-vapor region. Point C denotes this state on the P–v diagram.

Although we determined the regions in which various states lie using T, P, and v, other properties can be employed as well. The key, regardless of the particular properties given, is to find their relationships to the corresponding saturation state boundaries (i.e., the “steam dome”).

Example 2.19 Steam Power Plant Application

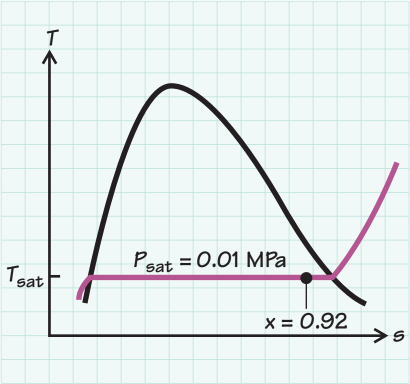
A turbine expands steam to a pressure of 0.01 MPa and a quality of 0.92. Determine the temperature and the specific volume at this state.

Solution

Known P, x

Find T, v

Sketch



Analysis The given state lies in the liquid–vapor region on the 0.01-MPa isobar as shown in the sketch. Knowing this, we use Table D.2, *Saturation Properties of Water and Steam—Pressure Increments*, to obtain the following data:

$$T = T_{sat}(P = P_{sat} = 0.01\text{ MPa}) = 318.96\text{ K},$$
$$v_f = 0.0010103\text{ m}^3/\text{kg},$$
$$v_g = 14.670\text{ m}^3/\text{kg}.$$

Using the given quality and these values for the specific volumes of the saturated liquid and saturated vapor, we calculate the specific volume from Eq. 2.49a as follows:

$$\begin{aligned} v &= (1 - x)\, v_f + x v_g \\ &= (1 - 0.92)\, 0.0010103\text{ m}^3/\text{kg} + 0.92\,(14.670\text{ m}^3/\text{kg}) \\ &= 13.496\text{ m}^3/\text{kg}. \end{aligned}$$

Comments The keys to this problem are, first, recognizing the region in which the given state lies, and, second, choosing the correct table to evaluate properties. The reader should verify the values obtained from Table D.2 for this example and also verify that the values agree with the NIST online database and NIST12 v. 5.2 software.

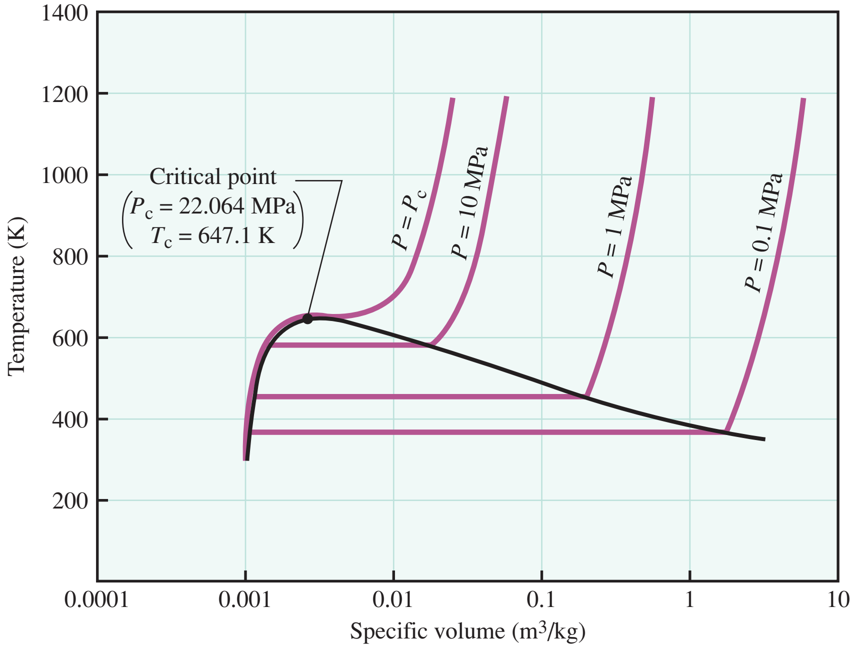
Self Test 2.19

☑ **Calculate the values of the specific internal energy *u* and the specific enthalpy *h* for the conditions given in Example 2.19.**

(Answer: u = 2257.57 kJ/kg, h = 2392.53 kJ/kg)

FIGURE 2.27

Temperature–specific volume diagram for H_2O showing isobars for 0.1, 1, and 10 MPa. Also shown is the critical pressure isobar.

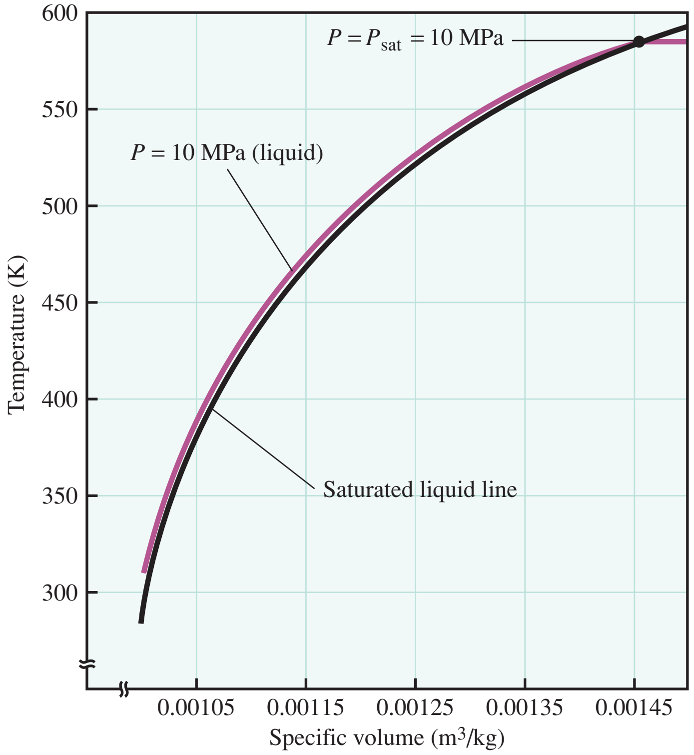


T–v Diagrams

Figure 2.27 presents a T–v diagram for H_2O showing several lines of constant pressure. In the liquid region, lines of constant pressure hug the saturated liquid line quite closely. This fact is illustrated more clearly in the expanded view of the liquid region provided in Fig. 2.28 where the 10-MPa constant-pressure line is shown together with the saturated liquid line. All of the constant-pressure lines for pressures less than 10 MPa, but greater than P_{sat} at any given temperature, are crowded between the two lines shown in Fig. 2.28; thus, we see that specific volume is much more

FIGURE 2.28

Isobars in T–v space in the compressed liquid region for H_2O lie close to the saturated liquid line. The 10-MPa isobar crosses the saturated liquid line when P_{sat} = 10 Ma and then proceeds horizontally across the steam dome (not shown).



sensitive to temperature than to pressure. As a consequence, values for specific volume for compressed liquids can be approximated as those at the saturated liquid state at the same temperature; that is,

$$v_{\text{liq}}(T) \cong v_f(T), \tag{2.51}$$

where v_f is the specific volume of the saturated liquid at T. This rule-of-thumb can be used when comprehensive compressed liquid data are not available. We discuss compressed liquid properties in more detail in a later section.

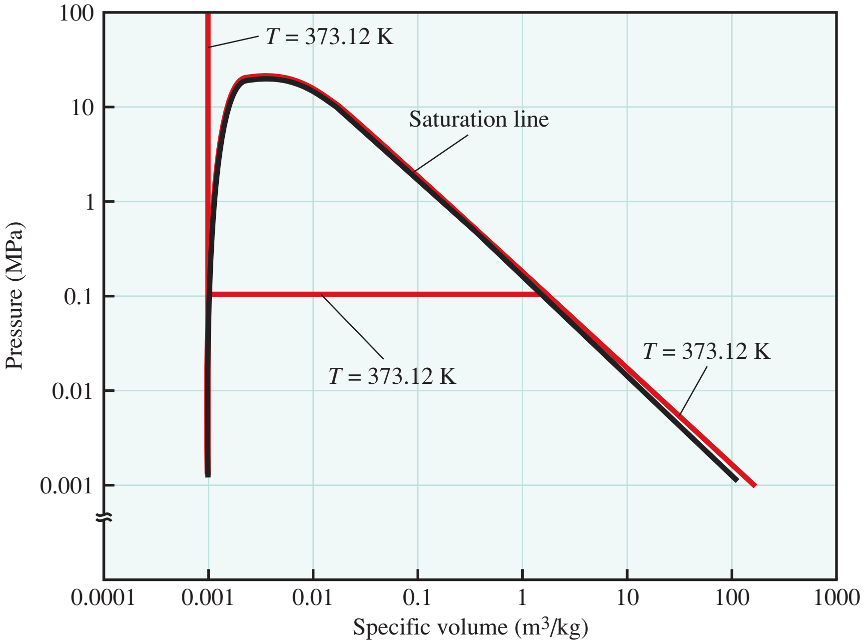
Returning to Fig. 2.27 we now examine the behavior of the constant-pressure lines on the other side of the steam dome. We first note the significant dependence of the specific volume on pressure along the saturated vapor line, where an order-of-magnitude increase in pressure results in approximately an order-of-magnitude decrease in specific volume. If the saturated vapor could be treated as an ideal gas, this relationship would follow $v^{-1} \propto P$. In the vapor region, specific volume increases with temperature along a line of constant pressure, and pressure increases with temperature along a line of constant volume. Although somewhat obscured by the use of the logarithmic scale for specific volume, the vapor region of Fig. 2.28 looks much like the ideal-gas T–v plot shown earlier (cf. Fig. 2.8). Of course, the real-gas behavior of steam affects the details of such a comparison.

P–v Diagrams

Figure 2.29 presents a P–v diagram for H_2O showing a single isotherm (T = 373.12 K or 99.97°C). The corresponding saturation pressure is 101,325 Pa (1 atm). The saturation condition thus corresponds to the normal boiling point of water. Note that both axes in Fig. 2.29 are logarithmic. Isotherms for temperatures greater than 373.12 K lie above and to the right of the isotherm shown. In the superheated vapor region, the isotherms lie relatively close to the saturated vapor line in the log–log coordinates of Fig. 2.29. Figure 2.30 presents an expanded view of the region $0.01 < P < 0.1$ MPa showing several isotherms in linear P–v space.

FIGURE 2.29

P–v diagram for H_2O showing T = 373.12 K (99.97°C) isotherm. An expanded view of several isotherms in the superheated vapor region (P = 0.01–0.1 MPa) is shown in Fig. 2.30.



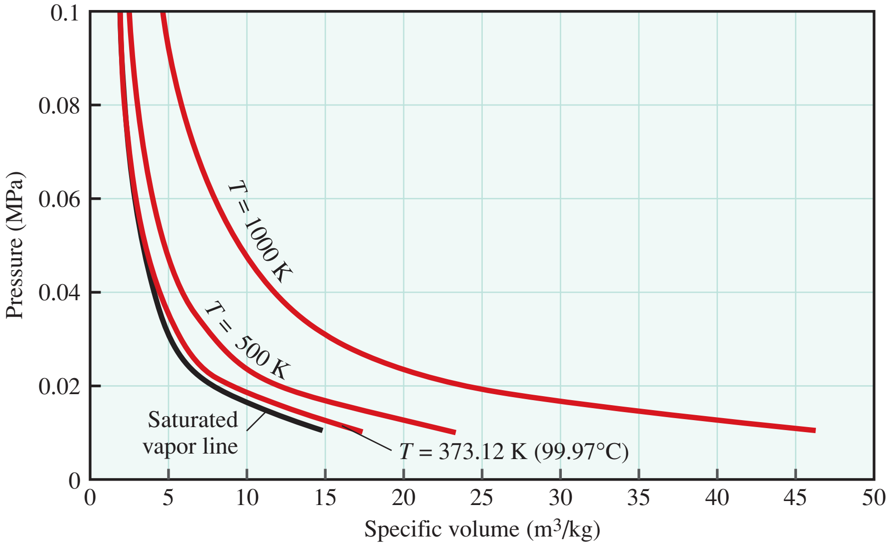
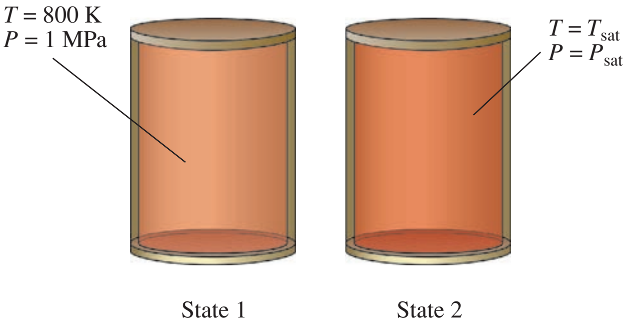


FIGURE 2.30
Isotherms in P–v space for the superheated region of H_2O exhibit a hyperbolic-like behavior (cf. ideal-gas behavior in Fig. 2.7).

Example 2.20

A 0.5-kg mass of steam at 800 K and 1 MPa is contained in a rigid vessel. The steam is cooled to the saturated vapor state. Plot the process on both T–v and P–v coordinates. Determine the volume of the vessel and the final temperature and pressure of the steam.



Solution

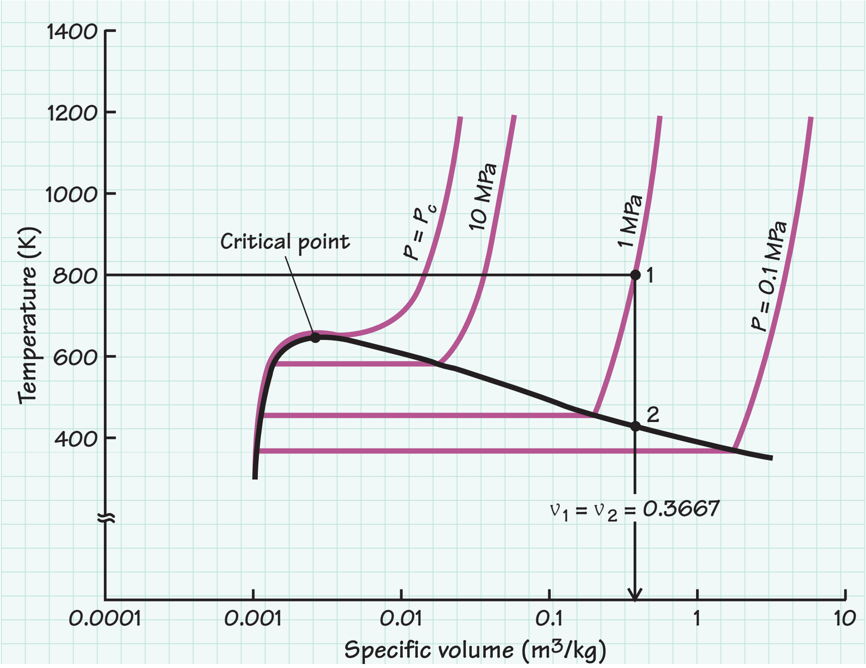
Known Steam, M, P_1, T_1, saturated vapor at state 2

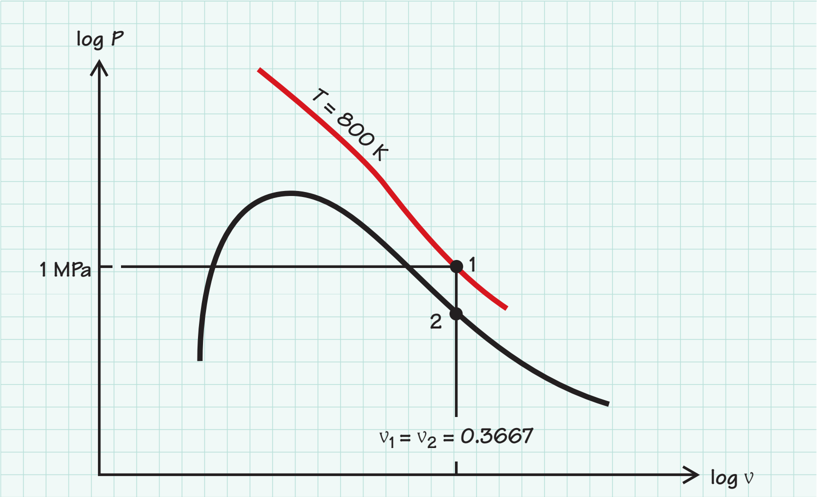
Find P_2, T_2, $\mathcal{V}$

Assumptions

i. Rigid tank (given)
ii. Simple compressible substance

Analysis Before we can create T–v and P–v sketches, we need to determine the region in which the state-1 point lies. Since the state-1 temperature (800 K) is greater than the critical temperature (T_c = 647.27 K) and the state-1 pressure (1 MPa) is less than the critical pressure (P_c = 22.064 MPa), state 1 must lie in the superheated vapor region. With this information, we now construct the following T–v and P–v plots:





We note that the cooling of the steam from state 1 to state 2 is a constant-volume process because the tank is rigid. Because the mass is also constant, the specific volume at state 1 equals the specific volume at state 2, as shown on the sketches. To find P_2, T_2, and $\mathcal{V}$ requires a numerical value for v_2 $(= v_1)$. Using data from Table D.3, we find the specific volume v_1:

T (K)	v (m³/kg)
780	0.35734
$800 = T_1$	$0.36677 = v_1$
820	0.37618

The NIST12 v. 5.2 software yields a value identical to the tabulated value. Since state 2 lies on the saturated vapor line, we know that $v_g(T_2, P_2) = v_2 = v_1$. From Table D.2, we see that the state-2 specific volume is between those of saturated vapor at 0.5 and 0.6 MPa; thus, we interpolate to find P_2 and T_2 as follows:

v_{sat} (m^3/kg)	P_{sat} (MPa)	T_{sat} (K)
0.37481	0.5	424.98
$0.36677 = v_2$	$0.514 = P_2$	$425.9 = T_2$
0.31558	0.6	431.98

Using the NIST database provides a more accurate result:

$$P_2 = 0.511 \text{ MPa},$$
$$T_2 = 425.8 \text{ K}.$$

To calculate the volume of the rigid vessel containing the steam, we apply the definition of specific volume

$$v \equiv \mathcal{V}/M,$$

or

$$\mathcal{V} = Mv.$$

Thus,

$$\mathcal{V} = (0.5 \text{ kg})\, 0.36677 \text{ m}^3/\text{kg} = 0.1834 \text{ m}^3.$$

Comments This example illustrates some of the thought processes involved in determining the region in which a state point lies. We also see the importance of recognizing that the process involved was a constant-volume process.

Self Test 2.20

☑ **The system of Example 2.20 is further cooled to a final temperature of 350 K. Determine the final pressure and the quality at this state.**

(Answer: $P = P_{sat}$ (350 K) = 41.68 kPa, $x = 0.095$)

2.6b Calorific and Second-Law Properties

The sources available for calorific properties—specific enthalpies and specific internal energies—and the second-law property—entropy—are the same as for state properties: Appendix D, the NIST online database [11], and NIST12. In the NIST data, both enthalpies and internal energies are provided; however, many sources provide only enthalpies, leaving it to the user to obtain internal energies from the definition

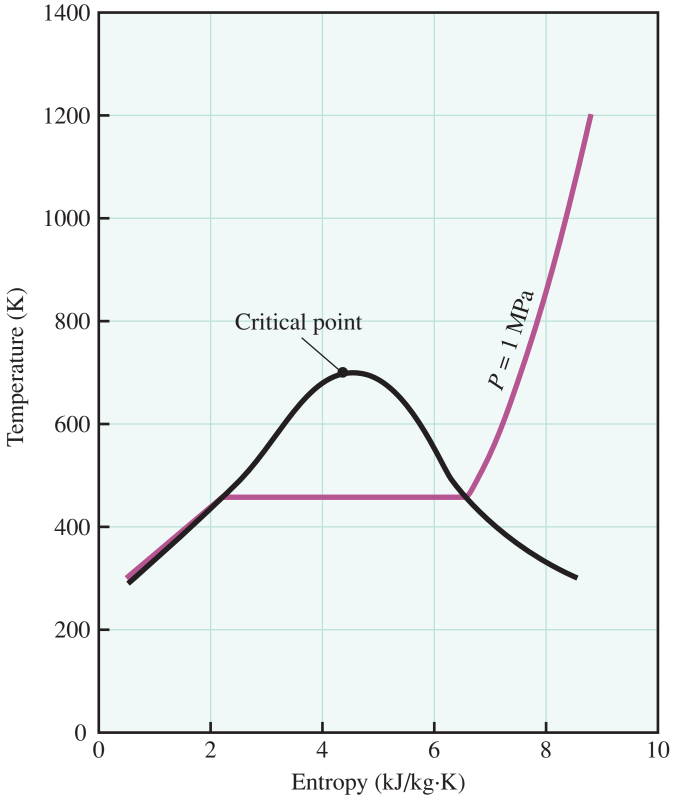
$$u(T, P) = h(T, P) - Pv.$$

Also frequently tabulated is the **enthalpy of vaporization,** h_{fg}, which is defined as

$$h_{fg} \equiv h_{vap} - h_{liq} = h_g - h_f. \tag{2.52}$$

Physically, this represents the amount of energy required to vaporize a unit mass of liquid at constant pressure. This quantity is also sometimes referred

FIGURE 2.31
Temperature–entropy (T–s) diagram for water showing liquid–vapor saturation lines and the 1-MPa isobar.



to as the latent heat of vaporization, a term coined during the reign of the caloric theory.[16]

T–s Diagrams

Of equal importance to *T–v* and *P–v* diagrams is the temperature–entropy, or *T–s*, diagram. For a reversible process, the integral of *Tds* provides the energy added as heat to a system; thus, the area under a reversible process line on *T–s* coordinates represents the energy added or removed by heat interactions. See Chapter 4 for a discussion of heat transfer and see Chapter 7 for a more expansive discussion of *T–s* diagrams.

Figure 2.31 presents a *T–s* diagram for water and shows an isobar traversing the compressed liquid region, across the steam dome, and up into the superheat region. Without an expanded scale, the 1-MPa isobar in the compressed liquid region is indistinguishable from the saturated liquid line; however, it does lie above and to the left of the saturated liquid line. Isobars for pressures greater than 1 MPa lie above the isobar shown, and those for lower pressures lie below. Although not shown, isochors (constant-volume lines) in the superheat region have steeper slopes than the isobars (see Fig. 2.11). Note that Fig. 2.31 employs linear scales for both temperature and entropy, rather than the semilog and log–log scales previously used in the analogous *T–v* (Fig. 2.27) and *P–v* (Fig. 2.29) diagrams, respectively.

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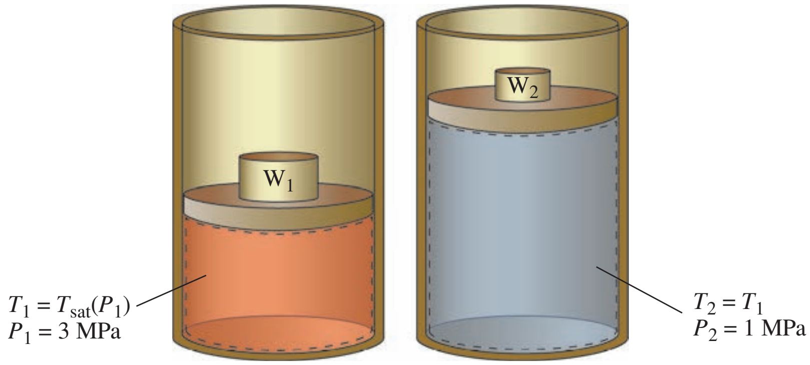
[16] See Chapter 4 for a brief history of the caloric theory and how it was superceded by modern constructs of energy.

Example 2.21

Consider an isothermal expansion of steam from an initial state of saturated vapor at 3 MPa to a pressure of 1 MPa. Plot the process on T–s and P–v coordinates and determine the initial and final specific volumes.



Solution

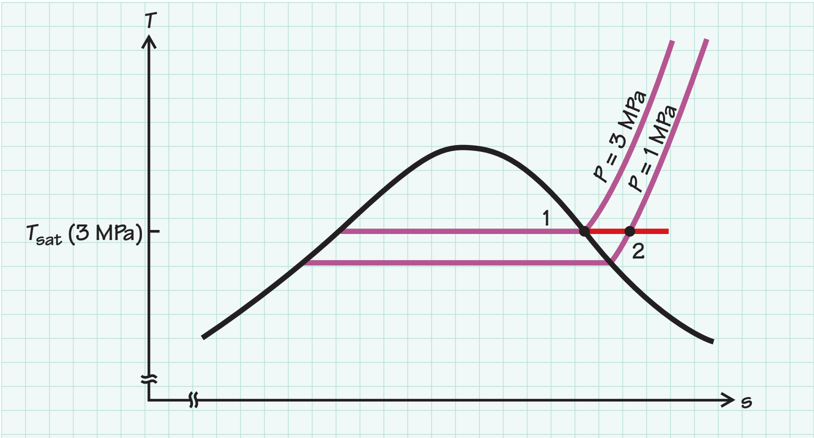
Known Saturated vapor at P_1, T_1 (= T_2), P_2

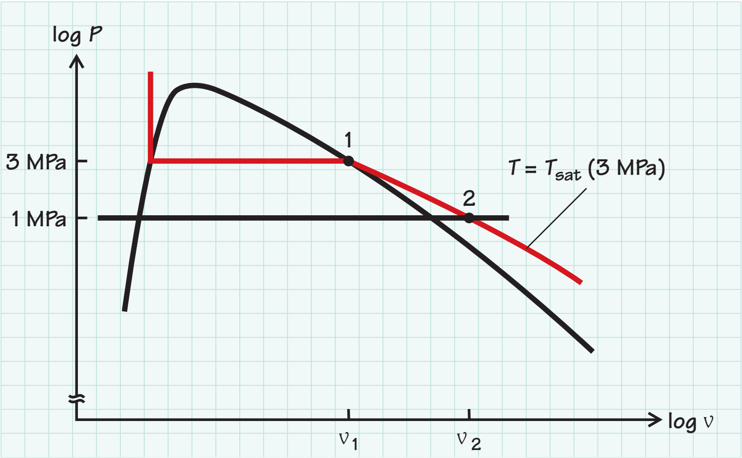
Find v_1 (= v_g), v_2

Assumption

Simple compressible substance at equilibrium

Analysis We begin by drawing the P_1 (= 3 MPa) and P_2 (= 1 MPa) isobars on a T–s diagram as shown. State 1 is identified on this diagram as a saturated vapor. For the isothermal process, a horizontal line is extended from the state-1 point. The location where this isotherm, $T = T_{sat}$ (3 MPa), crosses the 1-MPa isobar identifies the state-2 point. State 2 is in the superheated vapor region. On P–v coordinates, we draw the same $T = T_{sat}$ (3 MPa) isotherm. Where it crosses the 1-MPa isobar identifies the state-2 point in P–v space.





From Table D.2, we obtain the following properties:

$$P_1 = 3 \text{ MPa},$$

$$T_1 = 507.00 \text{ K},$$

$$v_1 = 0.066664 \text{ m}^3/\text{kg}.$$

To obtain the state-2 properties, we can interpolate to find v_2 in the superheated-vapor table for $P = 1$ MPa (see Table D.3). Alternatively, the NIST database can be used directly to determine v_2 by generating isothermal data ($T = 507.00$ K) with pressure increments containing $P = 1$ MPa. The result is

$$v_2 = 0.22434 \text{ m}^3/\text{kg}.$$

Comments We note the utility of defining constant-property lines on T–s and P–v diagrams. The reader should verify the state-2 property determinations using Table D.3 and the NIST online database and/or software.

Self Test 2.21

☑ **The system of Example 2.21 is allowed to expand isothermally until the final specific volume is 0.32 m^3/kg. Find the final pressure.**

(Answer: $P \cong 0.70$ MPa)

h–s Diagrams

Figure 2.32 illustrates an enthalpy–entropy diagram for water. Unlike all of the other previously shown property diagrams, the steam dome is skewed because both enthalpy and entropy increase during the liquid–vapor phase change. Note that the critical point does not lie at the topmost point on the saturation line in *h*–*s* space. In the analysis of many processes and devices, enthalpy and entropy are key properties and hence *h*–*s* diagrams can be helpful. Prior to the advent of digital computers, detailed *h*–*s* or **Mollier diagrams** showing numerous properties (e.g., *P, T, x,* etc.) were routinely used in thermodynamic analyses. Figure 2.33 illustrates such a diagram.

FIGURE 2.32
Enthalpy–entropy (h–s) diagram for water showing liquid and vapor saturation lines and the 1-MPa isobar. Also shown is the 453.03-K isotherm.

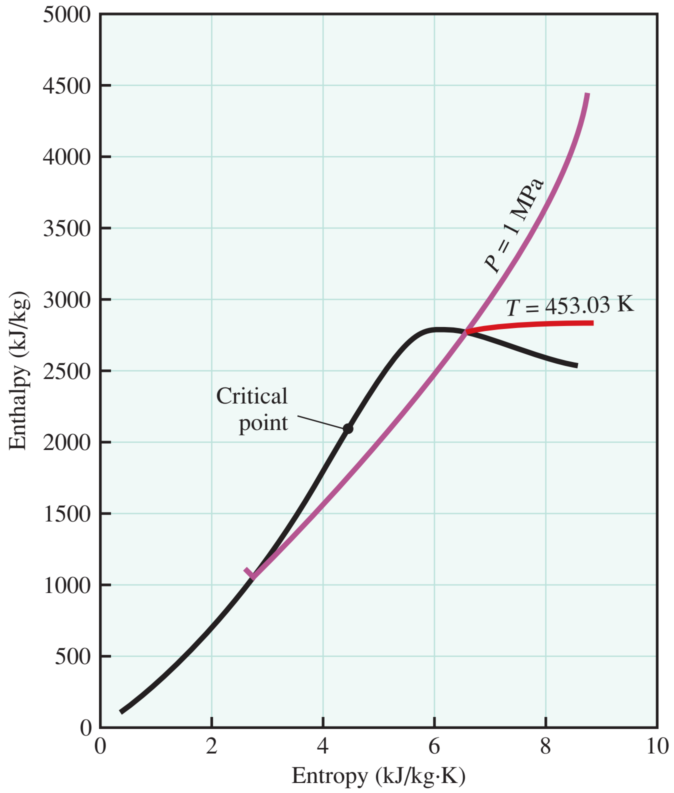
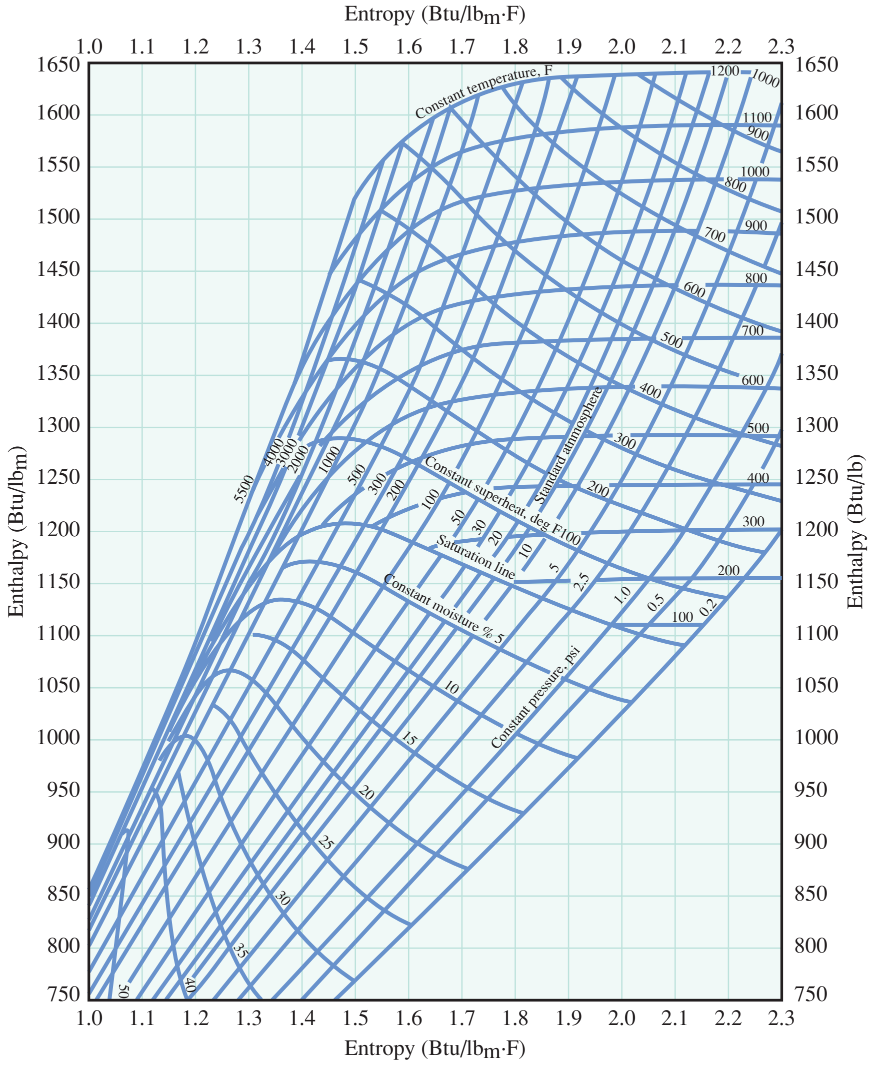
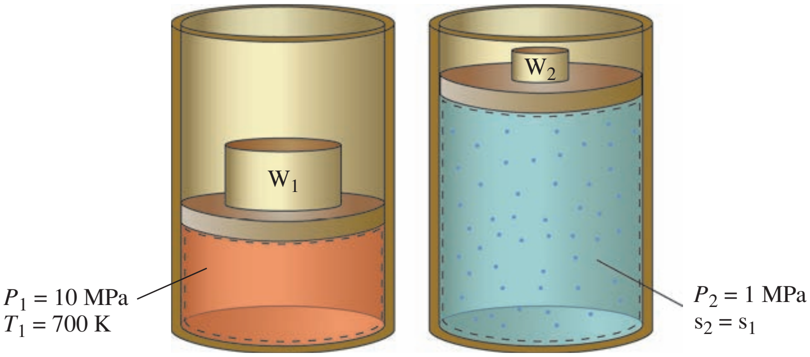


FIGURE 2.33
Mollier (h–s) diagram for water. **Courtesy of The Babcock & Wilcox Company.**



Example 2.22

Superheated steam, initially at 700 K and 10 MPa, is isentropically expanded to 1 MPa. Determine the values of v, h, T, and x at the final state. Sketch the process on a T–s diagram.

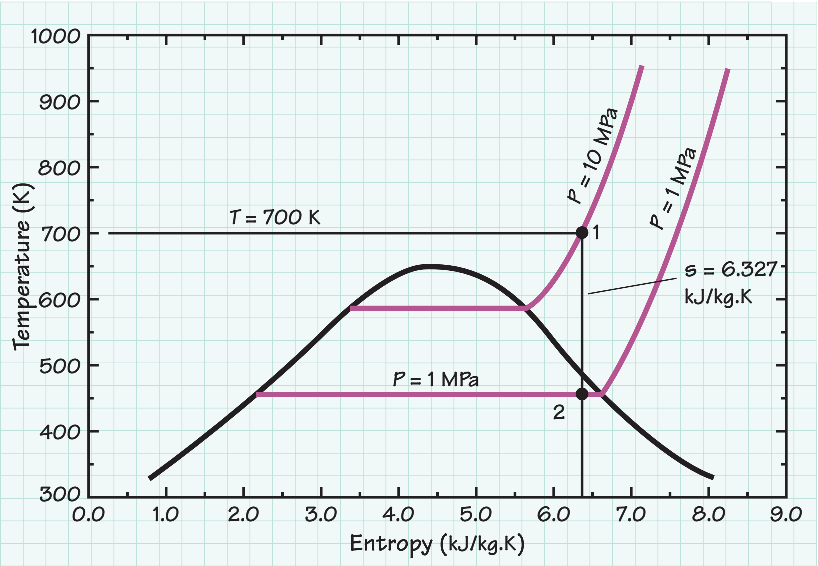


Solution

Known Superheated H_2O at T_1, P_1, isentropic expansion to P_2

Find v_2, h_2, T_2, x_2

Sketch



Assumption

Simple compressible substance at equilibrium

Analysis Our strategy here is to locate state 1 in T–s space, that is, find s_1 given T_1 and P_1. State 2 is then determined by the given pressure (P_2 = 1 MPa) and the fact that the process is isentropic (i.e., that $s_2 = s_1$). The relationship between state 1 and state 2 is shown in the sketch. Since we know two independent properties at state 2 (P_2, s_2), all other properties can be obtained.

To find s_1, we employ Table D.3 for the superheated steam at 10 MPa, which gives

$$s_1(T_1 = 700\text{ K}, P_1 = 10\text{ MPa}) = 6.3305\text{ kJ/kg}\cdot\text{K}.$$

Since $s_2 = s_1$ (=6.3305 kJ/kg·K), we see from Table D.2 that state 2 must be in the liquid–vapor mixture region since

$$s_f(P_{sat} = 1\text{ MPa}) < s_2 < s_g(P_{sat} = 1\text{ MPa}),$$

that is,

$$2.1381 < 6.3305 < 6.585.$$

With this knowledge, we calculate the quality from Eq. 2.49d as follows:

$$x = \frac{s_2 - s_f}{s_g - s_f}.$$

Numerically evaluating this expression yields

$$x = \frac{6.3305 - 2.1381}{6.585 - 2.1381} = 0.9428.$$

This value of quality is now used to determine v_2 and h_2 using Eq. 2.49c. The following table summarizes these calculations. Also shown are the saturated liquid and saturated vapor properties at 1 MPa.

x	s (kJ/kg·K)	v (m^3/kg)	h (kJ/kg)
0	2.1381	0.0011272	762.52
0.9421	$6.3305 = s_2$	$0.18330 = v_2$	$2661.8 = h_2$
1	6.585	0.19436	2777.1

Comments Once again we see how a process in which one property is held constant, in this case, entropy, is used to define the final state. This example also illustrates the use of a known mass-intensive property (s) to determine the quality, which, in turn, is used to calculate other mass-intensive properties (v and h).

Self Test 2.22

☑ **Determine the changes in the specific internal energy and the specific enthalpy for the process described in Example 2.22.**

(Answer: $\Delta u = -415.61$ kJ/kg, $\Delta h = -515.13$ kJ/kg)

2.7 LIQUID PROPERTY APPROXIMATIONS

Although accurate thermodynamic property data are available for many substances in the compressed liquid region (see Table 2.7), we now discuss some approximations. These approximations for liquid properties are useful to simplify some analyses, and they can be used when detailed compressed liquid data are not available.

For most liquids, the specific volume v and specific internal energy u are nearly independent of pressure; hence, they depend only on temperature, so that,

$$v(T, P) \cong v(T),$$
$$u(T, P) \cong u(T).$$

Since saturation properties are available for many liquids, v and u can be approximated using the corresponding saturation values where the saturation state is evaluated at the temperature of interest, that is,

$$v(T, P) \cong v_f(T_{sat} = T) \tag{2.53a}$$

and

$$u(T, P) \cong u_f(T_{sat} = T). \tag{2.53b}$$

The enthalpy can also be approximated using these relationships, together with the definition $h = u + Pv$; thus,

$$h(T, P) \cong h_f(T_{sat} = T) + (P - P_{sat})v_f(T_{sat} = T). \tag{2.53c}$$

Example 2.23

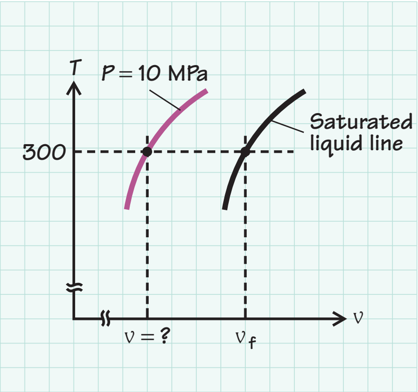
Determine the error associated with the evaluation of v and h from Eqs. 2.53a–2.53c for water at 10 MPa and 300 K.

Solution

Known H_2O (liquid), P, T

Find v and h (approximations and "exact")

Sketch



Assumption

Water is approximately incompressible

Analysis Using the NIST database, we obtain the following values for the compressed liquid at 10 MPa and 300 K:

$$v = 0.00099905\ \mathrm{m^3/kg},$$
$$h = 121.73\ \mathrm{kJ/kg}.$$

To obtain the approximate specific volume, we employ Eq. 2.53a together with Table D.1, which gives

$$v(T, P) \cong v_{\mathrm{f}}(T_{\mathrm{sat}} = T) = v_{\mathrm{f}}(300\ \mathrm{K}) = 0.0010035\ \mathrm{m^3/kg}.$$

We also employ values from Table D.2 to evaluate Eq. 2.54c for the approximate enthalpy:

$$\begin{aligned} h(T, P) &\cong h_{\mathrm{f}}(T) + [P - P_{\mathrm{sat}}(T)]v_{\mathrm{f}}(T) \\ &= 112.56 \times 10^3\ \mathrm{J/kg} + (10 \times 10^6\ \mathrm{Pa} - 3.5369 \\ &\quad \times 10^3\ \mathrm{Pa})\ 0.0010035\ \mathrm{m^3/kg} \\ &= 122.59 \times 10^3\ \mathrm{J/kg}\ \text{or}\ 122.59\ \mathrm{kJ/kg}. \end{aligned}$$

Verification of the units is left to the reader. The errors associated with the approximations are given in the following table:

Property	NIST Value	Approximation	Error
v ($\mathrm{m^3/kg}$)	0.00099905	0.0010035	+0.44%
h (kJ/kg)	121.73	122.59	+0.71%

Comments We see that the approximate values are quite close to the exact values, with errors of less than 1%. We also note that the high pressure (10 MPa) makes a significant contribution to the enthalpy.

Self Test 2.23

☑ **A beaker contains H_2O at atmospheric pressure and 10°C. Find the specific volume, specific internal energy, and specific enthalpy of the H_2O.**

(Answer: $v = 0.001\ \mathrm{m^3/kg}$, $u = 41.391\ \mathrm{kJ/kg}$, $h = 41.491\ \mathrm{kJ/kg}$)

2.8 SOLIDS

We have focused thus far on the thermodynamic properties of gases, liquids, and their mixtures. We now examine solids. Figure 2.34 presents a phase diagram for water showing the solid region, which is designated I; the liquid region, designated II; and the vapor region, III. A key feature of this diagram is the triple point. As you may recall, the triple point is the state at which all three phases (solid, liquid, and vapor) of a substance coexist in equilibrium. For water, the triple point temperature is 0.01°C (273.16 K) and the triple point pressure is 0.00604 atm (0.6117 kPa). The nearly vertical line that originates at the triple point, the **solidification** or **fusion line**, separates the solid region from the liquid region. Another line, the **sublimation line**, separates the solid from the vapor phase and ends at the triple point. A third line, which starts at the triple point and continues up to the critical point, comprises the saturation states that were defined in our discussion of liquid–vapor mixtures. The normal (i.e., 1 atm) freezing point

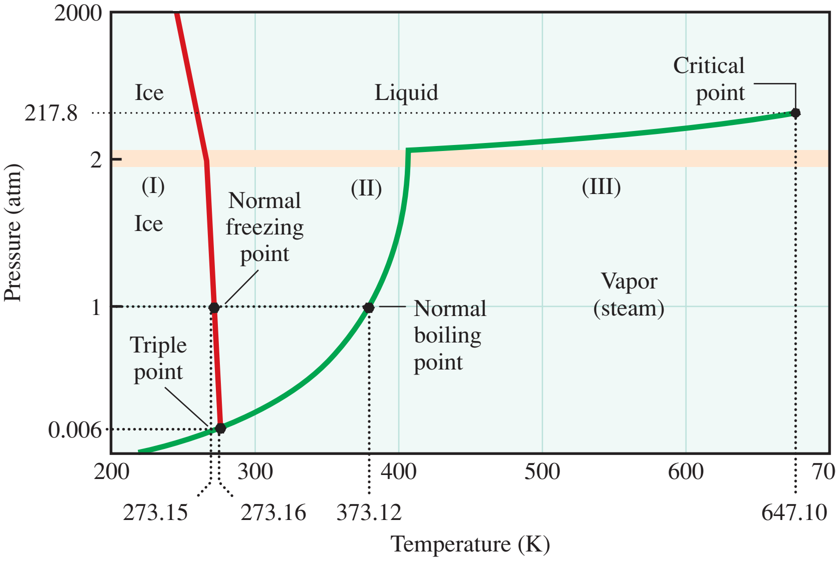


FIGURE 2.34
Phase diagram for water showing solid (I), liquid (II), and vapor (III) regions. Indicated on the diagram are the critical point ($P_c = 217.8$ atm, $T_c = 647.10$ K), the normal boiling (steam) point ($P_{boil} = 1$ atm, $T_{boil} = 373.12$ K), the normal freezing (ice) point ($P_{freeze} = 1$ atm, $T_{freeze} = 273.15$ K), and the triple point ($P_{triple} = 0.006$ atm, $T_{triple} = 273.16$ K). Note the scale change above 2 atm. **Adapted from Ref. [15] with permission.**

is also indicated on the phase diagram and corresponds to a temperature of 0°C (273.15 K).

Important properties associated with solid–liquid and solid–vapor phase changes are the enthalpy of fusion, h_{fusion}, and the enthalpy of sublimation, h_{sublim}, respectively:

$$h_{fusion} = h_{liq} - h_{solid}, \tag{2.54a}$$

$$h_{sublim} = h_{vap} - h_{solid}. \tag{2.54b}$$

Iodine sublimes from a bluish-black, metallic looking solid to a purple vapor. The vapor pressure of solid iodine at 90°C is 3.57 kPa.

Values of these quantities for H_2O at the triple point are 333.4 kJ/kg for h_{fusion} and 2834.3 kJ/kg for h_{sublim}.

In most thermal science applications, the thermodynamic properties of interest for solids are the density (reciprocal specific volume) and specific heats. The dependence of these properties on pressure is very slight over a wide range; in fact, the effect of pressure is so small that solid properties are usually assumed to be functions of temperature alone, that is,

$$\rho = \rho\ (T\text{ only}) \tag{2.55a}$$

and

$$c_p = c_p\ (T\text{ only}). \tag{2.55b}$$

Densities and constant-pressure specific heats are tabulated in Appendix I for a number of solids of engineering interest.

To simplify the thermal analysis of solid systems, we frequently assume that the solid is an **incompressible** substance. With this assumption, the density (or specific volume) is a constant, independent of both pressure and temperature; that is,

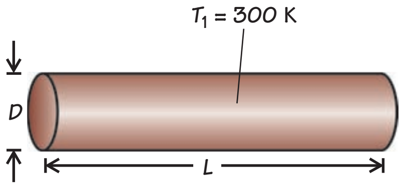
$$\rho = 1/v = \text{constant}. \tag{2.56a}$$

Furthermore,

$$c_p = c_v \equiv c = \text{constant}. \tag{2.56b}$$

When invoking the incompressible substance approximation, properties are usually evaluated at an appropriate average temperature. The proof that $c_p = c_v$ for an incompressible substance is left as an exercise for the reader (Problem 2.118).

Example 2.24



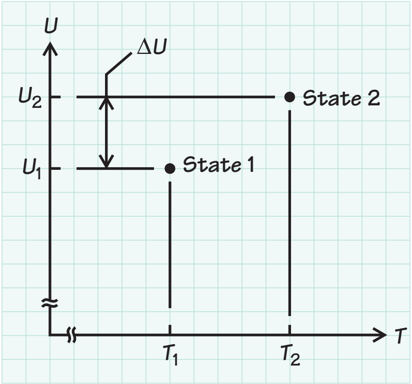
A pure copper rod of diameter $D = 25$ mm and length $L = 150$ mm is initially at a uniform temperature of 300 K. The rod is heated at 1 atm to a uniform temperature of 450 K. Estimate the change in internal energy $U([=]\text{ J})$ of the rod in going from the initial to the final state.

Solution

Known Pure Cu, L, D, T_1, T_2

Find $U_2 - U_1 \equiv \Delta U$

Sketch



Assumptions

Incompressible solid

Analysis We develop the required calorific equation of state for copper by starting with the definition of the constant-volume specific heat (Eq. 2.19a),

$$c_v \equiv \left(\frac{\partial u}{\partial T}\right)_v .$$

With the assumption of incompressibility, this becomes an ordinary derivative, which can be separated and integrated as follows:

$$\Delta u = \int_{u_1}^{u_2} du = \int_{T_1}^{T_2} c_v dT = c(T_2 - T_1).$$

For a system of mass M, the internal energy change is thus

$$\Delta U = M\Delta u = Mc(T_2 - T_1).$$

We find the mass of the rod as follows:

$$M = \rho\mathcal{V} = \rho\frac{\pi D^2}{4}L.$$

We use Appendix I (Table I.1) to obtain values for c and ρ. Because values of c are given for several temperatures, we interpolate for an average temperature $T[=(T_1 + T_2)/2]$ of 375 K:

T (K)	c_p (J/kg·K)
200	356
375	392
400	397

Because only a single value of the density is given in Table I.1, we use that value:

$$\rho(300\text{ K}) = 8933\text{ kg/m}^3 \cong \rho(375\text{ K}).$$

Evaluating the mass and internal energy change yields

$$M = 8933\frac{\pi(0.025)^2}{4}0.150 = 0.6577$$

$$[=]\frac{\text{kg}}{\text{m}^3}(\text{m}^2)\text{m} = \text{kg},$$

and

$$\Delta U = 0.6577\,(392)(450 - 300) = 38{,}700$$

$$[=]\text{kg}\frac{\text{J}}{\text{kg}\cdot\text{K}}\text{K} = \text{J}.$$

Comments Note the use of a c_p value based on an average temperature. This approach to find an average c_p is frequently used. That the temperature is uniform at both the start and end of the process also greatly simplifies this problem. (How would you solve the problem if a temperature *distribution* were given at the end of the heating process, rather than a single uniform temperature?)

Self Test 2.24

Redo Example 2.24 for an iron rod of the same dimensions. Compare your answer with that of Example 2.24 and discuss your results.

(Answer: $\Delta U = 41.4$ kJ. Even though the density of iron is lower than that of copper, more energy is required for the same process because iron has a higher c_p value.)

Example 12.15 in Chapter 12 shows that treating the water vapor in moist atmospheric air as an ideal gas is a good approximation.

2.9 IDEAL-GAS MIXTURES

So far we have confined our discussion of properties to pure substances; however, many practical devices involve mixtures of pure substances. Air conditioning and combustion systems are common examples of such. In the former application, water vapor becomes an important component of air, which already is a mixture of several components, whereas combustion systems deal with reactant mixtures of fuel and oxidizer and with product mixtures of various components. In both of these examples, we can treat the various gas streams as ideal-gas mixtures with reasonable accuracy for a wide range of conditions. For air conditioning and humidification systems, this results from the small amounts of water involved in the mixtures. For combustion, the high temperatures typically involved result in mixtures of low density. Applications of the concepts developed in this section are found in Chapters 3, 5, 11, and 12 for combustion systems and in Chapter 12 for air conditioning and humidification systems.

Condensation of water vapor from combustion products.

2.9a Specifying Mixture Composition

To characterize the composition of a mixture, we define two important and useful quantities: the constituent mole fractions and mass fractions. Consider a multicomponent mixture of gases composed of N_1 moles of species 1, N_2 moles of species 2, etc. The **mole fraction of species *i*, X_i,** is defined as the fraction of the total number of moles in the system that are species i:

Some specific examples in Chapter 12 include the operation of evaporative coolers (Example 12.17) and household dehumidifiers (Example 12.18).

$$X_i \equiv \frac{N_i}{N_1 + N_2 + \cdots} = \frac{N_i}{N_{\text{tot}}} \tag{2.57a}$$

Similarly, the **mass fraction of species *i*, Y_i,** is the fraction of the total mixture mass that is associated with species i:

$$Y_i \equiv \frac{M_i}{M_1 + M_2 + \cdots + M_i + \cdots} = \frac{M_i}{M_{\text{tot}}}. \tag{2.57b}$$

Note that, by definition, the sum of all the constituent mole (or mass) fractions must be unity; that is,

$$\sum_{i=1}^{J} X_i = 1, \tag{2.58a}$$

$$\sum_{i=1}^{J} Y_i = 1, \tag{2.58b}$$

where J is the total number of species in the mixture.

Conservation of mass for reacting systems uses mole and mass fractions. See Examples 3.14 and 3.15 in Chapter 3.

We can readily convert mole fractions and mass fractions from one to another using the molecular weights of the species of interest and the apparent molecular weight of the mixture:

$$Y_i = X_i \mathcal{M}_i / \mathcal{M}_{\text{mix}}, \tag{2.59a}$$

$$X_i = Y_i \mathcal{M}_{\text{mix}} / \mathcal{M}_i. \tag{2.59b}$$

The apparent mixture molecular weight, denoted $\mathcal{M}_{\text{mix}}$, is easily calculated from knowledge of either the species mole or mass fractions:

$$\mathcal{M}_{\text{mix}} = \sum_{i=1}^{J} X_i \mathcal{M}_i, \tag{2.60a}$$

or

$$\mathcal{M}_{\text{mix}} = \frac{1}{\sum_{i=1}^{J} (Y_i / \mathcal{M}_i)}. \tag{2.60b}$$

2.9b State (P–v–T) Relationships for Mixtures

In our treatment of mixtures, we assume a double ideality: first, that the pure constituent gases obey the ideal-gas equation of state (Eq. 2.8), and, second, that when these pure components mix, an ideal solution results. In an **ideal solution**, the behavior of any one component is uninfluenced by the presence of any other component.

Let us explore the characteristics of an ideal solution considering, first, the thermodynamic property pressure. Consider a fixed volume $\mathcal{V}$ containing two or more different species. If the mixture (solution) is ideal, gas molecules of species A are free to roam through the entire volume $\mathcal{V}$, as if no other species were present. The pressure that molecules A exert on the wall is less than the total pressure, however, since other non-A molecules also collide with the wall. We can thus define the **partial pressure** of species A, P_A, by applying the ideal-gas equation of state just to the A molecules:

$$P_A\mathcal{V} = N_A R_\mathrm{u} T. \tag{2.61}$$

Since each species behaves independently, similar expressions can be written for each,

$$\begin{aligned} P_B\mathcal{V} &= N_B R_\mathrm{u} T, \\ &\vdots \\ P_i\mathcal{V} &= N_i R_\mathrm{u} T, \end{aligned}$$

etc. Summing this set of equations for a mixture containing J species yields

$$(P_A + P_B + \cdots + P_i + \cdots + P_J)\mathcal{V} = (N_A + N_B + \cdots + N_\mathrm{i} + \cdots + N_\mathrm{J})R_\mathrm{u} T. \tag{2.62}$$

Because the sum of the number of moles of each constituent is the total number of moles in the system, N_tot, this equation becomes

$$\sum_{i=1}^{J} P_i\mathcal{V} = N_\mathrm{tot} R_\mathrm{u} T, \tag{2.63}$$

where P_i is the partial pressure of the ith species. Because the mixture as a whole obeys the ideal-gas law,

$$P\mathcal{V} = N_\mathrm{tot} R_\mathrm{u} T, \tag{2.64}$$

the sum of the **partial pressures** must be identical to the total pressure, that is,

$$\sum_{i=1}^{J} P_i = P. \tag{2.65}$$

This statement is known as *Dalton's law of partial pressures* and is schematically illustrated in Fig. 2.35. Here we see four containers, each having the same volume $\mathcal{V}$. Gas A fills one container, gas B another, and gas C the third. Each gas has the same temperature T. The absolute pressure of the gas in each container is measured to be P_A, P_B, and P_C, respectively. We now conduct the thought experiment in which gases A, B, and C are transferred to the fourth container, again at temperature T. The absolute pressure of the mixture in the fourth container is found to be the sum of the absolute pressures measured when the gases were segregated. That the contribution of a single species to the total pressure in a gas mixture is the same as that of the pure species occupying the same total volume at the same temperature is a defining characteristic of an ideal-gas mixture (i.e., an ideal solution). In nonideal mixtures (solutions), the total pressure is not necessarily equal to the sum of the pure component pressures as in the thought experiment.

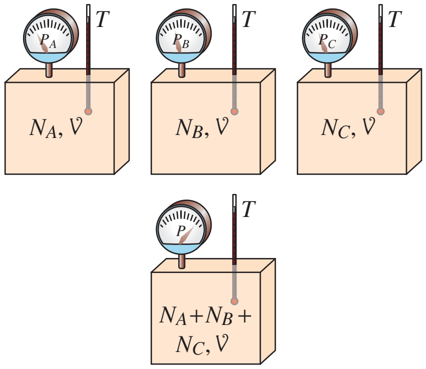


FIGURE 2.35
In an ideal-gas mixture, the sum of the pressures associated with each component isolated in the same volume at the same temperature is identical to the total pressure observed when all species are confined together in the same volume at the same temperature.

In Chapter 12, the partial pressure of water vapor is used to define the relative humidity of moist air. See Eq. 12.62.

The partial pressure can be related to the mixture composition and total pressure by dividing Eq. 2.61 by Eq. 2.64,

$$\frac{P_i \mathcal{V}}{P \mathcal{V}} = \frac{N_i R_u T}{N_{tot} R_u T},$$

which simplifies to

$$\boxed{\frac{P_i}{P} = \frac{N_i}{N_{tot}} \equiv X_i,} \tag{2.66a}$$

or

$$\boxed{P_i = X_i P.} \tag{2.66b}$$

Ideal-gas mixtures also exhibit the property that when component gases having different volumes but identical pressures and temperatures are brought together, the mixture volume is the sum of the pure component volumes (Fig. 2.36). Mathematically, we express this idea by writing the ideal-gas equation of state for each pure constituent,

$$P\mathcal{V}_A = N_A R_u T,$$
$$P\mathcal{V}_B = N_B R_u T,$$
$$P\mathcal{V}_C = N_C R_u T,$$

and summing to yield

$$P(\mathcal{V}_A + \mathcal{V}_B + \mathcal{V}_C) = (N_A + N_B + N_C) R_u T.$$

Since

$$P\mathcal{V}_{tot} = N_{tot} R_u T,$$

we conclude that the individual volumes, or partial volumes, must equal the total volume when combined, that is,

$$\mathcal{V}_{tot} = \mathcal{V}_A + \mathcal{V}_B + \mathcal{V}_C. \tag{2.67}$$

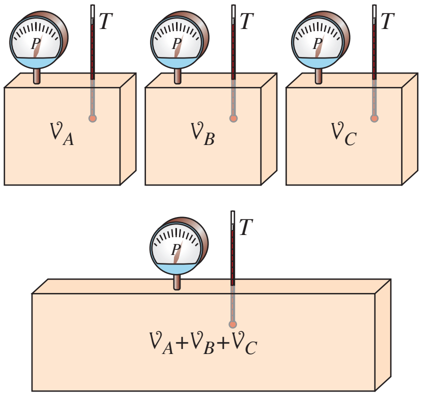


FIGURE 2.36
In an ideal-gas mixture, the sum of the volumes associated with each component isolated at the same temperature and the same pressure is identical to the total volume when all species are confined together at the same temperature and the same pressure.

This view of an ideal-gas mixture is frequently referred to as *Amagat's model*.

The partial volumes also can be related to the mixture composition by defining a volume fraction,

$$\mathcal{V}_i / \mathcal{V} = N_i / N_{tot}. \tag{2.68}$$

Comparing Eqs. 2.66a and 2.68, we see that the three measures of mixture composition—the ratio of the partial pressure to the total pressure, the volume fraction, and the mole fraction—are all equivalent for an ideal-gas mixture:

$$\boxed{P_i/\mathrm{P} = \mathcal{V}_i/\mathcal{V} = N_i/N \quad (= X_i).} \tag{2.69}$$

For insight into the behavior of nonideal mixtures, the reader is referred to Refs. [20, 21].

2.9c Standardized Properties

LEVEL 3

From our earlier discussion of the calorific equation of state for ideal gases, we see that a reference temperature is required to evaluate the specific internal energy and enthalpy (see Eqs. 2.31c and 2.33c). If one is concerned only with a single pure substance, as opposed to a reacting system where both reactant and product species are present, then Eqs. 2.31c and 2.33c would suffice to describe the internal energy and enthalpy changes for all thermodynamic processes, as only differences in states are of importance. Moreover, any choice of reference temperature would yield the same results. For example, the enthalpy change associated with a change of temperature from T_1 to T_2 is calculated from Eq. 2.33c as

$$h(T_2) - h(T_2) = \int_{T_{\text{ref}}}^{T_2} c_p dT - \int_{T_{\text{ref}}}^{T_1} c_p dT = \int_{T_1}^{T_2} c_p dT,$$

a straightforward calculation in which the reference temperature drops out. In reacting systems, however, we must include energy stored in chemical bonds in our accounting. To accomplish this, the concept of standardized enthalpies is extremely valuable. For any species, we define a **standardized enthalpy** that is the sum of an enthalpy that takes into account the energy associated with chemical bonds (or lack thereof), the **enthalpy of formation, h_f,** and an enthalpy associated only with a temperature change, the **sensible enthalpy change, Δh_s**. Thus, we write the molar standardized enthalpy for species i as

$$\underset{\substack{\text{Standardized}\\ \text{enthalpy at}\\ \text{temperature } T}}{\bar{h}_i(T)} = \underset{\substack{\text{Enthalpy of}\\ \text{formation at}\\ \text{standard}\\ \text{reference state}\\ (T_{\text{ref}},\, P^{\circ})}}{\bar{h}^{\circ}_{\text{f},i}(T_{\text{ref}})} + \underset{\substack{\text{Sensible}\\ \text{enthalpy change}\\ \text{in going from } T_{\text{ref}}\\ \text{to } T}}{\Delta\bar{h}_{\text{s},\,i}(T)}, \qquad (2.70)$$

where

$$\Delta\bar{h}_{\text{s},i} \equiv \bar{h}_i(T) - \bar{h}^{\circ}_{\text{f},\,i}(T_{\text{ref}}).$$

Table 2.8 Standard Reference State

$T_{\text{ref}} \equiv 298.15$ K
$P_{\text{ref}} \equiv 101{,}325$ Pa
For elements in their naturally occurring state (solid, liquid, or gas) at T_{ref} and P_{ref}*
$h_{\text{i}}\,(T_{\text{ref}}) \equiv 0$

*For example, the standard-state enthalpies for C(s), N_2(g), and O_2(g) are all zero.

To make practical use of Eq. 2.70, it is necessary to define a **standard reference state** (Table 2.8). We employ a standard-state temperature, $T_{\text{ref}} =$ 25°C (298.15 K), and standard-state pressure, $P_{\text{ref}} = P^{\circ} = 1$ atm (101,325 Pa), consistent with the JANAF [5], Chemkin [3], and NASA [6] thermodynamic databases. Although not needed to describe enthalpies, the standard-state pressure is required to calculate entropies at pressures other than one atmosphere (see Eq. 2.39a). In addition to defining T_{ref} and P_{ref}, we adopt the convention that enthalpies of formation are zero for the elements in their naturally occurring state at the reference-state temperature and pressure. For example, oxygen exists as diatomic molecules at 25°C and 1 atm; hence,

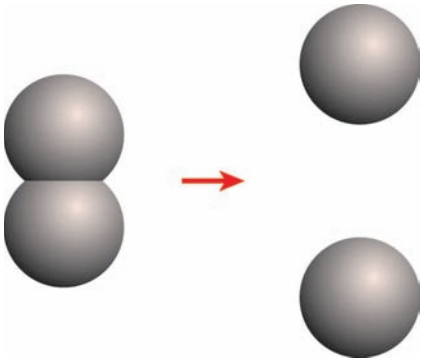
$$(\bar{h}^{\circ}_{\text{f},\,O_2})_{298} = 0,$$

where the superscript ° is used to denote that the value is for the standard-state pressure.[17]

To form oxygen atoms at the standard state requires the breaking of a rather strong chemical bond. The bond dissociation energy for O_2 at 298 K is 498,390 kJ/kmol$_{O_2}$. Breaking this bond creates two O atoms; thus, the enthalpy of formation for atomic oxygen is half the value of the O_2 bond dissociation energy:

$$(\bar{h}^{\circ}_{\text{f,O}}) = 249{,}195 \text{ kJ/kmol}_{\text{O}}.$$

Thus, enthalpies of formation have a clear physical interpretation as the net change in enthalpy associated with breaking the chemical bonds of the



Shared electrons form a covalent bond in molecular oxygen. An energy input is required to break this bond to form two oxygen atoms.

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[17] The use of this superscript is redundant for ideal-gas enthalpies, which exhibit no temperature dependence; for entropies, however, the superscript is important.

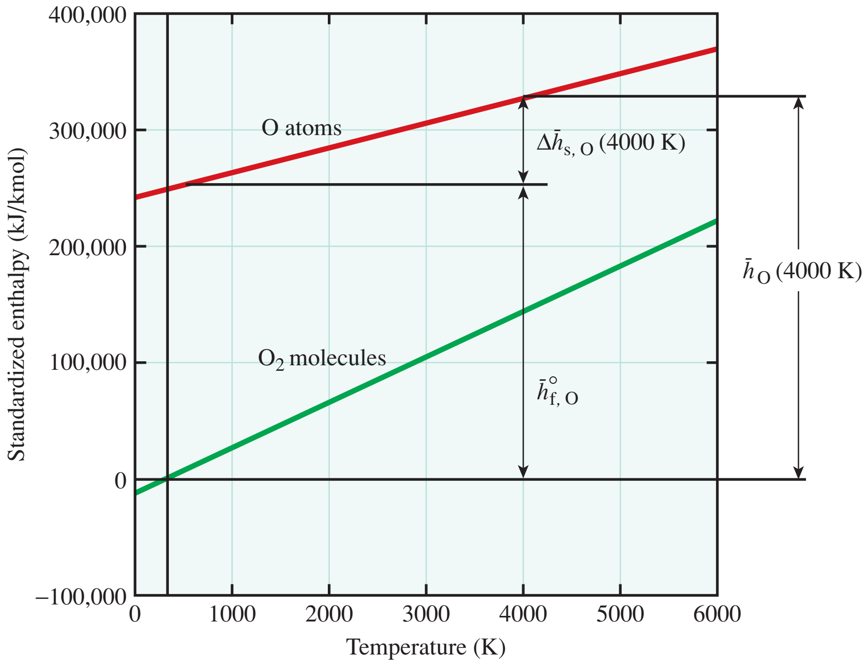


FIGURE 2.37
Graphical interpretation of standardized enthalpy, enthalpy of formation, and sensible enthalpy.

Standardized enthalpies are first used in conservation of energy for combustion systems. See Examples 5.7–5.9 in Chapter 5.

standard-state elements and forming new bonds to create the compounds of interest.

Representing the standardized enthalpy graphically provides a useful way to understand and use this concept. In Fig. 2.37, the standardized enthalpies for atomic oxygen (O) and diatomic oxygen (O_2) are plotted versus temperature starting from absolute zero. At 298.15 K, we see that $\bar{h}_{o_2}$ is zero (by definition of the standard-state reference condition), and the standardized enthalpy of atomic oxygen equals its enthalpy of formation, since the sensible enthalpy at 298.15 K is zero. At the temperature indicated (4000 K), we see the additional sensible enthalpy contribution to the standardized enthalpy. In Appendix B, enthalpies of formation at the reference state are given, and sensible enthalpies are tabulated as a function of temperature for a number of species of importance in combustion. Enthalpies of formation for reference temperatures other than the standard state 298.15 K are also tabulated.

Although the choice of a zero datum for the enthalpy of the elements at the reference state is arbitrary (being merely a pragmatic choice), the third law of thermodynamics is used to set zero values for entropies; thus, the standard-state entropy values are always larger than zero.

Example 2.25

Determine the standardized molar- and mass-specific enthalpies and entropies of N_2 and N at 3000 K and 2.5 atm.

Solution

Known N_2, N, T, P

Find $\bar{h}$, h, $\bar{s}$, s

Assumptions

Ideal-gas behavior

Analysis Tables B.7 and B.8 can be used to determine the molar-specific standard-state enthalpies and entropies for N_2 and N, respectively. The standard-state (1-atm) entropy can be converted to the value at 2.5 atm using the molar-specific form of Eq. 2.39a.

The sum of the enthalpies of formation and sensible enthalpies are the standardized enthalpies we seek (Eq. 2.70). At 3000 K, these values are

$$\begin{aligned}\bar{h}_{N_2} &= \bar{h}^{\circ}_{f,\,N_2}(298.15\text{ K}) + \Delta\bar{h}_{s,N_2}(3000\text{ K})\\ &= 0\text{ kJ/kmol} + 92{,}730\text{ kJ/kmol} = 92{,}730\text{ kJ/kmol}\end{aligned}$$

and

$$\begin{aligned}\bar{h}_{N} &= \bar{h}^{\circ}_{f,N}(298.15\text{ K}) + \Delta\bar{h}_{s,\,N}(3000\text{ K})\\ &= 472{,}628\text{ kJ/kmol} + 56{,}213\text{ kJ/kmol} = 528{,}841\text{ kJ/kmol.}\end{aligned}$$

Since the standard-state pressure is 1 atm, application of Eq. 2.39a yields

$$\bar{s}\,(T, P) - \bar{s}(T, 1\text{ atm}) = -R_u \ln\left(\frac{P\text{ (atm)}}{1\text{ atm}}\right),$$

or

$$\bar{s}\,(T, P) - \bar{s}^{\circ}(T) = -R_u \ln\left(\frac{P\text{ (atm)}}{1\text{ atm}}\right).$$

Thus,

$$\bar{s}\,(3000\text{ K, 2.5 atm}) = \bar{s}^{\circ}(3000\text{ K}) - R_u \ln 2.5.$$

Using the values from Tables B.7 and B.8, we evaluate this equation as follows:

$$\bar{s}_{N_2} = 266.810 - 8.31447 \ln 2.5 = 259.192\text{ kJ/kmol}\cdot\text{K}$$

and

$$\bar{s}_{N} = 201.199 - 8.31447 \ln 2.5 = 193.581\text{ kJ/kmol}\cdot\text{K.}$$

To compute the mass-specific enthalpies and entropies, we divide the molar-specific values by the molecular weight of the respective species; for example,

$$h_{N_2} = \frac{\bar{h}}{\mathcal{M}_{N_2}} = \frac{92{,}730\text{ kJ/kmol}}{28.013\text{ kg/kmol}} = 3310.25\text{ kJ/kg.}$$

The following table summarizes these calculations:

	$\mathcal{M}$ (kg/kmol)	$\bar{h}$ (kJ/kmol)	h (kJ/kg)	$\bar{s}$ (kJ/kmol·K)	s (kJ/kg·K)
N_2	28.013	92,730	3310.25	259.192	9.2526
N	14.007	528,841	37,755	193.581	13.8203

Comments This example illustrates the use of the tables in Appendix B to calculate standardized properties at temperatures and pressure not equal to the reference-state values. Because we assume ideal-gas behavior, the pressure has no effect on the enthalpy and, furthermore, the entropy is a simple function of pressure (see Eq. 2.39a). The conversion from the reference-state pressure (1 atm) to the pressure at the desired state (2.5 atm) is thus straightforward.

Self Test 2.25

Determine the standardized mass-specific enthalpies and entropies of O and O_2 at 2000 K and atmospheric pressure.

(Answer: $h_{O_2} = 1{,}849.09$ *kJ/kg,* $s_{O_2} = 8.396$ *kJ/kg·K,* $h_O = 17{,}806.8$ *kJ/kg,* $s_O = 12.571$ *kJ/kg·K)*

2.9d Calorific Relationships for Mixtures

The calorific relationships for ideal-gas mixtures are straightforward mass-fraction or mole-fraction weightings of the pure-species individual specific calorific properties:

$$u_{\text{mix}} = \sum_{i=1}^{J} Y_i u_i, \tag{2.71a}$$

$$h_{\text{mix}} = \sum_{i=1}^{J} Y_i h_i, \tag{2.71b}$$

$$c_{v,\text{mix}} = \sum_{i=1}^{J} Y_i c_{v,i}, \tag{2.71c}$$

$$c_{p,\text{mix}} = \sum_{i=1}^{J} Y_i c_{p,i}, \tag{2.71d}$$

or

$$\bar{u}_{\text{mix}} = \sum_{i=1}^{J} X_i \bar{u}_i, \tag{2.71e}$$

$$\bar{h}_{\text{mix}} = \sum_{i=1}^{J} X_i \bar{h}_i, \tag{2.71f}$$

$$\bar{c}_{v,\text{mix}} = \sum_{i=1}^{J} X_i \bar{c}_{v,i}, \tag{2.71g}$$

$$\bar{c}_{p,\text{mix}} = \sum_{i=1}^{J} X_i \bar{c}_{p,i}, \tag{2.71h}$$

The analysis of a jet engine combustor in Chapter 12 (Example 12.11) uses concepts developed here: mole and mass fractions and standardized properties of ideal-gas mixtures.

where the subscript i represents the ith species and J is the total number of species in the mixture. Since the specific heats, internal energies, and enthalpies of the constituent ideal-gas species depend only on temperature, the same is true for the mixture calorific properties; for example, $u_{\text{mix}} = u_{\text{mix}}$ (T only), etc. Molar-specific enthalpies for a number of species are tabulated in Appendix B.

2.9e Second-Law Relationships for Mixtures

The mixture entropy also is calculated as a weighted sum of the constituents:

$$s_{\text{mix}}(T, P) = \sum_{i=1}^{J} Y_i s_i(T, P_i), \tag{2.72a}$$

$$\bar{s}_{\text{mix}}(T, P) = \sum_{i=1}^{J} X_i \bar{s}_i(T, P_i). \tag{2.72b}$$

Unlike the ideal-gas calorific relationships, pressure is now required as a second independent variable. Here the pure-species entropies (s_i and $\bar{s}_i$) depend on the species partial pressures, as explicitly indicated in Eq. 2.72. Equation 2.39a can be applied to evaluate the constituent entropies in Eq. 2.72 from standard-state ($P_{\text{ref}} \equiv P^{\text{o}} = 1$ atm) values as

$$s_i(T, P_i) = s_i(T, P_{\text{ref}}) - R\ln\frac{P_i}{P_{\text{ref}}}, \tag{2.73a}$$

$$\bar{s}_i(T, P) = \bar{s}_i(T, P_{\text{ref}}) - R_{\text{u}}\ln\frac{P_i}{P_{\text{ref}}}, \tag{2.73b}$$

where $P_i = X_i P$. Ideal-gas, standard-state molar-specific entropies are tabulated in Appendix B for several species.

The Gibbs function is an important second-law property that has many uses in dealing with ideal-gas mixtures. For example, the Gibbs function is used to determine the equilibrium composition of reacting gas mixtures (see Chapter 7). Earlier in the present chapter (see Eq. 2.21) we defined the Gibbs function as

$$G \equiv H - TS,$$

or

$$g \equiv h - Ts, \tag{2.74a}$$

$$\bar{g} \equiv \bar{h} - T\bar{s}. \tag{2.74b}$$

For an ideal-gas mixture, the mass- or molar-specific Gibbs function is a weighted sum of the pure-species mass- or molar-specific Gibbs functions:

$$g_{\text{mix}}(T, P) = \sum_{i=1}^{J} Y_i g_i(T, P_i), \tag{2.75a}$$

$$\bar{g}_{\text{mix}}(T, P) = \sum_{i=1}^{J} X_i \bar{g}_i(T, P_i), \tag{2.75b}$$

where

$$g_i(T, P_i) = h_i(T) - Ts_i(T, P_i) = h_i(T) - T\left[s_i^{\circ}(T) - R\ln\frac{P_i}{P^{\circ}}\right] \tag{2.76a}$$

and

$$\bar{g}_i(T, P_i) = \bar{h}_i - T\left[\bar{s}_i^{\circ}(T) - R_{\text{u}}\ln\frac{P_i}{P^{\circ}}\right]. \tag{2.76b}$$

The connection to the mixture composition is through the ideal-gas relationship $P_i = X_i P$ (Eq. 2.66b).

2.10 SOME PROPERTIES OF REACTING MIXTURES

2.10a Enthalpy of Combustion

Knowing how to express the enthalpy for mixtures of reactants and mixtures of products allows us to define the enthalpy of reaction, or, when dealing specifically with combustion reactions, the enthalpy of combustion. The definition of the **enthalpy of reaction**, or the **enthalpy of combustion**, **ΔH_R**, is

$$\boxed{\Delta H_R(T) = H_{prod}(T) - H_{reac}(T),} \tag{2.77a}$$

where T may be any temperature, although a reference-state value of 298.15 K is frequently used. The enthalpy of combustion is illustrated graphically in Fig. 2.38. Note that the standardized enthalpy of the products lies below that of the reactants. For example, at 25°C and 1 atm, the reactants' enthalpy of a stoichiometric mixture of CH_4 and air is −74,831 kJ per kmol of fuel. At the same conditions (25°C, 1 atm), the combustion products have a standardized enthalpy of −877,236 kJ for the combustion of 1 kmol of fuel. Thus,

$$\Delta H_R = -877{,}236 - (-74{,}831) = -802{,}405 \text{ kJ (per kmol CH}_4\text{)}.$$

This value is usually expressed on a per-mass-of-fuel basis:

$$\Delta h_R(\text{kJ/kg}_{fuel}) = \Delta H_R/\mathcal{M}_{fuel}, \tag{2.77b}$$

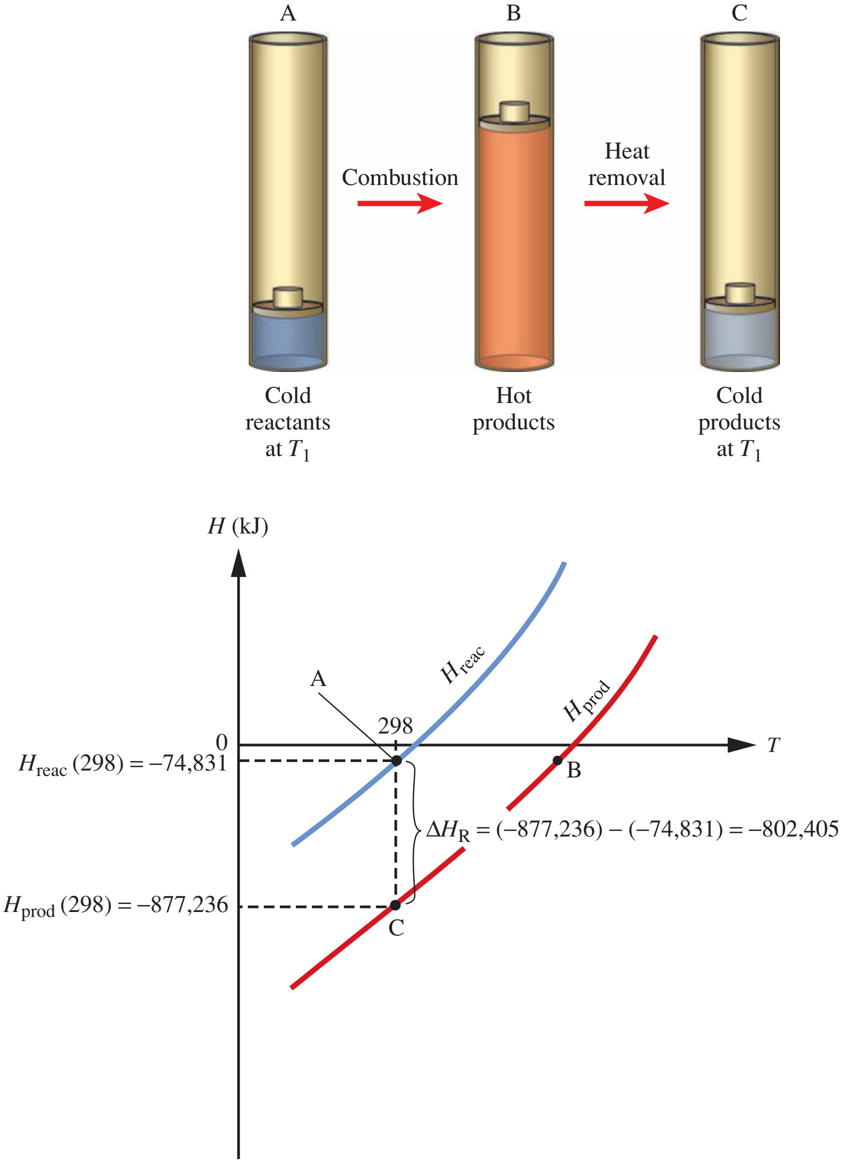


FIGURE 2.38
The enthalpy of reaction is illustrated using values for the reaction of one mole of methane with a stoichiometric quantity of air. The water in the products is assumed to be in the vapor state.

Methane, the largest component of natural gas, has a higher heating value of 55,528 kJ/kg.

or

$$\Delta h_R = (-802{,}405/16.043) = -50{,}016 \text{ kJ/kg}_{\text{fuel}}.$$

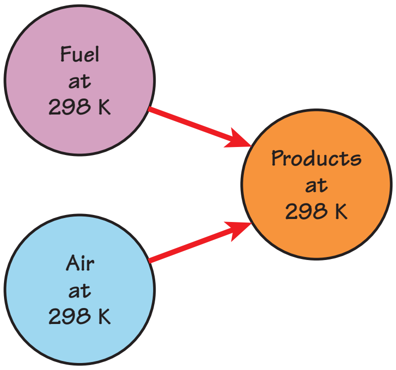
Note that the value of the enthalpy of combustion depends on the temperature chosen for its evaluation. Because the enthalpies of both the reactants and products vary with temperature, the distance between the H_{prod} and H_{reac} lines in Fig. 2.38 is not constant.

2.10b Heating Values

The **heat of combustion, Δh_c** (known also as the **heating value**), is numerically equal to the enthalpy of reaction, but with opposite sign. The **upper** or **higher heating value, HHV**, is the heat of combustion calculated assuming that all of the water in the products has condensed to liquid. In this scenario, the reaction liberates the most amount of energy, hence leading to the designation "upper." The **lower heating value, LHV**, corresponds to the case where none of the water is assumed to condense. For CH_4, the upper heating value is approximately 11% larger than the lower one. Standard-state heating values for a variety of hydrocarbon fuels are given in Appendix H.

Fuel heating values are used to define the efficiency of gas-turbine engines in Chapter 12. See Eq. 12.38.

Example 2.26



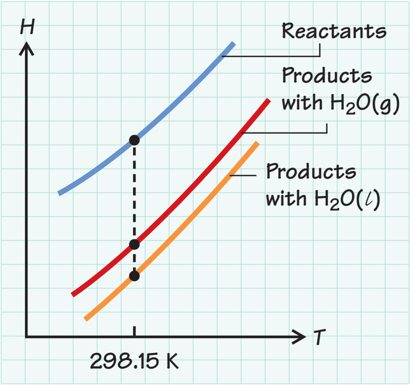
Determine the upper and lower heating values of gaseous *n*-decane ($C_{10}H_{22}$) for stoichiometric combustion with air at 298.15 K. For this condition, 15.5 kmol of O_2 reacts with each kmol of $C_{10}H_{22}$ to produce 10 kmol of CO_2 and 11 kmol of H_2O. Assume that air can be represented as a mixture of O_2 and N_2 in which there are 3.76 kmol of N_2 for each kmol of O_2. Express the results per unit mass of fuel. The molecular weight of *n*-decane is 142.284.

Solution

Known T, compositions of reactant and product mixtures, $\mathcal{M}_{C_{10}H_{22}}$

Find Δh_c (upper and lower)

Sketch



Assumption

Ideal-gas behavior

Conservation of elements is treated in detail in Chapter 3. See Example 3.14.

Analysis For 1 kmol of $C_{10}H_{22}$, stoichiometric combustion can be expressed from the given information as (see also Eqs. 3.53 and 3.54):

$$\begin{aligned} &C_{10}H_{22}(g) + 15.5\,(O_2 + 3.76\,N_2) \\ &\rightarrow 10\,CO_2 + 11\,H_2O\,(\ell \text{ or } g) + 15.5\,(3.76)\,N_2. \end{aligned}$$

For either the upper or lower heating value,

$$\Delta H_c = -\Delta H_R = H_{reac} - H_{prod},$$

where the numerical value of H_{prod} depends on whether the H_2O in the products is liquid (defining the higher heating value) or gaseous (defining the lower heating value). The sensible enthalpy changes for all species involved are zero since we desire ΔH_c at the reference state (298.15 K). Furthermore, the enthalpies of formation of the O_2 and N_2 are also zero at 298.15 K. Recognizing that

$$H_{reac} = \sum_{reac} N_i \bar{h}_i \quad \text{and} \quad H_{prod} = \sum_{prod} N_i \bar{h}_i,$$

we obtain

$$\Delta H_{c,H_2O(\ell)} = \mathrm{HHV} = (1)\bar{h}^{\circ}_{f,C_{10}H_{22}} - \left[10\bar{h}^{\circ}_{f,CO_2} + 11\bar{h}^{\circ}_{f,H_2O(\ell)}\right].$$

Note that the N_2 contribution as a reactant cancels with the N_2 contribution as a product. Table B.6 (Appendix B) gives the enthalpy of formation for gaseous water; the enthalpy of vaporization, h_{fg}, is obtained from Table D.1 or the NIST database. We thus calculate the enthalpy of formation of the liquid water as follows:

$$\begin{aligned} \bar{h}^{\circ}_{f,H_2O(\ell)} &= \bar{h}^{\circ}_{f,H_2O(g)} - \bar{h}_{fg} \\ &= -241{,}847 \text{ kJ/mol} - (45{,}876 - 1889) \text{ kJ/mol} \\ &= -285{,}834 \text{ kJ/mol}. \end{aligned}$$

Using this value together with enthalpies of formation given in Appendices B and H, we obtain the higher heating value:

$$\begin{aligned} \Delta H_{c,H_2O(\ell)} &= (1)(-249{,}659) - [10(-393{,}546) + 11(-285{,}834)] \\ &= 6{,}829{,}975 \\ [=]\ &\text{kmol}\left(\frac{\text{kJ}}{\text{kmol}}\right) = \text{kJ}. \end{aligned}$$

To express this on a per-mass-of-fuel basis, we need only divide by the number of moles of fuel in the combustion reaction and the fuel molecular weight, that is,

$$\begin{aligned} \Delta h_c &= \frac{\Delta H_c}{M_{C_{10}H_{22}}} = \frac{\Delta H_c}{N_{C_{10}H_{22}}\mathcal{M}_{C_{10}H_{22}}} \\ &= \frac{6{,}829{,}975}{(1)\ 142.284} = 48{,}002 \\ [=]\ &\frac{\text{kJ}}{\text{kmol(kg/kmol)}} = \text{kJ/kg}_{\text{fuel}}. \end{aligned}$$

For the lower heating value, we repeat these calculations using $\overline{h}^{\circ}_{f,H_2O(g)} = -241{,}847$ kJ/kmol in place of $\overline{h}^{\circ}_{f,H_2O(\ell)} = -285{,}834$ kJ/kmol. The result is

$$\Delta H_c = 6{,}345{,}986 \text{ kJ}$$

and

$$\Delta h_c = 44{,}601 \text{ kJ/kg}_{\text{fuel}}.$$

Comment We note that the difference between the higher and lower heating values is approximately 7%. What practical implications does this have, say, for a home heating furnace?

Self Test 2.26

☑ **Determine the enthalpy of reaction per unit mass of fuel for the conditions given in Example 2.26 when the products are at a temperature of 1800 K.**

(Answer: $\Delta h_R = -14{,}114$ kJ/kg fuel)

2.11 TRANSPORT PROPERTIES[18]

In addition to thermodynamic properties, we require **transport properties** to characterize many thermal-fluid systems. Of particular interest are the thermal conductivity k and the viscosity μ. These two properties are not defined by thermodynamic analyses of systems in equilibrium, as are all of the properties

Common materials in order of decreasing thermal conductivity: pure gold, copper alloy, steel, stone block, ceramic tile, and fiberglass insulation.

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[18] This section is appropriately used in conjunction with the study of conduction heat transfer in Chapter 5 and viscous fluid flow in Chapter 6.

discussed previously, but result from the dynamic, or rate, processes of thermal energy transfer and momentum transfer, respectively. Both thermal conductivity and viscosity can be predicted from models of the behavior of atoms, molecules, and electrons in the solid, liquid, and gaseous states of matter. Other commonly used transport properties are related in simple ways to the thermal conductivity and the viscosity. For example, the thermal diffusivity $\alpha(\equiv k/\rho c_p)$ is introduced in Chapter 5; the kinematic viscosity, also known as the momentum diffusivity, $\nu(\equiv \mu/\rho)$, is introduced in Chapter 6.

2.11a Thermal Conductivity

Physically, **thermal conductivity *k*** is the proportionality factor relating the rate of energy transfer per unit area by conduction, $\dot{Q}''_{\text{cond}}$, to its driving potential, the temperature gradient; that is,

$$\dot{Q}''_{\text{cond}} \propto -\nabla T \tag{2.78a}$$

or

$$\boxed{\dot{Q}''_{\text{cond}} = -k\nabla T.} \tag{2.78b}$$

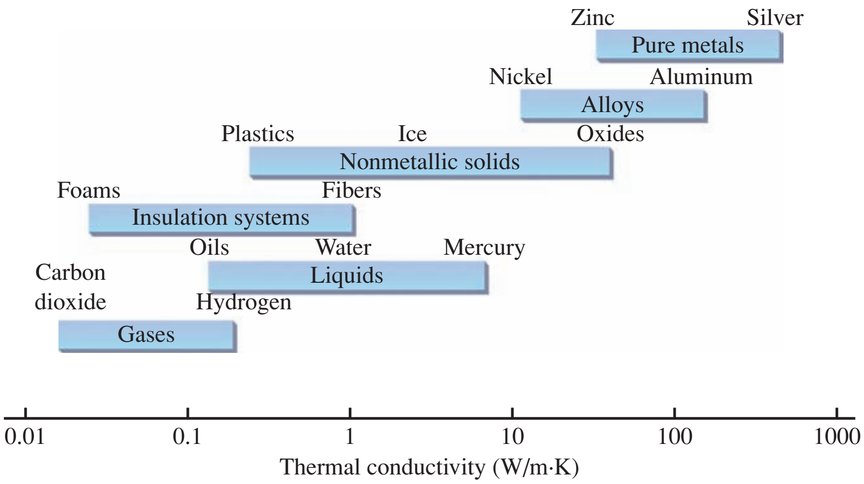
The SI units associated with the thermal conductivity are

$$k\,[=]\,\text{W/m}\cdot\text{K}.$$

Figure 2.39 illustrates the wide range of thermal conductivity values associated with various substances. From this figure, we see that gases have the smallest magnitudes (say, 0.02–0.13 W/m·K), liquids have intermediate values (say, 0.12–9 W/m·K), and pure metals have the highest values (say, 35–400 W/m·K). Falling between the most conducting pure metal and the least conducting gases are metal alloys and nonmetallic solids. Also indicated in Fig. 2.39 are insulation systems. These systems are neither pure substances nor intimate mixtures of pure substances but, rather, complex nonhomogeneous systems comprised, for example, of fiberglass fibers and air-filled voids, or various layers of foils and/or fabrics. For these systems, the thermal conductivity is an **effective conductivity** since the energy exchange across a layer of such material results from the combined effects of conduction, convection, and radiation.

Chapter 4 discusses these three modes of heat transfer: conduction, convection, and Radiation.

FIGURE 2.39
Typical ranges of thermal conductivity values for gases, liquids, insulation systems, nonmetallic solids, alloys, and pure metals. **Adapted from Ref. [19] with permission.**



In general, values of thermal conductivity depend on temperature, with weak, or essentially no, dependence on pressure. For gases, a simple kinetic-theory model of energy transfer can be used to explain the dependence of the thermal conductivity on temperature. In this model, molecules in regions of higher temperature have greater kinetic energies than nearby molecules in regions of lower temperature, where the differences in temperature are associated with the temperature gradient ∇T, or dT/dx for a 1-D system. With no net bulk motion, higher energy molecules collide with lower energy molecules, and vice versa. The net effect is an energy transfer from high to low temperature, as expressed by Eq. 2.78. Since the mechanism for energy transfer is the collision of molecules, we expect the energy transfer rate to be proportional to the collision rate. The collision rate, in turn, is proportional to the number of molecules per unit density, $N/\mathcal{V}$, and the mean molecular speed $\bar{v}_{\text{molec}}$. A more complete analysis [1] shows that

$$k \propto (N/\mathcal{V})\bar{v}_{\text{molec}}\ell_{\text{mf}},$$

where ℓ_{mf} is the mean free path, the average distance traveled by a molecule between collisions. Because the mean free path is inversely proportional to the number density $N/\mathcal{V}$, the temperature and pressure dependence inherent in $N/\mathcal{V}$ ($\propto T/P$) cancels in our simple model for conductivity. We are left with the conductivity being proportional to the mean molecular speed. The molecular speed, in turn, increases with temperature and with a decrease in the mass and size of the molecules involved. Thus, among the gases, small, light molecules, such as H_2 or He, at high temperatures exhibit the greatest conductivity. Appendix F provides tabulations of k for a range of temperatures for various gases; values for air are given in Appendix C. The NIST software and online database [11] can also be used to obtain values of thermal conductivity for selected gases (see Table 2.7).

The mechanism for energy transfer by conduction in liquids is similar to that of gases, except that the range of interaction is much shorter and the strength and frequency of the molecular collisions greater. Appendix G presents tabulations of k for water and a few other common liquids as functions of temperature. The NIST software and online database [11] also provide values of k for selected liquids (see Table 2.7).

In solids, the mechanism for energy transfer by conduction is the combined effects of lattice waves and the flow of free electrons. In amorphous solids, lattice waves are essentially the sole mechanism, whereas, for metals, electron flow dominates the transport. For metal alloys and nonmetallic crystalline solids, both mechanisms are important. Appendix I provides extensive tabulations of thermal conductivities for pure solids and for commonly used engineering materials such as insulations and building materials.

2.11b Viscosity[19]

In analogy to energy transport by conduction, the **viscosity** μ is the proportionality factor relating the rate at which momentum is transferred per unit area within a fluid to the application of a driving potential (i.e., a velocity

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[19] The *viscosity* as used here is sometimes referred to as the *absolute viscosity* or the *coefficient of viscosity*. These terms are used interchangeably.

gradient). Alternatively, the viscosity may be thought of as the proportionality factor in the stress–strain relationship associated with a fluid:

$$\text{stress} \propto \text{strain rate}, \tag{2.79a}$$

or

$$\text{stress} = \mu(\text{strain rate}). \tag{2.79b}$$

The SI units of viscosity are $N \cdot s/m^2$. For a more detailed definition of viscosity, the reader is referred to Chapter 6.

Ideas or constructs similar to those discussed here for gases and liquids apply to understanding viscosity except that, now, momentum transport replaces energy transport, and the velocity gradient replaces the temperature gradient. From such arguments, we again conclude that values of viscosity depend on temperature and are weakly sensitive, or insensitive, to pressure. Tabulations of viscosity are presented for air in Appendix C and for various gases and various liquids in Appendices F and G, respectively. Again, values are also available from the NIST software and online database [11] for selected fluids. Note that, for a solid, viscosity has no meaning, and the stress–strain relationship is defined by Young's modulus.

SUMMARY

This chapter introduced the reader to the myriad thermodynamic and thermophysical properties that are used throughout this book. The chapter also showed how these properties relate to one another through equations of state, calorific equations of state, and second-law (or Gibbs) relationships. The concept of an ideal gas was presented, and methods were presented to obtain properties for substances that do not behave as ideal gases. The properties of H_2O in both its liquid and vapor states were emphasized. You should be familiar with the use of both tables and computer-based resources to obtain property data for a wide variety of substances. You should also be proficient at sketching simple processes on thermodynamic coordinates. A more detailed summary of this chapter can be obtained by reviewing the learning objectives presented at the outset. It is recommended that you revisit this chapter many times in the course of your study of later chapters. Appropriate junctures for return are indicated in subsequent chapters.

Chapter 2
Key Concepts & Definitions Checklist[20]

2.1 Key Definitions

- ☐ Property ➤ ***Q2.2***
- ☐ State ➤ ***Q2.2***
- ☐ Process ➤ ***Q2.2***
- ☐ Pure substance ➤ ***Q2.3***
- ☐ Simple compressible substance ➤ ***Q2.3***
- ☐ Extensive and intensive properties ➤ ***Q2.6***
- ☐ Mass- and molar-specific properties ➤ ***Q2.7***

2.2 Frequently Used Thermodynamic Properties

- ☐ Common thermodynamic properties (list)
- ☐ Continuum limit ➤ ***Q2.5***
- ☐ Absolute, gage, and vacuum pressures ➤ ***2.3, 2.4***
- ☐ Zeroth law of thermodynamics ➤ ***Q2.12***
- ☐ Internal energy ➤ ***2.17***
- ☐ Enthalpy ➤ ***2.18***
- ☐ Constant-volume and constant-pressure specific heats ➤ ***Q2.11***
- ☐ Specific heat ratio ➤ ***Q2.13***
- ☐ Entropy ➤ ***Q2.14***
- ☐ Gibbs free energy or function ➤ ***Q2.15***

2.3 Concept of State Relationships

- ☐ State principle ➤ ***Q2.8***
- ☐ P–v–T relationships ➤ ***Q2.9, Q2.10***
- ☐ Calorific relationships ➤ ***Q2.9, Q2.10***
- ☐ Second-law relationships ➤ ***Q2.9, Q2.10, Q2.16***

2.4 Ideal Gases as Pure Substances

- ☐ Ideal gas definition ➤ ***2.23, 2.36***
- ☐ Ideal-gas equation of state (Table 2.4) ➤ ***2.27, 2.31***
- ☐ Particular gas constant ➤ ***2.36***
- ☐ P–v and T–v diagrams ➤ ***2.35***
- ☐ u, c_v, T relationships (Eqs. 2.31a–2.31e) ➤ ***2.46***
- ☐ h, c_p, T relationships (Eqs. 2.33a–2.33e) ➤ ***2.41, 2.42***
- ☐ u–T and h–T diagrams ➤ ***2.22, 2.46***
- ☐ T–dS relationships (Eqs. 2.35 and 2.36) ➤ ***Q2.21***
- ☐ Δs relationships (Eqs. 2.39 and 2.40) ➤ ***2.54, 2.56***
- ☐ Isentropic process relationships (Table 2.5) ➤ ***2.57, 2.58***
- ☐ T–s and P–v diagrams (Figs. 2.11 and 2.12) ➤ ***2.59***
- ☐ Polytropic processes ➤ ***2.60***

2.5 Nonideal Gas Properties

- ☐ Critical point ➤ ***Q2.24***
- ☐ Use of tables and NIST databases ➤ ***2.73, 2.74***
- ☐ Van der Waals equation of state ➤ ***2.75***
- ☐ Generalized compressibility ➤ ***2.72***

2.6 Pure Substances Involving Liquid and Vapor Phases

- ☐ Regions and phase boundaries ➤ ***Q2.27***
- ☐ T–v and P–v diagrams ➤ ***Q2.28, 2.83***
- ☐ Quality and liquid–vapor mixture properties ➤ ***Q2.25, 2.99***
- ☐ Use of tables and NIST databases ➤ ***2.79, 2.80***
- ☐ T–s and h–s diagrams ➤ ***Q2.29***

2.7 Liquid Property Approximations

- ☐ Specific volume, internal energy, and enthalpy approximations ➤ ***2.116***

2.8 Solids

- ☐ Fusion and sublimation properties ➤ ***Q2.32***

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[20] Numbers following arrows refer to Questions (prefaced with a Q) and Problems at the end of the chapter.

2.9 Ideal-Gas Mixtures

- ☐ Partial pressures and mole and volume fractions ➤ ***2.126***
- ☐ Standardized properties ➤ ***Q2.37, 2.132***
- ☐ Enthalpy of formation ➤ ***Q2.38***
- ☐ Sensible enthalpy change ➤ ***Q2.38***
- ☐ Standard reference state (Table 2.8) ➤ ***Q2.39***
- ☐ Mixture properties (Eqs. 2.71–2.76) ➤ ***2.135***

2.10 Some Properties of Reacting Mixtures

- ☐ Enthalpy of reaction ➤ ***2.141, Q2.40***
- ☐ Heat of combustion and higher and lower heating values ➤ ***Q2.41, 2.143***

2.11 Transport Properties ➤ ***2.144***

- ☐ Thermal conductivity
- ☐ Viscosity

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

23. Look, D. C., Jr., and Sauer, H. J., Jr., *Engineering Thermodynamics*, PWS, Boston, 1986.

Nomenclature

$\mathbf{a}$	Acceleration vector (m/s^2)
a	Specific Helmholtz free energy (J/kg or van der Waals constant (Pa · m^6/kmol^2)
A	Helmoltz free energy (J) or area (m^2)
b	Van der Waals constant (m^3/kmol)
c	Specific heat (J/kg · K)
c_p	Constant-pressure specific heat (J/kg · K)
$\bar{c}_p$	Molar constant-pressure specific heat (J/kmol · K)
c_v	Constant-volume specific heat (J/kg · K)
$\bar{c}_v$	Molar constant-volume specific heat (J/kmol · K)
e	Specific energy (J/kg)
$\bar{e}$	Molar-specific energy (J/kmol)
E	Energy (J)
F	Force (N)
g	Specific Gibbs function (J/kg)
$\bar{g}$	Molar-specific Gibbs function (J/kmol)
G	Gibbs function (J)
h	Specific enthalpy (J/kg)
$\bar{h}$	Molar-specific enthalpy (J/kmol)
H	Enthalpy (J)
HHV	Higher heating value (J/kg$_{\text{fuel}}$)
k	Thermal conductivity (W/m · K)
k_B	Boltzmann constant, 1.3806503 × 10^{-23} (J/K)
ℓ_{mf}	Mean free path (m)
LHV	Lower heating value (J/kg$_{\text{fuel}}$)
M	Mass (kg)
$\mathcal{M}$	Molecular weight (kg/kmol)
m_u	Unified atomic mass unit (kg)
n	Number of particles or polytropic exponent (dimensionless)
N	Number of moles (kmol)

$\mathcal{N}_{AV}$	Avagodro's number (see Eq. 2.7)
P	Pressure (Pa)
$\dot{Q}''_{cond}$	Conduction heat flux (W/m^2)
R	Particular gas constant (J/kg · K)
R_u	Universal gas constant, 8,314.472 (J/kmol · K)
s	Specific entropy (J/kg · K)
$\bar{s}$	Molar-specific entropy (J/kmol · K)
S	Entropy (J/K)
t	Time (s)
T	Temperature (K)
u	Specific internal energy (J/kg)
$\bar{u}$	Molar-specific internal energy (J/kmol)
U	Internal energy (J)
v	Velocity (m/s)
$\bar{v}_{molec}$	Mean molecular speed (m/s)
v	Specific volume (m^3/kg)
$\bar{\mathrm{v}}$	Molar-specific volume (m^3/kmol)
$\mathcal{V}$	Volume (m^3)
x	Quality (dimensionless) or spatial coordinate (m)
X	Mole fraction (dimensionless)
y	Spatial coordinate (m)
Y	Mass fraction (dimensionless)
z	Spatial coordinate (m)
Z	Compressibility factor, $P\mathrm{v}/RT$ (dimensionless)

GREEK

β	Arbitrary property
γ	Specific-heat ratio (dimensionless)
Δ	Difference or increment
ΔH_R	Enthalpy of reaction (or of combustion) (J)

Δh_R	Enthalpy of reaction (or of combustion) per mass of fuel (J/kg_{fuel})
Δh_c	Heat of combustion or heating value (J/kg_{fuel})
μ	Viscosity ($N \cdot s/m^2$)
ρ	Density (kg/m^3)

SUBSCRIPTS

abs	absolute
atm	atmospheric
avg	average
c	critical
f	fluid (liquid) or formation
fg	difference between saturated vapor and saturated liquid states
g	gas (vapor)
gage	gage
i	species *i*
liq	liquid
mix	mixture
molec	molecule
prod	products
reac	reactants
ref	reference state
rot	rotational
s	sensible
sat	saturated state
sublim	sublimation
tot	total
trans	translational
vac	vacuum
vap	vapor
vib	vibrational

SUPERSCRIPTS

°	Denotes standard-state pressure ($P° =$ 1 atm)

QUESTIONS

2.1 Review the most important equations presented in this chapter (i.e., those with a red background). What physical principles do they express? What restrictions apply?

2.2 Discuss how the following concepts are related: properties, states, and process.

2.3 Distinguish between a pure substance and a simple compressible substance.

2.4 Explain the continuum limit to a classmate.

2.5 Without direct reference to any textbook, write an explanation of the continuum limit.

2.6 Explain the difference between extensive and intensive properties. List five (or more) properties of each type.

2.7 How do the properties u and $\bar{u}$ differ? The properties v and $\bar{v}$?

2.8 Write out the state principle for a simple compressible substance.

2.9 Explain the distinction between an equation of state and a calorific equation of state.

2.10 What are the three types of thermodynamic state relationships? What properties are typically used in each?

2.11 Distinguish between constant-volume and constant-pressure specific heats.

2.12 What is the practical significance of the zeroth law of thermodynamics?

2.13 Define the specific-heat ratio. What Greek symbol is used to denote this ratio?

2.14 Write out a qualitative definition of the thermodynamic property entropy.

2.15 Using symbols, define the Gibbs free energy (or function) in terms of other thermodynamic properties.

2.16 Consider an ideal gas. Indicate which of the following thermodynamic properties are pressure dependent: density, specific volume, molar-specific internal energy, mass-specific enthalpy, mass-specific entropy, constant-volume specific heat, and constant-pressure specific heat.

2.17 Sketch two isotherms on a P–v plot for an ideal gas. Label each where $T_2 > T_1$.

2.18 Sketch two isobars on a T–v plot for an ideal gas. Label each where $P_2 > P_1$.

2.19 What is the microscopic interpretation of internal energy for a monatomic gas?

2.20 What is the microscopic interpretation of internal energy for a gas comprising diatomic molecules?

2.21 Write out the so-called first and second Gibbs (or T–dS) relationships.

2.22 List fluids that you know are used as working fluids in thermal-fluid devices.

2.23 Compare your list of fluids from Question 2.22 with the fluids for which property data are available from the NIST online database.

2.24 What is the physical significance of the critical point? Locate the critical point on a P–v diagram.

2.25 Write out a physical interpretation of the thermodynamic property quality.

2.26 Explain the meaning of quality to a classmate.

2.27 Draw from memory (or familiarity) a T–v diagram for H_2O. Show an isobar that begins in the compressed-liquid region and ends in the superheated-vapor region. Label all lines and regions and indicate the critical point.

2.28 Draw from memory (or familiarity) a P–v diagram for H_2O. Show an isotherm that begins in the compressed-liquid region and ends in the superheated-vapor region. Label all lines and regions and indicate the critical point.

2.29 Draw from memory (or familiarity) a T–s diagram for H_2O. Show an isobar that begins in the compressed-liquid region and ends in the superheated-vapor region. Also draw an isotherm that crosses your isobar at a state well within the superheated-vapor region. Label each.

2.30 Explain the principle of corresponding states and how this principle relates to the use of the generalized compressibility chart.

2.31 List and explain the factors that result in the breakdown of the application of the ideal-gas approximation to real gases.

2.32 Distinguish between the enthalpy of fusion and the enthalpy of sublimation.

2.33 Consider an ideal-gas mixture. Explain the differences and similarities among the following measures of composition: mole fraction, volume fraction, and mass fraction.

2.34 How does the partial pressure of a constituent in an ideal-gas mixture relate to the mole fraction of that constituent?

2.35 Compare and contrast Dalton's and Amagat's views of an ideal-gas mixture.

2.36 Explain in words how the mass-specific and molar-specific enthalpies of an ideal-gas mixture relate to the corresponding properties of the constituent species.

2.37 Explain the concept of standardized properties applied to chemically reacting systems.

2.38 Distinguish between enthalpies of formation and sensible enthalpies.

2.39 List the conditions that define the standard reference state for properties of species involved in reacting systems.

2.40 What is the sign (positive or negative) associated with the enthalpy of reaction for exothermic reactions? For endothermic reactions? Explain.

2.41 Explain what is meant by the heating value of a fuel. What distinguishes the "higher" heating value from the "lower" heating value?

Chapter 2 Problem Subject Areas

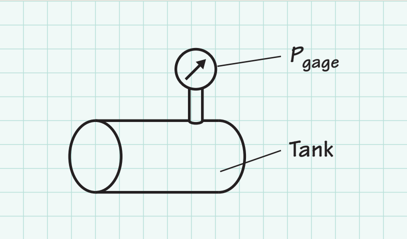
2.1–2.16	**State properties: definitions, units, and conversions**
2.17–2.22	**Calorific properties: definitions and units**
2.23–2.39	**Ideal gases: equation of state**
2.40–2.56	**Ideal gases: calorific and second-law state relationships**
2.57–2.71	**Ideal gases: isentropic and polytropic processes**
2.72–2.78	**Real gases: tabulated properties, generalized compressibility, and van der Waals equation of state**
2.79–2.114	**Pure substances with liquid and vapor phases**
2.115–2.116	**Liquid property approximations**
2.117–2.118	**Solids**
2.119–2.125	**Ideal-gas mixtures: specifying composition**
2.126–2.131	**Ideal-gas mixtures: P–v–T relationships**
2.132–2.133	**Ideal-gas mixtures: standardized properties**
2.134–2.140	**Ideal-gas mixtures: enthalpies and entropies**
2.141–2.143	**Ideal-gas mixtures: enthalpy of combustion and heating values**
2.144–2.145	**Transport properties**

PROBLEMS

2.1 The specific volume of water vapor at 150 kPa and 120°C is 1.188 m^3/kg. Determine the molar-specific volume and the density of the water vapor.

2.2 Determine the number of molecules in 1 kg of water.

2.3 An air compressor fills a tank to a gage pressure of 100 psi. The barometric pressure is 751 mm Hg. What is the absolute pressure in the tank in kPa?



2.4 An instrument used to measure the concentration of the pollutant nitric oxide uses a vacuum pump to create a vacuum of 28.3 in Hg in a reaction chamber. What is the absolute pressure in the chamber if the barometric pressure is 1 standard atmosphere? Express your result in psia, mm Hg, and Pa.

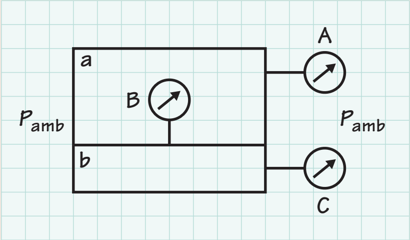
2.5 Find the specific volume (in both ft^3/lb_m and m^3/kg) of 45 lb_m of a substance of density 10 kg/m^3, where the acceleration of gravity is 30 ft/s^2.

2.6 Assume that a pressure gage and a barometer read 227.5 kPa and 26.27 in Hg, respectively. Calculate the absolute pressure in psia, psfa (pounds-force per square foot absolute), and atm.

2.7 The pressure in a partially evacuated enclosure is 26.8 in Hg vacuum when the local barometer reads 29.5 in Hg. Determine the absolute pressure in in Hg, psia, and atm.

2.8 A vertical cylinder containing air is fitted with a piston of 68 lb_m and cross-sectional area of 35 in^2. The ambient pressure outside the cylinder is 14.6 psia and the local acceleration due to gravity is 31.1 ft/s^2. What is the air pressure inside the cylinder in psia and in psig?

2.9 The accompanying sketch shows a compartment divided into two sections *a* and *b*. The ambient pressure P_{amb} is 30.0 in Hg (absolute). Gage *C* reads 620,528 Pa and gage *B* reads 275,790.3 Pa. Determine the reading of gage *A* and convert this reading to an absolute value.



2.10 A cylinder containing a gas is fitted with a piston having a cross-sectional area of 0.029 m^2. Atmospheric pressure is 0.1035 MPa and the acceleration due to gravity is 30.1 ft/s^2. To produce an absolute pressure in the gas of 0.1517 MPa, what mass (kg) of piston is required?

2.11 For safety, cans of whipped cream (with propellant) should not be stored above 120 F. What is this temperature expressed on the Rankine, Celsius, and Kelvin temperature scales?

2.12 Albuterol inhalers, used for the control of asthma, are to be stored and used between 15°C and 30°C. What is the acceptable temperature range on the Fahrenheit scale?

2.13 How fast, on average, do nitrogen molecules travel at room temperature (25°C)? How does this speed compare to the average speed of a modern jet aircraft that travels 2500 miles in 5 hours?

2.14 A thermometer reads 72 F. Specify the temperature in °C, K, and R.

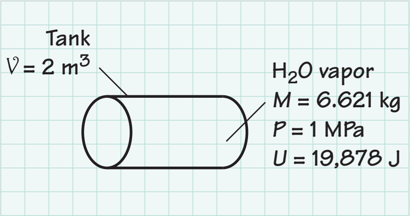
2.15 Convert the following Celsius temperatures to Fahrenheit: (a) −30°C, (b) −10°C, (c) 0°C, (d) 200°C, and (e) 1050°C.

2.16 At what temperature are temperatures expressed in Fahrenheit and Celsius numerically equal?

2.17 At 600 K and 0.10 MPa, the mass-specific internal energy of water vapor is 2852.4 kJ/kg and the specific volume is 2.7635 m^3/kg. Determine the density and mass-specific enthalpy of the water vapor. Also determine the molar-specific internal energy and enthalpy.

2.18 At 0.3 MPa, the mass-specific internal energy and enthalpy of a substance are 3313.6 J/kg and 3719.2 J/kg, respectively. Determine the density of the substance at these conditions.

2.19 A tank having a volume of 2 m^3 contains 6.621 kg of water vapor at 1 MPa. The internal energy of the water vapor is 19,878 J. Determine the density, the mass-specific internal energy, and the mass-specific enthalpy of the water vapor.



2.20 The constant-volume molar-specific heat of nitrogen (N_2) at 1000 K is 24.386 kJ/kmol·K and the specific-heat ratio γ is 1.3411. Determine the constant-pressure molar-specific heat and the constant-pressure mass-specific heat of the N_2.

2.21 For temperatures between 300 and 1000 K and at 1 atm, the molar specific enthalpy of O_2 is expressed by the following polynomial:

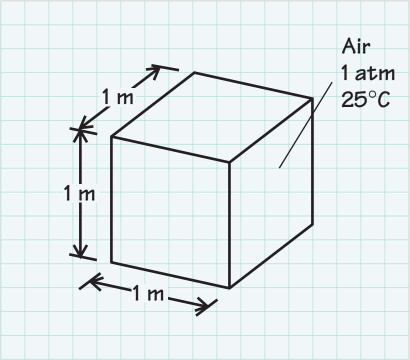
$$\begin{aligned}\bar{h}_{O_2} = R_u(&3.697578\,T + 3.0675985 \times 10^{-4}\,T^2\\ &-4.19614 \times 10^{-8}\,T^3 + 4.4382025 \times 10^{-12}\,T^4\\ &-2.27287 \times 10^{-16}\,T^5 - 1233.9301),\end{aligned}$$

where $\bar{h}$ is expressed in kJ/kmol and T in kelvins.

Determine the constant-pressure molar-specific heat $\bar{c}_p$ at 500 K and at 1000 K. Compare the magnitudes of the values at the two temperatures and discuss. Also determine c_p, the constant-pressure *mass*-specific heat.

2.22 Plot a graph of the molar specific enthalpy for O_2 given in Problem 2.21 for the temperature range 300–1000 K (i.e., plot $\bar{h}_{O_2}$ versus T). (Spreadsheet software is recommended.) Use your plot to graphically determine $\bar{c}_p$ at 500 K and at 1000 K. Use a pencil and ruler to perform this operation. How do these estimated values for $\bar{c}_p$ compare with your computations in Problem 2.21?

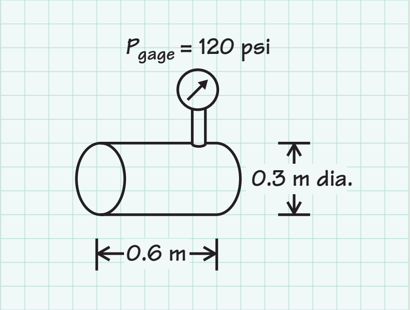
2.23 What is the mass of a cubic meter of air at 25°C and 1 atm?



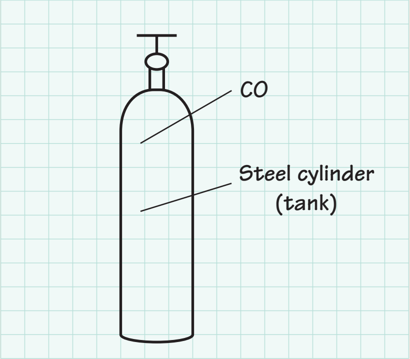
2.24 A. Determine the density of air at Mile High Stadium in Denver, Colorado, on a warm summer evening when the temperature is 78 F. The barometric pressure is 85.1 kPa.

B. Assume to a first approximation that the drag force exerted on a well-hit baseball arcing to the outfield, or beyond, is proportional to the air density. Discuss the implications of this for balls hit at Mile High Stadium in Denver versus balls hit in Yankee Stadium in New York (which is at sea level).

2.25 A compressor pumps air into a tank until a pressure gage reads 120 psi. The temperature of the air is 85 F, and the tank is a 0.3-m-diameter cylinder 0.6 m long. Determine the mass of the air contained in the tank in grams.

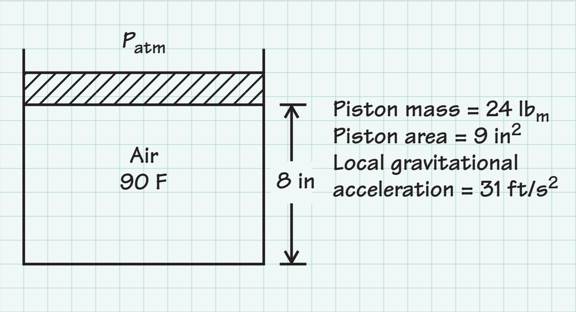


2.26 Determine the number of kmols of carbon monoxide contained in a 0.027-m^3 compressed-gas cylinder at 200 psi and 72 F. Assume ideal-gas behavior.



2.27 A piston-cylinder assembly contains of 9.63 m^3 air at 29.4°C. The piston has a cross-sectional area of 0.029 in^2 and a mass of 160.6 kg. The gravitational acceleration is 9.144 m/s^2. Determine the mass of air trapped within the cylinder. Atmospheric pressure is 0.10135 MPa.

2.28 Consider the piston–cylinder arrangement shown in the sketch. Determine the absolute pressure of the air (psia) and the mass of air in the cylinder (lb$_m$). The atmospheric pressure is 14.6 psia.



2.29 Determine the mass of air in a room that is 15 m by 15 m by 2.5 m. The temperature and pressure are 25°C and 1 atm, respectively.

2.30 Carbon monoxide is discharged from an exhaust pipe at 49°C and 0.8 kPa. Determine the specific volume (m^3/kg) of the CO.

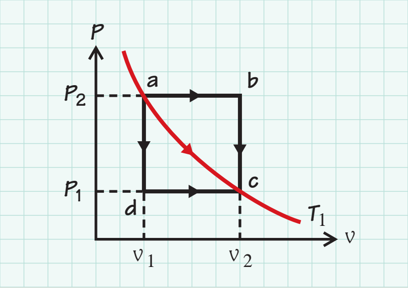
2.31 A cylinder–piston arrangement contains nitrogen at 21°C and 1.379 MPa. The nitrogen is compressed from 98 to 82 cm^3 with a final temperature of 27°C. Determine the final pressure (kPa).

2.32 The temperature of an ideal gas remains constant while the pressure changes from 101 to 827 kPa. If the initial volume is 0.08 m^3, what is the final volume?

2.33 Nitrogen (3.2 kg) at 348°C is contained in a vessel having a volume of 0.015 m^3. Use the ideal-gas equation of state to determine the pressure of the N$_2$.

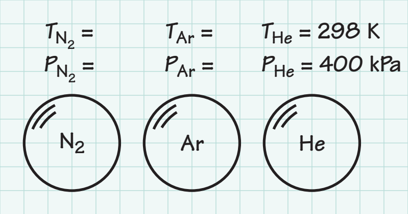
2.34 On P–v coordinates, sketch a process in which the product of the pressure and specific volume are constant from state 1 to state 2. Assume an ideal gas. Also assume $P_1 > P_2$ Show this same process on P–T and T–v diagrams.

2.35 Consider the five processes a–b, b–c, c–d, d–a, and a–c as sketched on the P–v coordinates. Show the same processes on P–T and T–v coordinates assuming ideal-gas behavior.

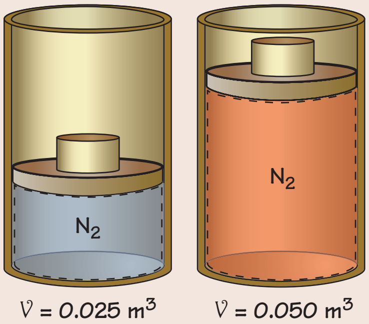


2.36 Starting with Eq. 2.28c, derive all other forms of the ideal-gas law, (i.e., Eqs. 2.28a, 2.28b, 2.28d, and 2.28e).

2.37 Consider three 0.03-m^3 tanks filled, respectively, with N$_2$, Ar, and He. Each tank is filled to a pressure of 400 kPa at room temperature, 298 K. Determine the mass of gas contained in each tank. Also determine the number of moles of gas (kmol) in each tank.



2.38 Nitrogen slowly expands from an initial volume of 0.025 m^3 to 0.05 m^3 at a constant pressure of 400 kPa. Determine the final temperature if the initial temperature is 500 K. Plot the process on P–v and T–v coordinates using spreadsheet software.



2.39 Repeat Problem 2.38 for a constant-temperature process (500 K). Determine the final pressure for an initial pressure of 400 kPa.

2.40 The constant-pressure specific heat of a gas is 0.24 Btu/lb$_m$·R at room temperature. Determine the specific heat in units of kJ/kg·K.

2.41 Compute the mass-specific enthalpy change associated with N_2 undergoing a change in state from 400 to 800 K. Assume the constant-pressure specific heat is constant for your calculation. Use the arithmetic average of values at 400 and 800 K from Table B.7.

2.42 Compare the specific enthalpy change calculated in Problem 2.41 with the change determined directly from the ideal-gas tables (Table B.7). Also compare these values with that obtained from the NIST software or online database at 1 atm.

2.43 Use Table C.2 to calculate the mass-specific enthalpy change for air undergoing a change of state from 300 to 1000 K. How does this value compare with that estimated using the constant-pressure specific heat at the average temperature, $T_{\text{avg}} = (300 + 1000)/2$?

2.44 Determine the mass-specific internal energy for O_2 at 900 K for a reference-state temperature of 298.15 K. Also determine the constant-volume specific heat (mass basis).

2.45 Hydrogen is compressed in a cylinder from 101 kPa and 15°C to 5.5 MPa and 121°C. Determine Δv, Δu, Δh, and Δs for the process.

2.46 As air flows across the cooling coil of an air conditioner at the rate of 3856 kg/hr, its temperature drops from 26°C to 12°C. Determine the internal energy change in kJ/hr. Plot the process on h–T coordinates.

2.47 Air cools an electronics compartment by entering at 60 F and leaving at 105 F. The pressure is essentially constant at 14.7 psia. Determine (a) the change in internal energy of the air as it flows through the compartment and (b) the change in specific volume.

2.48 Nitrogen is compressed adiabatically in a cylinder having an initial volume of 0.25 ft^3. The initial pressure and temperature are 20 psia and 100 F, respectively. The final volume is 0.1 ft^3 and the final pressure is 100 psia. Assuming ideal-gas behavior and using average specific heats, determine the following:

A. Final temperature (F)
B. Mass of nitrogen (lb$_\text{m}$)
C. Change in enthalpy (Btu)
D. Change in entropy (Btu/R)
E. Change in internal energy (Btu)

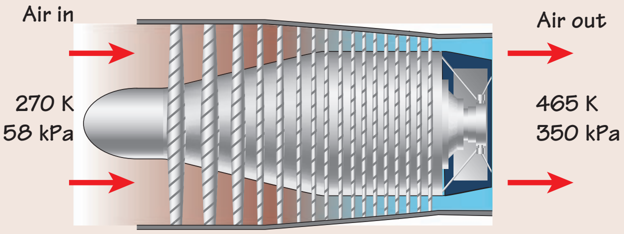
2.49 In a closed (fixed-mass) system, an ideal gas undergoes a process from 75 psia and 5 ft^3 to 25 psia and 9.68 ft^3. For this process, $\Delta H = -62$ Btu and $c_{v,\text{avg}} = 0.754$ Btu/lb$_\text{m}\cdot$R. Determine (a) ΔU, (b) $c_{p,\text{avg}}$, and (c) the specific gas constant R.

2.50 In a fixed-mass system, 4 lb$_\text{m}$ of air is heated at constant pressure from 30 psia and 40 F to 140 F. Determine the change in internal energy (Btu) for this process assuming $\bar{c}_{v,\text{avg}} = 4.96$ Btu/lbmol$\cdot$R and $k = 1.4$.

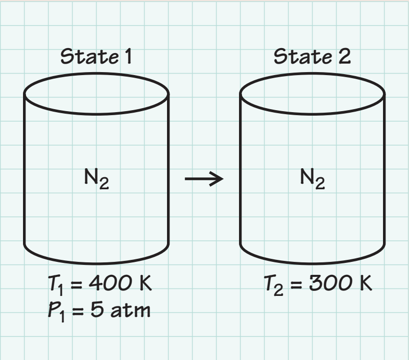
2.51 Use Table C.2 to calculate the mass-specific entropy change for air undergoing a change of state from 300 to 1000 K. The initial and final pressures are both 1 atm.

2.52 Calculate the mass-specific enthalpy and entropy changes for air undergoing a change of state from 400 K and 2 atm to 800 K and 7.2 atm.

2.53 Air is compressed in the compressor of a turbojet engine. The air enters the compressor at 270 K and 58 kPa and exits the compressor at 465 K and 350 kPa. Determine the mass-specific enthalpy, internal energy, and entropy changes associated with the compression process.

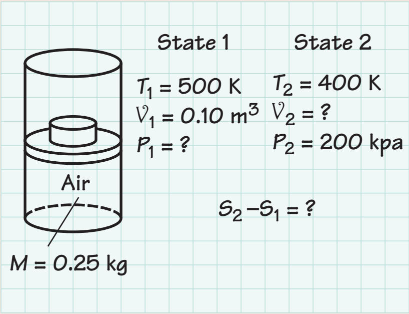


2.54 Consider 0.3 kg of N_2 in a rigid container at 400 K and 5 atm. The N_2 is cooled to 300 K. Determine the specific entropy change of the N_2 associated with this cooling process.



2.55 A fixed mass of air undergoes a state change from 400 K and 1 atm to 500 K and 1.5 atm. Determine the specific entropy change associated with this process.

2.56 A fixed mass of air (0.25 kg) at 500 K is contained in a piston–cylinder assembly having a volume of 0.10 m^3. A process occurs to cause a change of state. The final state pressure and temperature are 200 kPa and 400 K, respectively. Determine the entropy change associated with this process. Use both the ideal-gas approximations (Eqs. 2.40a and 2.40b) and the air tables (Table C.2) to calculate ΔS. Note that the data in Table C.2 are for a pressure of 1 atm. Compare the results of the two methods. Also, what is the volume at the final state?



2.57 Nitrogen undergoes an isentropic process from an initial state at 425 K and 150 kPa to a final state at 600 K. Determine the density of the N_2 at the final state.

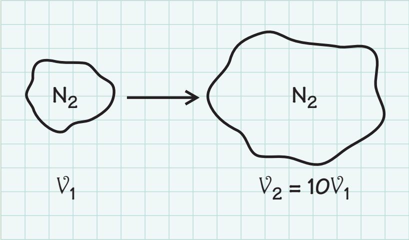
2.58 Starting with the relationship Pv^γ = constant, derive Eq. 2.42a.

2.59 The following processes constitute the air-standard Diesel cycle:

1–2: isentropic compression,
2–3: constant-volume energy addition (T and P increase),
3–4: constant-pressure energy addition (v increases),
4–5: isentropic expansion, and
5–1: constant-volume energy rejection (T and P decrease).

Plot these processes on P–v and T–s coordinates. How does this cycle differ from the Otto cycle presented in Example 2.12?

2.60 Consider the expansion of N_2 to a volume ten times larger than its initial volume. The initial temperature and pressure are 1800 K and 2 MPa, respectively. Determine the final-state temperature and pressure for (a) an isentropic expansion ($\gamma = 1.4$) and (b) a polytropic expansion with $n = 1.25$.



2.61 Consider a T–s diagram. Show that the constant specific volume line (v) must have a steeper slope than a line of constant pressure (P).

2.62 Air is drawn into the compressor of a jet engine at 55 kPa and −23°C. The air is compressed isentropically to 275 kPa. Determine (a) the temperature after compression (°C), (b) the specific volume before compression (m^3/kg), and (c) the change in specific enthalpy for the process (kJ/kg).

2.63 An automobile engine has a compression ratio ($\mathcal{V}_1/\mathcal{V}_2$) of 8.0. If the compression is isentropic and the initial temperature and pressure are 30°C and 101 kPa, respectively, determine (a) the temperature and the pressure after compression and (b) the change in enthalpy for the process.

2.64 Air is compressed in a piston–cylinder system having an initial volume of 80 in^3. Initial pressure and temperature are 20 psia and 140 F. The final volume is one-eighth of the initial volume at a pressure of 175 psia. Determine the following:

A. Final temperature (F)
B. Mass of air (lb_m)
C. Change in internal energy (Btu)
D. Change in enthalpy (Btu)
E. Change in entropy ($Btu/lb_m \cdot R$)

2.65 An ideal gas expands in a polytropic process (n = 1.4) from 850 to 500 kPa. Determine the final volume if the initial volume is 100 m^3.

2.66 An ideal gas (3 lb_m) in a closed system is compressed such that $\Delta s = 0$ from 14.7 psia and 70 F to 60 psia. For this gas, $c_p = 0.238$ Btu/lbm·F, $c_v = 0.169$ Btu/lb_m·F, and $R = 53.7$ ft·lb_f/lb_m·R. Compute (a) the final volume if the initial volume is 40.3 ft^3 and (b) the final temperature.

2.67 Air expands from 172 kPa and 60°C to 101 kPa and 5°C. Determine the change in the mass-specific entropy s of the air (kJ/kg·K) assuming constant average specific heats.

2.68 A piston–cylinder assembly contains oxygen initially at 0.965 MPa and 315.5°C. The oxygen then expands such that the entropy s remains constant to a final pressure of 0.1379 MPa. Determine the change in internal energy per kg of oxygen.

2.69 During the compression stroke in an internal combustion engine, air initially at 41°C and 101 kPa is compressed isentropically to 965 kPa. Determine (a) the final temperature (°C), (b) the change in enthalpy (kJ/kg), and (c) the final volume (m^3/kg).

2.70 Air is heated from 49°C to 650°C at a constant pressure of 620 kPa. Determine the enthalpy and entropy changes for this process. Ignore the variation in specific heat and use the value at 27°C.

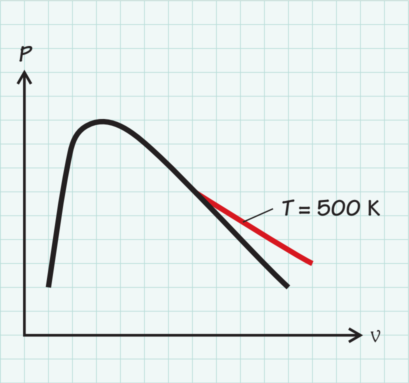
Also determine the percentage error associated with the use of this constant specific heat.

2.71 Air expands through a air turbine from inlet conditions of 690 kPa and 538°C to an exit pressure of 6.9 kPa in an isentropic process. Determine the inlet specific volume, the outlet specific volume, and the change in specific enthalpy.

2.72 Determine the density of methane (CH_4) at 300 K and 40 atm. Compare results obtained by assuming ideal-gas behavior, by using the generalized compressibility chart, and by using the NIST software or online database. Discuss.

2.73 Compare the value of the specific volume of superheated steam at 2 MPa and 500 K found in Appendix D with that calculated assuming ideal-gas behavior. Discuss.

2.74 Consider steam. Plot the 500-K isotherm in P–v space using the NIST online database as your data source. Also plot on the same graph the 500-K isotherm assuming ideal-gas behavior. Start (actually end) the isotherm at the saturated vapor line. Use a sufficiently large range of pressures so that the real isotherm approaches the fictitious ideal-gas isotherm at large specific volumes. Use spreadsheet software for your calculations and plot.



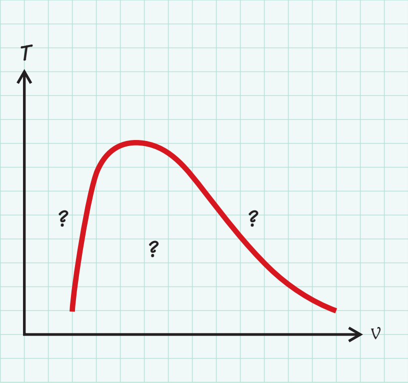
2.75 Use the van der Waals equation of state to determine the density of propane (C_3H_8) at 400 K and 12.75 MPa. How does this value compare with that obtained from the NIST online database?

2.76 Carbon dioxide (CO_2) is heated in a constant-pressure process from 15°C and 101.3 kPa to 86°C Determine, per unit mass, the changes in (a) enthalpy, (b) internal energy, (c) entropy, and (d) volume all in SI units.

2.77 A large tank contains nitrogen at −65°C and 91 MPa. Can you assume that this nitrogen is an ideal gas? What is the specific volume error in this assumption?

2.78 Is steam at 10 MPa and 500°C an ideal gas? Discuss.

2.79 Given the following property data for H_2O designate the region in T–v or P–v space (i.e., compressed liquid, liquid–vapor mixture, superheated vapor, etc.) and find the value(s) of the requested property or properties. Use the tables in Appendix D or the NIST database as necessary. Provide units with your answers.



A. $T = 310$ K, $v = 22.903$ m^3/kg
Region = ?
$P = ?$

B. $T = 310$ K, $v = 15$ m^3/kg
Region = ?
$h = ?$

C. $T = 310$ K, $P = 10$ kPa
Region = ?
$v = ?$

D. $T = 310$ K, $P = 4$ kPa
Region = ?
$u = ?$

E. $T = 647.096$ K, $P = 22.064$ MPa
Region = ?
$v = ?$

F. $T = 800$ K, $P = 25$ MPa
Region = ?
$\rho = ?$

G. $T = 800$ K, $P = 5$ MPa
Region = ?
$s = ?$

H. $T = 743.2$ K, $P = 4.61$ MPa
Region = ?
$h = ?$

2.80 Determine the remaining properties for each of the following states of H_2O:

A.	$P =$	?	psia	B.	$P =$	200	psia
	$T =$	200	F		$T =$	?	F
	$v =$	?	ft^3/lb$_m$		$v =$	?	ft^3/lb$_m$
	$h =$	?	Btu/lb$_m$		$h =$	?	Btu/lb$_m$
	$u =$	?	Btu/lb$_m$		$u =$	480	Btu/lb$_m$
	$s =$	1.87	Btu/lb$_m$·R		$s =$	?	Btu/lb$_m$·R

C. $P =$ 2000 psia
$T =$ 100 F
$v =$? ft^3/lb$_m$
$h =$? Btu/lb$_m$
$s =$? Btu/lb$_m\cdot$R

D. $P =$ 1 psia
$T =$ 100 F
$v =$? ft^3/lb$_m$
$h =$? Btu/lb$_m$
$s =$? Btu/lb$_m\cdot$R

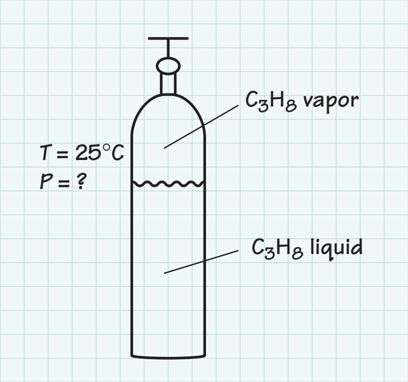
E. $P =$? kPa
$T =$ 95 °C
$v =$? m^3/kg
$h =$? kJ/kg
$s =$ 1.28933 kJ/kg·K

F. $P =$ 1379 kPa
$T =$? °C
$v =$? m^3/kg
$h =$ 1116.5 kJ/kg
$s =$? kJ/kg·K

G. $P =$ 6.895 kPa
$T =$ 38 °C
$v =$? m^3/kg
$h =$? kJ/kg
$s =$? kJ/kg·K

H. $P =$ 13,979 kPa
$T =$ 38 °C
$v =$? m^3/kg
$h =$? kJ/kg
$s =$? kJ/kg·K

2.81 A. At room temperature (25°C), what pressure (in both kPa and psi) is required to liquefy propane (C_3H_8)?
B. Determine values of the specific volume of the saturated vapor and saturated liquid. Also determine their ratios.
C. Determine h_{fg} for these same conditions.



2.82 Plot the 1-atm isobar for H_2O on T–v coordinates. Start in the compressed-liquid region, continue across the liquid-vapor dome, and end well into the superheated-vapor region. *Hint:* Use a log scale for specific volume.

2.83 For H_2O complete the following:

A. $P =$ 1000 psia
$T =$ 150 F
$v =$ ft^3/lb$_m$
$h =$ Btu/lb$_m$
$s =$ Btu/lb$_m\cdot$R

B. $P =$ 30 psia
$T =$ 150 F
$v =$ ft^3/lb$_m$
$h =$ Btu/lb$_m$
$s =$ Btu/lb$_m\cdot$R

C. $P =$ psia
$T =$ 250 F
$v =$ ft^3/lb$_m$
$h =$ Btu/lb$_m$
$s =$ 1.21 Btu/lb$_m\cdot$R

D. $P =$ 30 psia
$T =$ F
$v =$ 1.4 ft^3/lb$_m$
$h =$ Btu/lb$_m$
$s =$ Btu/lb$_m\cdot$R

E. $P =$ 200 kPa
$T =$ 600 °C
$v =$ m^3/kg
$h =$ kJ/kg
$s =$ kJ/kg·K

F. $P =$ 400 kPa
$T =$ °C
$v =$ m^3/kg
$h =$ kJ/kg
$s =$ 4.000 kJ/kg·K

G. $P =$ kPa
$T =$ 500 °C
$v =$ 0.1161 m^3/kg
$h =$ kJ/kg
$s =$ kJ/kg·K

H. $P =$ kPa
$T =$ 200 °C
$v =$ m^3/kg
$h =$ 1500 kJ/kg
$s =$ kJ/kg·K

2.84 Steam in a boiler has an enthalpy of 2558 kJ/kg and an entropy of 6.530 kJ/kg·K. What is its internal energy in kJ/kg?

2.85 Water at 30 psig is heated from 62 to 115 F. Determine the change in enthalpy in Btu/lb$_m$.

2.86 A hot water heater has 2.0 gal/min entering at 50 F and 40 psig. The water leaves the heater at 160 F and 39 psig. Determine the change in enthalpy in Btu/lb$_m$.

2.87 Water at 6.90 MPa and 95°C enters the steam-generating unit of a power plant and leaves the unit as steam at 6.90 MPa and 850°C. Determine the following properties in SI units:

Inlet	**Outlet**
$v =$? m^3/kg	$v =$? m^3/kg
$h =$? kJ/kg	$h =$? kJ/kg
$u =$? kJ/kg	$u =$? kJ/kg
$s =$? kJ/kg·K	$s =$? kJ/kg·K
Region: ?	Region: ?

2.88 In a proposed automotive steam engine, the steam after expansion would reach a state at which the pressure is 20 psig and the volume occupied per pound mass is 4.8 ft^3. Atmospheric pressure is 15 psia. Determine the following properties of the steam at this state:

$T =$? F
$u =$? Btu/lb$_m$
Region: ?

2.89 A water heater operating under steady-flow conditions delivers 10 liters/min at 75°C and 370 kPa. The input conditions are 10°C and 379 kPa. What are the corresponding changes in internal energy and enthalpy per kilogram of water supplied?

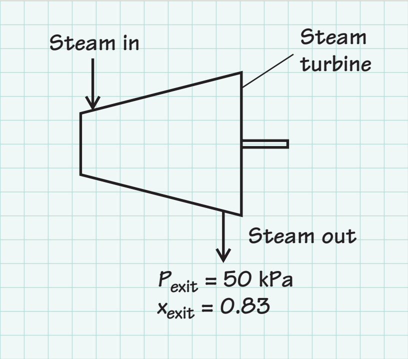
2.90 Water at 3.4 MPa is pumped through pipes embedded in the concrete of a large dam. The water, in picking up the heat of hydration of the curing, increases in temperature from 10°C to 40°C. Determine (a) the change in enthalpy (kJ/kg) and (b) the change in entropy of the water (kJ/kg·K).

2.91 Steam enters the condenser of a modern power plant with a temperature of 32°C and a quality of 0.98 (98% by mass vapor). The condensate (water) leaves at 7 kPa and 27°C. Determine the change in specific volume between inlet and outlet of the condenser in m^3/kg.

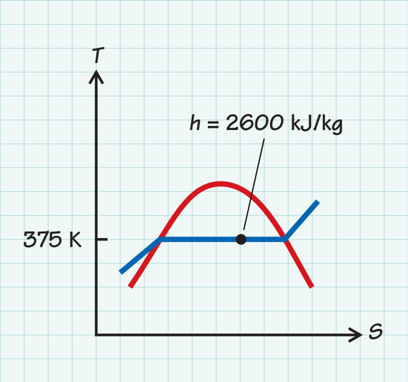
2.92 What is the temperature or quality of H_2O in the following states?

A. 20°C, 2000 kJ/kg (u)
B. 2 MPa, 0.1 m^3/kg
C. 140°C, 0.5089 m^3/kg
D. 4 MPa, 25 kg/m^3
E. 2 MPa, 0.111 m^3/kg

2.93 Wet steam exits a turbine at 50 kPa with a quality of 0.83. Determine the following properties of the wet steam: T, v, h, u, and s. Give units.

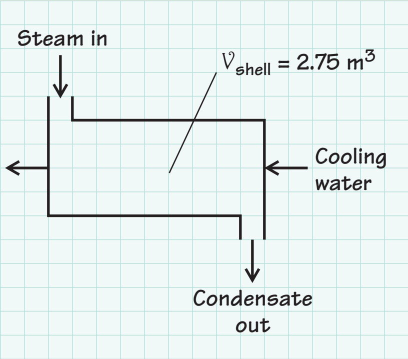


2.94 Wet steam at 375 K has a specific enthalpy of 2600 kJ/kg. Determine the quality of the mixture and the specific entropy s.

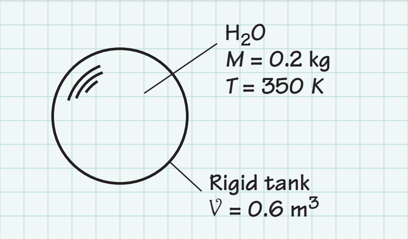


2.95 Consider H_2O at 1 MPa. Plot the following properties as a function of quality x: T(K), h (kJ/kg), s (kJ/kg·K), and v (m^3/kg). Discuss.

2.96 Steam is condensing in the shell of a heat exchanger at 305 K under steady conditions. The volume of the shell is 2.75 m^3. Determine the mass of the liquid in the shell if the specific enthalpy of the mixture is 2500 kJ/kg.



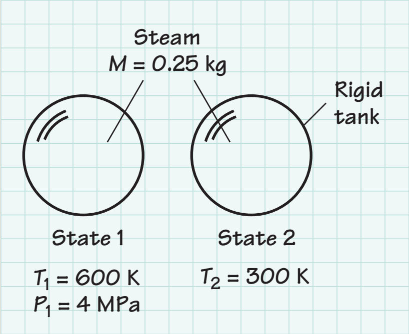
2.97 A 0.6-m^3 tank contains 0.2 kg of H_2O at 350 K. Determine the pressure in the tank and the enthalpy of the H_2O.



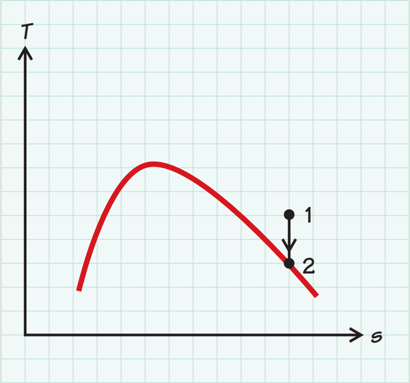
2.98 A 7.57-m^3 rigid tank contains 0.546 kg of H_2O at 37.8°C. The H_2O is then heated to 204.4°C. Determine (a) the initial and final pressures of the H_2O in the tank (MPa) and (b) the change in internal energy (kJ).

2.99 A 2.7-kg mass of H_2O is in a 0.566-m^3 container (liquid and vapor in equilibrium) at 700 kPa. Calculate (a) the volume and mass of liquid and (b) the volume and mass of vapor in the container.

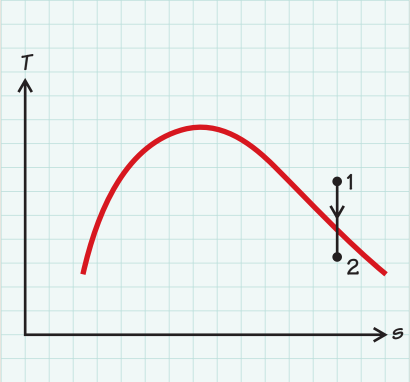
2.100 Consider 0.25 kg of steam contained in a rigid container at 600 K and 4 MPa. The steam is cooled to 300 K. Determine the entropy change of the H_2O associated with this cooling process. Note: Find $S_2 - S_1$, not $s_2 - s_1$.



2.101 Steam expands isentropically from 2 MPa and 500 K to a final state in which the steam is saturated vapor. What is the temperature of the steam at the final state?



2.102 Steam expands isentropically from 2 MPa and 500 K to a final state in which the quality is 0.90. Determine the final-state temperature, pressure, and specific volume.



2.103 Steam expands isentropically from 6 MPa and 1000 K to 1 MPa. Determine the temperature at the final state. Also determine the specific enthalpy change for the process, (i.e., $h_2 - h_1$).

2.104 A piston–cylinder assembly contains steam initially at 0.965 MPa and 315.6°C. The steam then expands in an isentropic process to a final pressure of 0.138 MPa. Determine the change in specific internal energy (kJ/kg and Btu/lb_m).

2.105 A rigid vessel contains saturated R-22 at 15.6°C. Determine (a) the volume and mass of liquid and (b) the volume and mass of vapor at the point necessary to make the R-22 pass through the critical state (or point) when heated.

2.106 Determine the specific enthalpy (Btu/lb_m) of superheated ammonia vapor at 1.3 MPa and 65°C. Use the NIST database.

2.107 Determine the specific entropy of evaporation of steam at standard atmospheric pressure (kJ/kg·K).

2.108 A liquid–vapor mixture of H_2O at 2 MPa is heated in a constant-volume process. The final state is the critical point. Determine the initial quality of the liquid-vapor mixture.

2.109 An 85-m^3 rigid vessel contains 10 kg of water (both liquid and vapor in thermal equilibrium at a pressure of 0.01 MPa). Calculate the volume and mass of both the liquid and vapor.

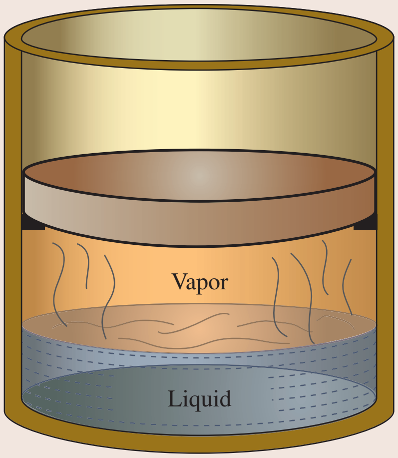
2.110 Determine the moisture content $(1 - x)$ of the following:

H_2O: 400 kPa, $h = 1700$ kJ/kg
H_2O: 1850 $\text{lb}_\text{f}/\text{in}^2$, $s = 1$ Btu/lb_m·R
R-134a: 10 F, 40 $\text{lb}_\text{m}/\text{ft}^3$

2.111 Determine the moisture content of the following:

H_2O: $h = 950$ Btu/lb_m, $s = 1.705$ Btu/lb_m·F
H_2O: $h = 1187.7$ Btu/lb_m, 0.38714 $\text{ft}^3/\text{lb}_\text{m}$
R-134a: 59 F, 0.012883 $\text{ft}^3/\text{lb}_\text{m}$

2.112 Consider 0.136 kg of H_2O (liquid and vapor in equilibrium) contained in a vertical piston–cylinder arrangement at 50°C, as shown in the sketch. Initially, the volume beneath the 113.4-kg piston (area of 11.15 cm^2) is 0.03 m^3. With an atmospheric pressure of 101.325 kPa ($g = 9.14\ \text{m/s}^2$), the piston rests on the stops. Energy is transferred to this arrangement until there is only saturated vapor inside.



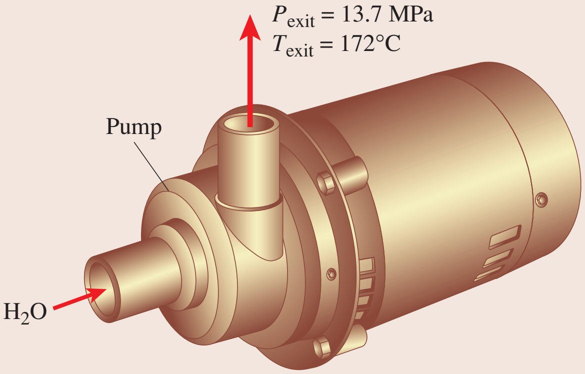
A. Show this process on a T–$\mathcal{V}$ diagram.
B. What is the temperature of the H_2O when the piston first rises from the stops?

2.113 H_2O expands isentropically through a steam turbine from inlet conditions of 700 kPa and 550°C to an exit pressure of 7 kPa. Determine the specific volume and specific enthalpy at both the inlet and outlet conditions.

2.114 Fifty kilograms of H_2O liquid and vapor in equilibrium at 300°C occupies a volume of m^3. What is the percentage of liquid, that is, the moisture content, $1 - x$?

2.115 Consider water at 400 K and a pressure of 5 atm. Estimate the enthalpy of the water using the *saturated liquid* tables from Appendix D. Compare this result with the value obtained from the NIST database or the compressed liquid tables in Appendix D. Repeat for the density.

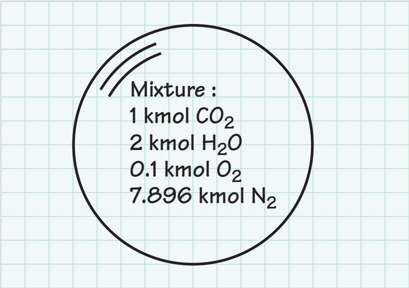
2.116 Water exits a water pump at 13.7 MPa and 172°C. Use Eqs. 2.53a–2.53c to estimate the specific volume, internal energy, and enthalpy of the water. Compare with the exact values obtained from the NIST database and calculate the percent error associated with each.



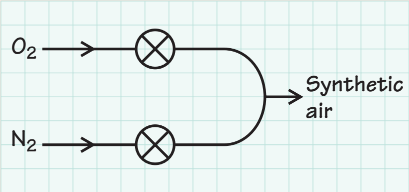
2.117 Consider a block of pure aluminum measuring 25 × 300 × 200 mm. Estimate the change in internal energy associated with a temperature change from 600 to 400 K.

2.118 Formally show that $c_p = c_v$ for an incompressible solid.

2.119 A mixture of ideal gases contains 1 kmol of CO_2, 2 kmol of H_2O, 0.1 kmol of O_2, and 7.896 kmol of N_2. Determine the mole fractions and the mass fractions of each constituent. Also determine the apparent molecular weight of the mixture.



2.120 Determine the apparent molecular weight of synthetic air created by mixing 1 kmol of O_2 with 3.76 kmol of N_2. Also determine the mole and mass fractions of the O_2 in the mixture.



2.121 On a hot (95 F) summer day the relative humidity reaches an uncomfortable 85%. At this condition, the water vapor mole fraction is 0.056. Treating the moist air as an ideal-gas mixture of water vapor and dry air, determine the mass fraction of water vapor and the apparent molecular weight of the *moist* air. Treat the *dry* air as a simple substance with a molecular weight of 28.97 kg/kmol.

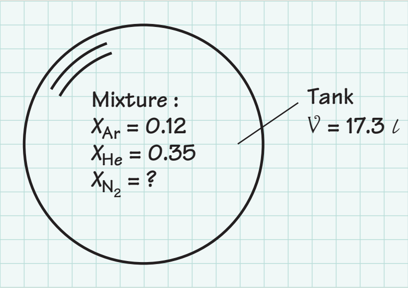
2.122 A 0.5-m^3 rigid vessel contains 1 kg of carbon monoxide and 1.5 kg of air at 15°C. The composition of the air on a mass basis is 23.3% O_2 and 76.7% N_2. What are the partial pressures (kPa) of each component?

2.123 A gas mixture of O_2, N_2, and CO_2 contains 5.5, 3, and 1.5 kmol of each species, respectively. Determine volume fractions of each component. Also determine the mass (kg) and molecular weight (kg/kmol) of the mixture.

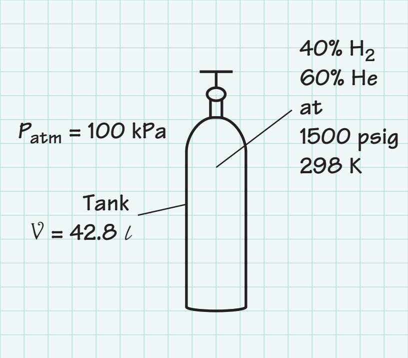
2.124 For air containing 75.53% N_2, 23.14% O_2, 1.28% Ar, and 0.05% CO_2, by mass, determine the gas constant and its molecular weight. How do these values compare if the mass-based composition is 76.7% N_2 and 23.3% O_2?

2.125 The gravimetric (mass) analysis of a gaseous mixture yields $CO_2 =$ 32%, $O_2 =$ 56.5%, and $N_2 =$ 11.5%. The mixture is at a pressure of 3 psia. Determine (a) the volumetric composition and (b) the partial pressure of each component.

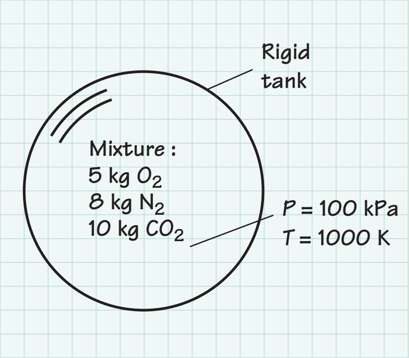
2.126 A 17.3-liter tank contains a mixture of argon, helium, and nitrogen at 298 K. The argon and helium mole fractions are 0.12 and 0.35, respectively. If the partial pressure of the nitrogen is 0.8 atm, determine (a) the total pressure in the tank, (b) the total number of moles (kmol) in the tank, and (c) the mass of the mixture in the tank.



2.127 An instrument for the analysis of trace hydrocarbons in air, or in the products of combustion, uses a flame ionization detector. The flame in this device is fueled by a mixture of 40% (vol.) hydrogen and 60% (vol.) helium. The fuel mixture is contained in a 42.8-liter tank at 1500 psig and 298 K. The atmospheric pressure is 100 kPa. Determine (a) the partial pressure of each constituent in the tank and (b) the total mass of the mixture. Assume ideal-gas behavior for the mixture.



2.128 A rigid tank contains 5 kg of O_2, 8 kg of N_2, and 10 kg of CO_2 at 100 kPa and 1000 K. Assume that the mixture behaves as an ideal gas. Determine (a) the mass fraction of each component, (b) the mole fraction of each component, (c) the partial pressure of each component, (d) the average molar mass (apparent molecular weight) and the gas constant of the mixture, and (e) the volume of the mixture in m^3.



2.129 A 3-ft^3 rigid vessel contains a 50–50 mixture of N_2 and CO (by volume). Determine the mass of each component for $T = 65$ F and $P = 30$ psia.

2.130 A 1-m^3 tank contains nitrogen at 30°C and 500 kPa. In an isothermal process, CO_2 is forced into this tank until the pressure is 1000 kPa. What is the mass (kg) of each gas present at the end of this process?

2.131 A 0.08-m^3 rigid vessel contains a 50–50 (by volume) mixture of nitrogen and carbon monoxide at 21°C and 2.75 MPa. Determine the mass of each component.

2.132 Determine the standardized enthalpies and entropies of the following pure species at 4 atm and 2500 K: H_2, H_2O, and OH.

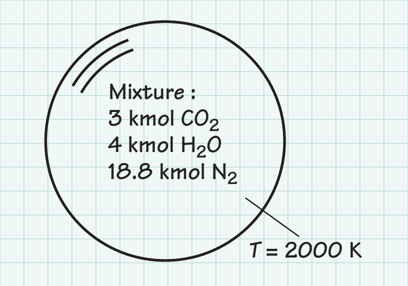
2.133 Use the curve-fit coefficients for the standardized enthalpy from Table H.2 to verify the enthalpies of formation at 298.15 K in Table H.1 for methane, propane, and hexane.

2.134 Determine the total standardized enthalpy H (kJ) for a fuel–air reactant mixture containing 1 kmol CH_4, 2.5 kmol O_2, and 9.4 kmol N_2 at 500 K and 1 atm. Also determine the mass-specific standardized enthalpy h (kJ/kg) for this mixture.

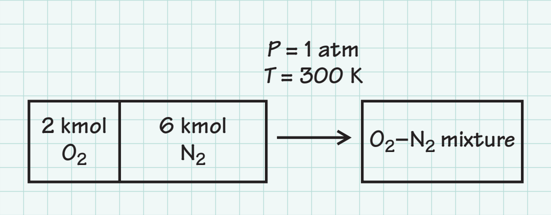
2.135 A mixture of products of combustion contains the following constituents at 2000 K: 3 kmol of CO_2, 4 kmol of H_2O, and 18.8 kmol of N_2.

Determine the following quantities:

A. The mole fraction of each constituent in the mixture
B. The total standardized enthalpy *H* of the mixture
C. The mass-specific standardized enthalpy *h* of the mixture



2.136 Calculate the change in entropy for mixing 2 kmol of O_2 with 6 kmol of N_2. Both species are initially at 1 atm and 300 K, as is the final mixture.



2.137 A mixture of 15% CO_2, 12% O_2, and 73% N_2, (by volume) expands to a final volume six times greater than its initial volume. The corresponding temperature change is 1000°C to 750°C. Determine the entropy change (kJ/kg·K).

2.138 Determine the change in entropy (kJ/kg·K) of a mixture of 60% N_2 and 40% CO_2 by volume for a reversible adiabatic increase in volume by a factor of 5. The initial temperature is 540°C.

2.139 A partition separating a chamber into two compartments is removed. The first compartment initially contains oxygen at 600 kPa and 100°C; the second compartment initially contains nitrogen at the same pressure and temperature. The oxygen compartment volume is twice that of the one containing nitrogen. The chamber is isolated from the surroundings. Determine the change of entropy associated with the mixing of the O_2 and N_2. *Hint:* Assume that the process is isothermal.

2.140 Consider two compartments of the same chamber separated by a partition. Both compartments contain nitrogen at 600 kPa and 100°C; however, the volume of one compartment is twice that of the other. The partition is removed. Assuming the chamber is isolated from the surroundings, determine the entropy change of the N_2 associated with this process.

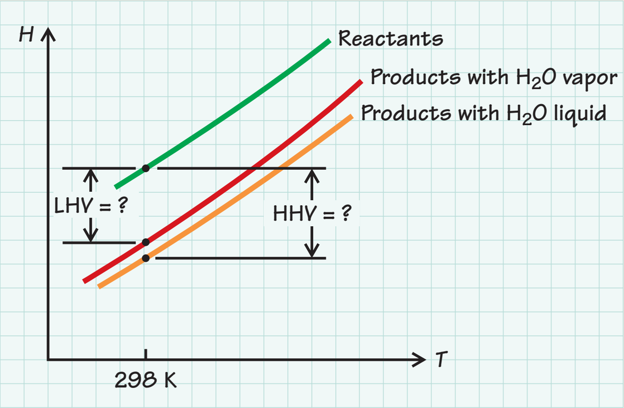
2.141 In the stoichiometric combustion of 1 kmol of methane with air (2 kmol of O_2 and 7.52 kmol of N_2). the following combustion products are formed: 1 kmol CO_2, 2 kmol H_2O, and 7.52 kmol N_2. The H_2O is in the vapor state. Determine the following:

A. The enthalpy of reaction (kJ)
B. The apparent molecular weight of the product mixture
C. The enthalpy of reaction per mass of mixture
D. The enthalpy of reaction per mass of fuel

2.142 Repeat Problem 2.141 for the stoichiometric combustion of propane with air where the following reaction occurs:

$$C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 18.8\,N_2.$$

2.143 Determine the higher and lower heating values for the stoichiometric combustion of methane with air (see Problem 2.141) and for the combustion of propane with air (see Problem 2.142).



2.144 Use the NIST software or online database to determine the thermal conductivity k and the viscosity μ of H_2O for the following conditions. Express your results in SI units.

A. 1 MPa and 300 K
B. 1 MPa and 400 K
C. 0.1 MPa and 300 K
D. 3 kPa and 300 K

2.145 Use the NIST online database to determine the thermal conductivity k and viscosity μ of N_2 for the following conditions. Express your results in SI units.

A. 1 atm and 300 K
B. 1 atm and 500 K
C. 1 atm and 1000 K
D. 2 atm and 1000 K
E. 5 atm and 1000 K
F. 100 atm and 1000 K

Use your results to discuss the influence of temperature and pressure on the thermal conductivity and viscosity of N_2.

Appendix 2A
Molecular Interpretation of Entropy

The purpose of this appendix is to introduce the reader to a molecular interpretation of entropy without getting bogged down in details. A rigorous development can be found in Ref. [16], for example, and a very readable elementary treatment is provided by Wark [17].

We begin by stating our final result that the entropy S is given by the following expression:

$$S = k_B \ln W_{mp}, \tag{2A.1}$$

where k_B is Boltzmann's constant and W_{mp} is the most probable **thermodynamic probability**, a concept that requires some elaboration. Continuing to work backward, we define the thermodynamic probability as the number of microstates associated with a given macrostate. We are now at the heart of this issue: What do we mean by a microstate or by a macrostate? Answering these questions allows us to come full circle back to Eq. 2A.1, our statistical definition of entropy.

To understand the concepts of microstates and macrostates, we consider an isolated group of N particles comprising our thermodynamic system. Furthermore, we assume that the individual particles in our system have various energy levels, ε_i, as dictated by quantum mechanics. Although any individual particle may have any particular allowed energy, the system energy must remain fixed and is constrained by

$$\sum N_i \varepsilon_i = U, \tag{2A.2}$$

where N_i is the number of particles that have the specific energy level ε_i. We continue now with a specific, but hypothetical, example in which our system contains only three particles, A, B, and C, and has a total system energy of six units, or quanta. Furthermore, we assume that the allowed energy levels are equally spaced intervals of one unit, beginning with unity. Thus, any individual particle can have energy of one, two, three, or four quanta. Clearly, energy levels above four are disallowed because, if one or more particles possessed this energy, the overall system constraint of six units would be violated. For example, if particle A possesses five units, the least possible total system energy is seven units, since the least energy particles B and C can possess is one unit ($5 + 1 + 1 = 7$)

We now consider the number of ways the overall system can be configured, assuming particles A, B, and C are distinguishable. Using Table 2A.1 as a guide, we see that there are a total of ten ways that our three particles can be arranged while maintaining the total system energy at six units. Each one of these ten arrangements is identified as a **microstate**. We further note that some

Table 2A.1 Macrostates and Microstates Associated with a System of Three Particles and a Total Energy of Six Units

Macrostate 1

ε_i						
4	—	—	—	—	—	—
3	A	B	C	B	A	C
2	B	A	A	C	C	B
1	C	C	B	A	B	A
$\sum N_i \varepsilon_i =$	6	6	6	6	6	6

$W = 6$

Macrostate 2

ε_i			
4	A	B	C
3	—	—	—
2	—	—	—
1	B,C	A,C	B,A
$\sum N_i \varepsilon_i =$	6	6	6

$W = 3$

Macrostate 3

ε_i	
4	—
3	—
2	A,B,C
1	—
$\sum N_i \varepsilon_i =$	6

$W = 1$

of these microstates are similar; if we remove the restriction that A, B, and C are distinguishable, there are six identical microstates in which one particle possesses three units of energy, another particle possesses two units of energy, and the third particle possesses one unit. The identification of a state purely by enumeration of the number of particles at each energy level without regard to the identification of the individual particle is defined as a **macrostate**. Employing this definition, we see that there are two other macrostates associated with our system: macrostate 2, in which one particle has four units of energy and two particles possess one unit, and macrostate 3, in which each particle has two units of energy. The probability of our system being found in a particular macrostate is related to the number of microstates comprising the macrostate. For our example, there are six internal arrangements that can be identified with macrostate 1, three for macrostate 2, and only one arrangement possible for macrostate 3.

Recall that one of our goals at the outset of this discussion was to understand the definition of thermodynamic probability as the number of microstates associated with a given macrostate. We come to closure on this goal by generalizing and defining the **thermodynamic probability *W*** for a system containing a total of N particles as follows:

$$W = \frac{N!}{N_1!\,N_2!\ldots N_i!\ldots N_M},\tag{2A.3}$$

where N_i represents the number of particles having energies associated with the ith energy level. For our example, formal application of Eq. 2A.3 to the three macrostates shown in Table 2A.1 yields (recognizing that $0! = 1$)

$$W_1 = \frac{3!}{1!\,1!\,1!\,0!} = 6,$$

$$W_2 = \frac{3!}{2!\,0!\,0!\,1!} = 3,$$

and

$$W_3 = \frac{3!}{0!\,3!\,0!\,0!} = 1.$$

If we normalize these results by the total number of microstates, a conventional concept of probability gives us:

$$P_1 = \frac{W_1}{W_1 + W_2 + W_3} = 0.6,$$

$$P_2 = \frac{W_2}{W_1 + W_2 + W_3} = 0.3,$$

and

$$P_3 = \frac{W_3}{W_1 + W_2 + W_3} = 0.1.$$

Thus we see that the probability of finding the system in macrostate 1 is 0.6, whereas the probability of finding the system in macrostates 2 and 3 are 0.3 and 0.1, respectively. As the number of particles increases, the probability of the most probable macrostate overwhelms that of all of the other possible macrostates.

We conclude our discussion of entropy with two observations. First, the practical evaluation of the defining relationship for entropy (Eq. 2A.1) requires a knowledge of how particles in a macroscopic system distribute among all of the allowed energy states (i.e., quantum levels) to determine the most probable thermodynamic probability. Various theories provide such distribution functions (e.g., Maxwell–Boltzmann, Bose–Einstein, and Fermi-Dirac statistics). Discussion of these is beyond the scope of this book and the interested reader is referred to Refs. [16, 17], for example. Our second observation is that Boltzmann's definition of entropy (Eq. 2A.1) does indeed say something about "disorder" as being a favored condition.[21] By definition, the most probable macrostate is the one that has the greatest number of microstates. We can view this most probable macrostate as a state of maximum "disorder"—there is no other possible state that has as many different possible arrangements of particles.

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[21] The idea of disorder is frequently invoked in nontechnical definitions of entropy. For example, one dictionary definition of entropy is a measure of the degree of disorder in a substance or a system [18].