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Engineering Thermodynamics

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Although various aspects of what is now known as thermodynamics have been of interest since antiquity, formal study began only in the early 19th century through consideration of the motive power of *heat*: the capacity of hot bodies to produce *work*. Today the scope is larger, dealing generally with *energy and entropy*, and with relationships among the *properties* of matter. Moreover, in the past 25 years engineering thermodynamics has undergone a revolution, both in terms of the presentation of fundamentals and in the manner that it is applied. In particular, the second law of thermodynamics has emerged as an effective tool for engineering analysis and design.

2.1 Fundamentals

Classical thermodynamics is concerned primarily with the macrostructure of matter. It addresses the gross characteristics of large aggregations of molecules and not the behavior of individual molecules. The microstructure of matter is studied in kinetic theory and statistical mechanics (including quantum thermodynamics). In this chapter, the classical approach to thermodynamics is featured.

Basic Concepts and Definitions

Thermodynamics is both a branch of physics and an engineering science. The scientist is normally interested in gaining a fundamental understanding of the physical and chemical behavior of fixed, quiescent quantities of matter and uses the principles of thermodynamics to relate the *properties* of matter. Engineers are generally interested in studying *systems* and how they interact with their *surroundings.* To facilitate this, engineers have extended the subject of thermodynamics to the study of systems through which matter flows.

System

In a thermodynamic analysis, the *system is* the subject of the investigation. Normally the system is a specified quantity of matter and/or a region that can be separated from everything else by a well-defined surface. The defining surface is known as the *control surface* or *system boundary.* The control surface may be movable or fixed. Everything external to the system is the *surroundings.* A system of fixed mass is referred to as a *control mass* or as a *closed system.* When there is flow of mass through the control surface, the system is called a *control volume,* or *open, system.* An *isolated* system is a closed system that does not interact in any way with its surroundings.

State, Property

The condition of a system at any instant of time is called its *state.* The state at a given instant of time is described by the properties of the system. A *property is any* quantity whose numerical value depends on the state but not the history of the system. The value of a property is determined in principle by some type of physical operation or test.

Extensive properties depend on the size or extent of the system. Volume, mass, energy, and entropy are examples of extensive properties. An extensive property is additive in the sense that its value for the whole system equals the sum of the values for its parts. *Intensive* properties are independent of the size or extent of the system. Pressure and temperature are examples of intensive properties.

A mole is a quantity of substance having a mass numerically equal to its molecular weight. Designating the molecular weight by $\mathcal{M}$ and the number of moles by n, the mass m of the substance is $m = n\mathcal{M}$. One kilogram mole, designated kmol, of oxygen is 32.0 kg and one pound mole (lbmol) is 32.0 lb. When an extensive property is reported on a unit mass or a unit mole basis, it is called a *specific* property. An overbar is used to distinguish an extensive property written on a per-mole basis from its value expressed per unit mass. For example, the volume per mole is $\bar{v}$, whereas the volume per unit mass is v, and the two specific volumes are related by $\bar{v} = \mathcal{M}v$.

Process, Cycle

Two states are identical if, and only if, the properties of the two states are identical. When any property of a system changes in value there is a change in state, and the system is said to undergo a *process.* When a system in a given initial state goes through a sequence of processes and finally returns to its initial state, it is said to have undergone a *cycle.*

Phase and Pure Substance

The term *phase* refers to a quantity of matter that is homogeneous throughout in both chemical composition and physical structure. Homogeneity in physical structure means that the matter is all *solid,* or all *liquid,* or all *vapor* (or equivalently all *gas). A* system can contain one or more phases. For example, a system of liquid water and water vapor (steam) contains *two* phases. A *pure substance* is one that is uniform and invariable in chemical composition. *A* pure substance can exist in more than one phase, but its chemical composition must be the same in each phase. For example, if liquid water and water vapor form a system with two phases, the system can be regarded as a pure substance because each phase has the same composition. The nature of phases that coexist in equilibrium is addressed by the *phase rule* (Section 2.3, Multicomponent Systems).

Equilibrium

Equilibrium means a condition of balance. In thermodynamics the concept includes not only a balance of forces, but also a balance of other influences. Each kind of influence refers to a particular aspect of thermodynamic (complete) equilibrium. *Thermal* equilibrium refers to an equality of temperature, *mechanical* equilibrium to an equality of pressure, and *phase* equilibrium to an equality of chemical potentials (Section 2.3, Multicomponent Systems). *Chemical* equilibrium is also established in terms of chemical potentials (Section 2.4, Reaction Equilibrium). For complete equilibrium the several types of equilibrium must exist individually.

To determine if a system is in thermodynamic equilibrium, one may think of testing it as follows: isolate the system from its surroundings and watch for changes in its observable properties. If there are no changes, it may be concluded that the system was in equilibrium at the moment it was isolated. The system can be said to be at an *equilibrium state.* When a system is *isolated,* it cannot interact with its surroundings; however, its state can change as a consequence of spontaneous events occurring internally as its intensive properties, such as temperature and pressure, tend toward uniform values. When all such changes cease, the system is in equilibrium. At equilibrium. temperature and pressure are uniform throughout. If gravity is significant, a pressure variation with height can exist, as in a vertical column of liquid.

Temperature

A scale of temperature independent of the *thermometric substance* is called a *thermodynamic* temperature scale. The Kelvin scale, a thermodynamic scale, can be elicited from the second law of thermodynamics (Section 2.1, The Second Law of Thermodynamics, Entropy). The definition of temperature following from the second law is valid over all temperature ranges and provides an essential connection between the several *empirical* measures of temperature. In particular, temperatures evaluated using a *constant-volume gas thermometer* are identical to those of the Kelvin scale over the range of temperatures where gas thermometry can be used.

The empirical *gas scale* is based on the experimental observations that (1) at a given temperature level all gases exhibit the same value of the product $p\bar{v}$ (p is pressure and $\bar{v}$ the specific volume on a molar basis) if the pressure is low enough, and (2) the value of the product $p\bar{v}$ increases with the temperature level. On this basis the gas temperature scale is defined by

$$T = \frac{1}{\bar{R}} \lim_{p \to 0} \left(p\bar{v} \right)$$

where T is temperature and $\bar{R}$ is the *universal gas constant.* The absolute temperature at the *triple point of water* (Section 2.3, *P-v-T* Relations) is fixed by international agreement to be 273.16 K on the *Kelvin* temperature scale. $\bar{R}$ is then evaluated experimentally as $\bar{R}$ = 8.314 kJ/kmol · K (1545 ft · lbf/lbmol ·°R).

The *Celsius termperature scale* (also called the centigrade scale) uses the degree Celsius (°C), which has the same magnitude as the kelvin. Thus, temperature *differences* are identical on both scales. However, the zero point on the Celsius scale is shifted to 273.15 K, as shown by the following relationship between the Celsius temperature and the Kelvin temperature:

$$T(°\text{C}) = T(\text{K}) - 273.15 \tag{2.1}$$

On the Celsius scale, the triple point of water is 0.01°C and 0 K corresponds to –273.15°C.

Two other temperature scales are commonly used in engineering in the U.S. By definition, the *Rankine scale*, the unit of which is the degree rankine (°R), is proportional to the Kelvin temperature according to

$$T(°\mathrm{R}) = 1.8T(\mathrm{K}) \tag{2.2}$$

The Rankine scale is also an absolute thermodynamic scale with an absolute zero that coincides with the absolute zero of the Kelvin scale. In thermodynamic relationships, temperature is always in terms of the Kelvin or Rankine scale unless specifically stated otherwise.

A degree of the same size as that on the Rankine scale is used in the *Fahrenheit scale*, but the zero point is shifted according to the relation

$$T(°\mathrm{F}) = T(°\mathrm{R}) - 459.67 \tag{2.3}$$

Substituting Equations 2.1 and 2.2 into Equation 2.3 gives

$$T(°\mathrm{F}) = 1.8T(°\mathrm{C}) + 32 \tag{2.4}$$

This equation shows that the Fahrenheit temperature of the *ice point* (0°C) is 32°F and of the *steam point* (100°C) is 212°F. The 100 Celsius or Kelvin degrees between the ice point and steam point corresponds to 180 Fahrenheit or Rankine degrees.

To provide a standard for temperature measurement taking into account both theoretical and practical considerations, the International Temperature Scale of 1990 (ITS-90) is defined in such a way that the temperature measured on it conforms with the thermodynamic temperature, the unit of which is the kelvin, to within the limits of accuracy of measurement obtainable in 1990. Further discussion of ITS-90 is provided by Preston-Thomas (1990).

The First Law of Thermodynamics, Energy

Energy is a fundamental concept of thermodynamics and one of the most significant aspects of engineering analysis. Energy can be *stored* within systems in various macroscopic forms: kinetic energy, gravitational potential energy, and internal energy. Energy can also be *transformed* from one form to another and *transferred* between systems. For closed systems, energy can be transferred by *work* and *heat transfer.* The total amount of energy is *conserved* in all transformations and transfers.

Work

In thermodynamics, the term *work* denotes a means for transferring energy. Work is an effect of one system on another that is identified and measured as follows: work is done by a system on its surroundings if the *sole effect* on everything external to the system *could have been* the raising of a weight. The test of whether a work interaction has taken place is not that the elevation of a weight is actually changed, nor that a force actually acted through a distance, but that the sole effect *could be* the change in elevation of a mass. The magnitude of the work is measured by the number of standard weights that could have been raised. Since the raising of a weight is in effect a force acting through a distance, the work concept of mechanics is preserved. This definition includes work effects such as is associated with rotating shafts, displacement of the boundary, and the flow of electricity.

Work done *by* a system is considered positive: $W > 0$. Work done *on* a system is considered negative: $W < 0$. The time rate of doing work, or *power,* is symbolized by $\dot{W}$ and adheres to the same sign convention.

Energy

A closed system undergoing a process that involves only work interactions with its surroundings experiences an *adiabatic* process. On the basis of experimental evidence, it can be postulated that *when* *a closed system is altered adiabatically, the amount of work is fixed by the end states of the system and is independent of the details of the process.* This postulate, which is one way the *first law of thermodynamics* can be stated, can be made regardless of the type of work interaction involved, the type of process, or the nature of the system.

As the work in an adiabatic process of a closed system is fixed by the end states, an extensive property called *energy* can be defined for the system such that its change between two states is the work in an adiabatic process that has these as the end states. In engineering thermodynamics the change in the energy of a system is considered to be made up of three macroscopic contributions: the change in *kinetic energy, KE,* associated with the motion of the system *as a whole* relative to an external coordinate frame, the change in gravitational *potential energy, PE,* associated with the position of the system *as a whole* in the Earth's gravitational field, and the change in *internal energy, U,* which accounts for all other energy associated with the system. Like kinetic energy and gravitational potential energy, internal energy is an extensive property.

In summary, the change in energy between two states of a closed system in terms of the work W_{ad} of an adiabatic process between these states is

$$\left(KE_2 - KE_1\right) + \left(PE_2 - PE_1\right) + \left(U_2 - U_1\right) = -W_{ad} \tag{2.5}$$

where 1 and 2 denote the initial and final states, respectively, and the minus sign before the work term is in accordance with the previously stated sign convention for work. Since any arbitrary value can be assigned to the energy of a system at a given state 1, no particular significance can be attached to the value of the energy at state 1 or at *any* other state. Only *changes* in the energy of a system have significance.

The specific energy (energy per unit mass) is the sum of the specific internal energy, u, the specific kinetic energy, $\mathrm{v}^2/2$, and the specific gravitational potential energy, gz, such that

$$\text{specific energy} = u + \frac{\mathrm{v}^2}{2} + \mathrm{gz} \tag{2.6}$$

where the velocity v and the elevation z are each relative to specified datums (often the Earth's surface) and g is the acceleration of gravity.

A property related to internal energy u, pressure p, and specific volume v is *enthalpy,* defined by

$$h = u + pv \tag{2.7a}$$

or on an extensive basis

$$H = U + pV \tag{2.7b}$$

Heat

Closed systems can also interact with their surroundings in a way that cannot be categorized as work, as, for example, a gas (or liquid) contained in a closed vessel undergoing a process while in contact with a flame. This type of interaction is called a *heat interaction,* and the process is referred to as *nonadiabatic.*

A fundamental aspect of the energy concept is that energy is conserved. Thus, since a closed system experiences precisely the same energy change during a nonadiabatic process as during an adiabatic process between the same end states, it can be concluded that the *net* energy transfer to the system in each of these processes must be the same. It follows that heat interactions also involve energy transfer.

Denoting the amount of energy transferred *to* a closed system in heat interactions by Q, these considerations can be summarized by the *closed system energy balance:*

$$\left(U_2 - U_1\right) + \left(KE_2 - KE_1\right) + \left(PE_2 - PE_1\right) = Q - W \tag{2.8}$$

The closed system energy balance expresses the conservation of energy principle for closed systems of all kinds.

The quantity denoted by Q in Equation 2.8 accounts for the amount of energy transferred to a closed system during a process by means other than work. On the basis of experiments it is known that such an energy transfer is induced only as a result of a temperature difference between the system and its surroundings and occurs only in the direction of decreasing temperature. This means of energy transfer is called an *energy transfer by heat.* The following sign convention applies:

$Q > 0$: heat transfer *to* the system

$Q < 0$: heat transfer *from* the system

The time rate of heat transfer, denoted by $\dot{Q}$, adheres to the same sign convention.

Methods based on experiment are available for evaluating energy transfer by heat. These methods recognize two basic transfer mechanisms: *conduction* and *thermal radiation.* In addition, theoretical and empirical relationships are available for evaluating energy transfer involving *combined* modes such as *convection.* Further discussion of heat transfer fundamentals is provided in Chapter 4.

The quantities symbolized by W and Q account for *transfers* of energy. The terms *work* and *heat* denote different *means* whereby energy is transferred and not *what* is transferred. Work and heat are not properties, and it is improper to speak of work or heat "contained" in a system. However, to achieve economy of expression in subsequent discussions, W and Q are often referred to simply as work and heat transfer, respectively. This less formal approach is commonly used in engineering practice.

Power Cycles

Since energy is a property, over each cycle there is no net change in energy. Thus, Equation 2.8 reads for *any* cycle

$$Q_{cycle} = W_{cycle}$$

That is, for *any* cycle the net amount of energy received through heat interactions is equal to the net energy transferred out in work interactions. A *power cycle,* or *heat* engine, is one for which a net amount of energy is transferred out by work: $W_{cycle} > 0$. This equals the net amount of energy transferred in by heat.

Power cycles are characterized both by addition of energy by heat transfer, Q_A, and inevitable rejections of energy by heat transfer, Q_R:

$$Q_{cycle} = Q_A - Q_R$$

Combining the last two equations,

$$W_{cycle} = Q_A - Q_R$$

The *thermal efficiency* of a heat engine is defined as the ratio of the net work developed to the total energy added by heat transfer:

$$\eta = \frac{W_{cycle}}{Q_A} = 1 - \frac{Q_R}{Q_A} \tag{2.9}$$

The thermal efficiency is strictly less than 100%. That is, some portion of the energy Q_A supplied is invariably rejected $Q_R \neq 0$.

The Second Law of Thermodynamics, Entropy

Many statements of the second law of thermodynamics have been proposed. Each of these can be called a statement of the second law *or* a corollary of the second law since, if one is invalid, all are invalid. In every instance where a consequence of the second law has been tested directly or indirectly by experiment it has been verified. Accordingly, the basis of the second law, like every other physical law, is experimental evidence.

Kelvin-Planck Statement

The Kelvin-Plank statement of the second law of thermodynamics refers to a *thermal reservoir.* A thermal reservoir is a system that remains at a constant temperature even though energy is added or removed by heat transfer. A reservoir is an idealization, of course, but such a system can be approximated in a number of ways — by the Earth's atmosphere, large bodies of water (lakes, oceans), and so on. Extensive properties of thermal reservoirs, such as internal energy, can change in interactions with other systems even though the reservoir temperature remains constant, however.

The Kelvin-Planck statement of the second law can be given as follows: *It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir.* In other words, a *perpetual-motion machine of the second kind* is impossible. Expressed analytically, the Kelvin-Planck statement is

$$W_{cycle} \leq 0 \qquad (\text{single reservoir})$$

where the words *single reservoir* emphasize that the system communicates thermally only with a single reservoir as it executes the cycle. The "less than" sign applies when *internal irreversibilities* are present as the system of interest undergoes a cycle and the "equal to" sign applies only when no irreversibilities are present.

Irreversibilities

A process is said to be *reversible* if it is possible for its effects to be eradicated in the sense that there is some way by which *both* the system and its surroundings can be *exactly restored* to their respective initial states. A process is *irreversible* if there is no way to undo it. That is, there is no means by which the system and its surroundings can be exactly restored to their respective initial states. A system that has undergone an irreversible process is not necessarily precluded from being restored to its initial state. However, were the system restored to its initial state, it would not also be possible to return the surroundings to their initial state.

There are many effects whose presence during a process renders it irreversible. These include, but are not limited to, the following: heat transfer through a finite temperature difference; unrestrained expansion of a gas or liquid to a lower pressure; spontaneous chemical reaction; mixing of matter at different compositions or states; friction (sliding friction as well as friction in the flow of fluids); electric current flow through a resistance; magnetization or polarization with hysteresis; and inelastic deformation. The term *irreversibility* is used to identify effects such as these.

Irreversibilities can be divided into two classes, *internal* and *external.* Internal irreversibilities are those that occur within the system, while external irreversibilities are those that occur within the surroundings, normally the immediate surroundings. As this division depends on the location of the boundary there is some arbitrariness in the classification (by locating the boundary to take in the immediate surroundings, all irreversibilities are internal). Nonetheless, valuable insights can result when this distinction between irreversibilities is made. When internal irreversibilities are absent during a process, the process is said to be *internally reversible*. At every intermediate state of an internally reversible process of a closed system, all intensive properties are uniform throughout each phase present: the temperature, pressure, specific volume, and other intensive properties do not vary with position. The discussions to follow compare the actual and internally reversible process concepts for two cases of special interest.

For a gas as the system, the work of expansion arises from the force exerted by the system to move the boundary against the resistance offered by the surroundings:

$$W = \int_1^2 F dx = \int_1^2 pA dx$$

where the force is the product of the moving area and the pressure exerted by the system there. Noting that Adx is the change in total volume of the system,

$$W = \int_1^2 p dV$$

This expression for work applies to both actual and internally reversible expansion processes. However, for an internally reversible process p is not only the pressure at the moving boundary but also the pressure of the entire system. Furthermore, for an internally reversible process the volume equals mv, where the specific volume v has a single value throughout the system at a given instant. Accordingly, the work of an internally reversible expansion (or compression) process is

$$W = m\int_1^2 p dv \tag{2.10}$$

When such a process of a closed system is represented by a continuous curve on a plot of pressure vs. specific volume, the area *under* the curve is the magnitude of the work per unit of system mass (area a-b-c′-d′ of Figure 2.3, for example).

Although improved thermodynamic performance can accompany the reduction of irreversibilities, steps in this direction are normally constrained by a number of practical factors often related to costs. For example, consider two bodies able to communicate thermally. With a *finite* temperature difference between them, a spontaneous heat transfer would take place and, as noted previously, this would be a source of irreversibility. The importance of the heat transfer irreversibility diminishes as the temperature difference narrows; and as the temperature difference between the bodies vanishes, the heat transfer approaches *ideality*. From the study of heat transfer it is known, however, that the transfer of a finite amount of energy by heat between bodies whose temperatures differ only slightly requires a considerable amount of time, a large heat transfer surface area, or both. To approach *ideality*, therefore, a heat transfer would require an exceptionally long time and/or an exceptionally large area, each of which has cost implications constraining what can be achieved practically.

Carnot Corollaries

The two corollaries of the second law known as *Carnot* corollaries state: (1) the thermal efficiency of an irreversible power cycle is always less than the thermal efficiency of a reversible power cycle when each operates between the same two thermal reservoirs; (2) all reversible power cycles operating between the same two thermal reservoirs have the same thermal efficiency. A cycle is considered *reversible* when there are no irreversibilities within the system as it undergoes the cycle, and heat transfers between the system and reservoirs occur ideally (that is, with a vanishingly small temperature difference).

Kelvin Temperature Scale

Carnot corollary 2 suggests that the thermal efficiency of a reversible power cycle operating between two thermal reservoirs depends only on the temperatures of the reservoirs and not on the nature of the substance making up the system executing the cycle or the series of processes. With Equation 2.9 it can be concluded that the ratio of the heat transfers is also related only to the temperatures, and is independent of the substance and processes:

$$\left(\frac{Q_C}{Q_H}\right)_{\substack{rev\\cycle}} = \psi\left(T_C, T_H\right)$$

where Q_H *is* the energy transferred to the system by heat transfer from a *hot* reservoir at temperature T_H, and Q_C is the energy rejected from the system to a *cold* reservoir at temperature T_C. The words *rev cycle* emphasize that this expression applies only to systems undergoing reversible cycles while operating between the two reservoirs. Alternative temperature scales correspond to alternative specifications for the function ψ in this relation.

The *Kelvin temperature scale is* based on $\psi(T_C, T_H) = T_C/T_H$. Then

$$\left(\frac{Q_C}{Q_H}\right)_{\substack{rev\\cycle}} = \frac{T_C}{T_H} \tag{2.11}$$

This equation defines only a ratio of temperatures. The specification of the Kelvin scale is completed by assigning a numerical value to one standard reference state. The state selected is the same used to define the *gas scale:* at the triple point of water the temperature is specified to be 273.16 K. If a reversible cycle is operated between a reservoir at the reference-state temperature and another reservoir at an unknown temperature T, then the latter temperature is related to the value at the reference state by

$$T = 273.16\left(\frac{Q}{Q'}\right)_{\substack{rev\\cycle}}$$

where Q is the energy received by heat transfer from the reservoir at temperature T, and Q' is the energy rejected to the reservoir at the reference temperature. Accordingly, a temperature scale is defined that is valid over all ranges of temperature and that is independent of the thermometric substance.

Carnot Efficiency

For the special case of a reversible power cycle operating between thermal reservoirs at temperatures T_H and T_C on the Kelvin scale, combination of Equations 2.9 and 2.11 results in

$$\eta_{\max} = 1 - \frac{T_C}{T_H} \tag{2.12}$$

called the *Carnot efficiency.* This is the efficiency of *all* reversible power cycles operating between thermal reservoirs at T_H and T_C. Moreover, it is the *maximum theoretical* efficiency that any power cycle, real or ideal, could have while operating between the same two reservoirs. As temperatures on the Rankine scale differ from Kelvin temperatures only by the factor 1.8, the above equation may be applied with either scale of temperature.

The Clausius Inequality

The Clausius inequality provides the basis for introducing two ideas instrumental for quantitative evaluations of processes of systems from a second law perspective: *entropy* and *entropy generation.* The Clausius inequality states that

$$\oint \left(\frac{\delta Q}{T} \right)_b \leq 0 \tag{2.13a}$$

where δQ represents the heat transfer at a part of the system boundary during a portion of the cycle, and T is the absolute temperature at that part of the boundary. The symbol δ is used to distinguish the differentials of *nonproperties,* such as heat and work, from the differentials of properties, written with the symbol d. The subscript b indicates that the integrand is evaluated at the boundary of the system executing the cycle. The symbol $\oint$ indicates that the integral is to be performed over all parts of the boundary and over the entire cycle. The Clausius inequality can be demonstrated using the Kelvin-Planck statement of the second law, and the significance of the inequality is the same: the equality applies when there are no internal irreversibilities as the system executes the cycle, and the inequality applies when internal irreversibilities are present.

The Clausius inequality can be expressed alternatively as

$$\oint \left(\frac{\delta Q}{T} \right)_b = -S_{gen} \tag{2.13b}$$

where S_{gen} can be viewed as representing the *strength* of the inequality. The value of S_{gen} is positive when internal irreversibilities are present, zero when no internal irreversibilities are present, and can never be negative. Accordingly, S_{gen} is a measure of the irreversibilities present within the system executing the cycle. In the next section, S_{gen} is identified as the *entropy* generated (or *produced*) by internal irreversibilities during the cycle.

Entropy and Entropy Generation

Entropy

Consider two cycles executed by a closed system. One cycle consists of an internally reversible process A from state 1 to state 2, followed by an internally reversible process C from state 2 to state 1. The other cycle consists of an internally reversible process B from state 1 to state 2, followed by the same process C from state 2 to state 1 as in the first cycle. For these cycles, Equation 2.13b takes the form

$$\left(\int_1^2 \frac{\delta Q}{T} \right)_A + \left(\int_2^1 \frac{\delta Q}{T} \right)_C = -S_{gen} = 0$$

$$\left(\int_1^2 \frac{\delta Q}{T} \right)_B + \left(\int_2^1 \frac{\delta Q}{T} \right)_C = -S_{gen} = 0$$

where S_{gen} has been set to zero since the cycles are composed of internally reversible processes. Subtracting these equations leaves

$$\left(\int_1^2 \frac{\delta Q}{T} \right)_A = \left(\int_1^2 \frac{\delta Q}{T} \right)_B$$

Since A and B are arbitrary, it follows that the integral of $\delta Q/T$ has the same value for *any* internally reversible process between the two states: the value of the integral depends on the end states only. It can be concluded, therefore, that the integral defines the change in some property of the system. Selecting the symbol S to denote this property, its change is given by

$$S_2 - S_1 = \left(\int_1^2 \frac{\delta Q}{T} \right)_{\substack{int\\rev}} \tag{2.14a}$$

where the subscript *int rev* indicates that the integration is carried out for any internally reversible process linking the two states. This extensive property is called *entropy.*

Since entropy is a property, the change in entropy of a system in going from one state to another is the same for *all* processes, both internally reversible and irreversible, between these two states. In other words, once the change in entropy between two states has been evaluated, this is the magnitude of the entropy change for *any* process of the system between these end states.

The definition of entropy change expressed on a differential basis is

$$dS = \left(\frac{\delta Q}{T} \right)_{\substack{int\\rev}} \tag{2.14b}$$

Equation 2.14b indicates that when a closed system undergoing an internally reversible process *receives* energy by heat transfer, the system experiences an *increase* in entropy. Conversely, when energy is *removed* from the system by heat transfer, the entropy of the system *decreases.* This can be interpreted to mean that an entropy transfer is *associated* with (or accompanies) heat transfer. The direction of the entropy transfer is the same as that of the heat transfer. In an *adiabatic* internally reversible process of a closed system the entropy would remain constant. A constant entropy process is called an *isentropic* process.

On rearrangement, Equation 2.14b becomes

$$(\delta Q)_{\substack{int\\rev}} = TdS$$

Then, for an internally reversible process of a closed system between state 1 and state 2,

$$Q_{\substack{int\\rev}} = m \int_1^2 Tds \tag{2.15}$$

When such a process is represented by a continuous curve on a plot of temperature vs. specific entropy, the area *under* the curve is the magnitude of the heat transfer per unit of system mass.

Entropy Balance

For a cycle consisting of an actual process from state 1 to state 2, during which internal irreversibilities are present, followed by an internally reversible process from state 2 to state 1, Equation 2.13b takes the form

$$\int_1^2 \left(\frac{\delta Q}{T} \right)_b + \int_2^1 \left(\frac{\delta Q}{T} \right)_{\substack{int\\rev}} = -S_{gen}$$

where the first integral is for the actual process and the second integral is for the internally reversible process. Since no irreversibilities are associated with the internally reversible process, the term S_{gen} accounting for the effect of irreversibilities during the cycle can be identified with the actual process only.

Applying the definition of entropy change, the second integral of the foregoing equation can be expressed as

$$S_1 - S_2 = \int_2^1 \left(\frac{\delta Q}{T}\right)_{\substack{int\\rev}}$$

Introducing this and rearranging the equation, the *closed system entropy balance* results:

$$\underbrace{S_2 - S_1}_{\substack{\text{entropy}\\\text{change}}} = \underbrace{\int_1^2 \left(\frac{\delta Q}{T}\right)_b}_{\substack{\text{entropy}\\\text{transfer}}} + \underbrace{S_{gen}}_{\substack{\text{entropy}\\\text{generation}}} \tag{2.16}$$

When the end states are fixed, the entropy change on the left side of Equation 2.16 can be evaluated independently of the details of the process from state 1 to state 2. However, the two terms on the right side depend explicitly on the nature of the process and cannot be determined solely from knowledge of the end states. The first term on the right side is associated with heat transfer to or from the system during the process. This term can be interpreted as the *entropy transfer associated with (or accompanying) heat transfer.* The direction of entropy transfer is the same as the direction of the heat transfer, and the same sign convention applies as for heat transfer: a positive value means that entropy is transferred into the system, and a negative value means that entropy is transferred out.

The entropy change of a system is not accounted for solely by entropy transfer, but is also due to the second term on the right side of Equation 2.16 denoted by S_{gen}. The term S_{gen} is positive when internal irreversibilities are present during the process and vanishes when internal irreversibilities are absent. This can be described by saying that entropy is *generated* (or produced) within the system by the action of irreversibilities. The second law of thermodynamics can be interpreted as specifying that entropy is generated by irreversibilities and conserved only in the limit as irreversibilities are reduced to zero. Since S_{gen} measures the effect of irreversibilities present within a system during a process, its value depends on the nature of the process and not solely on the end states. Entropy generation is *not* a property.

When applying the entropy balance, the objective is often to evaluate the entropy generation term. However, the value of the entropy generation for a given process of a system usually does not have much significance by itself. The significance is normally determined through comparison. For example, the entropy generation within a given component might be compared to the entropy generation values of the other components included in an overall system formed by these components. By comparing entropy generation values, the components where appreciable irreversibilities occur can be identified and rank ordered. This allows attention to be focused on the components that contribute most heavily to inefficient operation of the overall system.

To evaluate the entropy transfer term of the entropy balance requires information regarding both the heat transfer and the temperature on the boundary where the heat transfer occurs. The entropy transfer term is not always subject to direct evaluation, however, because the required information is either unknown or undefined, such as when the system passes through states sufficiently far from equilibrium. In practical applications, it is often convenient, therefore, to enlarge the system to include enough of the immediate surroundings that the temperature on the boundary of the *enlarged system* corresponds to the ambient temperature, T_{amb}. The entropy transfer term is then simply Q/T_{amb}. However, as the irreversibilities present would not be just those for the system of interest but those for the enlarged system, the entropy generation term would account for the effects of internal irreversibilities within the system *and* external irreversibilities present within that portion of the surroundings included within the enlarged system.

A form of the entropy balance convenient for particular analyses is the *rate form:*

$$\frac{dS}{dt} = \sum_j \frac{\dot{Q}_j}{T_j} + \dot{S}_{gen} \tag{2.17}$$

where *dS/dt* is the time rate of change of entropy of the system. The term $\dot{Q}_j / T_j$ represents the time rate of entropy transfer through the portion of the boundary whose instantaneous temperature is T_j. The term $\dot{S}_{gen}$ accounts for the time rate of entropy generation due to irreversibilities within the system.

For a system *isolated* from its surroundings, the entropy balance is

$$\left(S_2 - S_1\right)_{isol} = S_{gen} \tag{2.18}$$

where S_{gen} is the total amount of entropy generated within the isolated system. Since entropy is generated in all actual processes, the only processes of an isolated system that actually can occur are those for which the entropy of the isolated system increases. This is known as the *increase of entropy principle.*

2.2 Control Volume Applications

Since most applications of engineering thermodynamics are conducted on a control volume basis, the control volume formulations of the mass, energy, and entropy balances presented in this section are especially important. These are given here in the form of *overall* balances. Equations of change for mass, energy, and entropy in the form of differential equations are also available in the literature (see, e.g., Bird et al., 1960).

Conservation of Mass

When applied to a control volume, the principle of mass conservation states: *The time rate of accumulation of mass within the control volume equals the difference between the total rates of mass flow in and out across the boundary.* An important case for engineering practice is one for which inward and outward flows occur, each through one or more ports. For this case the conservation of mass principle takes the form

$$\frac{dm_{cv}}{dt} = \sum_i \dot{m}_i - \sum_e \dot{m}_e \tag{2.19}$$

The left side of this equation represents the time rate of change of mass contained within the control volume, $\dot{m}_i$ denotes the mass flow rate at an inlet, and $\dot{m}_e$ is the mass flow rate at an outlet.

The *volumetric flow rate* through a portion of the control surface with area dA is the product of the velocity component normal to the area, $\mathrm{v_n}$, times the area: $\mathrm{v_n}\,dA$. The *mass* flow rate through dA is $\rho(\mathrm{v_n}\,dA)$. The mass rate of flow through a port of area A is then found by integration over the area

$$\dot{m} = \int_A \rho \mathrm{v_n}\, dA$$

For *one-dimensional* flow the intensive properties are uniform with position over area A, and the last equation becomes

$$\dot{m} = \rho \mathrm{v} A = \frac{\mathrm{v}A}{v} \tag{2.20}$$

where v denotes the specific volume and the subscript n has been dropped from velocity for simplicity.

Control Volume Energy Balance

When applied to a control volume, the principle of energy conservation states: *The time rate of accumulation of energy within the control volume equals the difference between the total incoming rate of energy transfer and the total outgoing rate of energy transfer.* Energy can enter and exit a control volume by work and heat transfer. Energy also enters and exits with flowing streams of matter. Accordingly, for a control volume with one-dimensional flow at a single inlet and a single outlet,

$$\frac{d(U + KE + PE)_{cv}}{dt} = \dot{Q}_{cv} - \dot{W} + \dot{m}\left(u_i + \frac{\mathrm{v}_i^2}{2} + \mathrm{g}\mathrm{z}_i\right) - \dot{m}\left(u_e + \frac{\mathrm{v}_e^2}{2} + \mathrm{g}\mathrm{z}_e\right) \tag{2.21}$$

where the underlined terms account for the specific energy of the incoming and outgoing streams. The terms $\dot{Q}_{cv}$ and $\dot{W}$ account, respectively, for the net rates of energy transfer by heat and work over the boundary (control surface) of the control volume.

Because work is always done on or by a control volume where matter flows across the boundary, the quantity $\dot{W}$ of Equation 2.21 can be expressed in terms of two contributions: one is the work associated with the force of the fluid pressure as mass is introduced at the inlet and removed at the exit. The other, denoted as $\dot{W}_{cv}$, includes *all other* work effects, such as those associated with rotating shafts, displacement of the boundary, and electrical effects. The work rate concept of mechanics allows the first of these contributions to be evaluated in terms of the product of the pressure force, *pA*, and velocity at the point of application of the force. To summarize, the work term $\dot{W}$ of Equation 2.21 can be expressed (with Equation 2.20) as

$$\begin{aligned} \dot{W} &= \dot{W}_{cv} + \left(p_e A_e\right)\mathrm{v}_e - \left(p_i A_i\right)\mathrm{v}_i \\ &= \dot{W}_{cv} + \dot{m}_e\left(p_e v_e\right) - \dot{m}_i\left(p_i v_i\right) \end{aligned} \tag{2.22}$$

The terms $\dot{m}_i$ (pv_i) and $\dot{m}_e$ $(p_e v_e)$ account for the work associated with the pressure at the inlet and outlet, respectively, and are commonly referred to as *flow work.*

Substituting Equation 2.22 into Equation 2.21, and introducing the specific enthalpy *h*, the following form of the control volume energy rate balance results:

$$\frac{d(U + KE + PE)_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_i\left(h_i + \frac{\mathrm{v}_i^2}{2} + \mathrm{g}\mathrm{z}_i\right) - \dot{m}_e\left(h_e + \frac{\mathrm{v}_e^2}{2} + \mathrm{g}\mathrm{z}_e\right) \tag{2.23}$$

To allow for applications where there may be several locations on the boundary through which mass enters or exits, the following expression is appropriate:

$$\frac{d(U + KE + PE)_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \sum_i \dot{m}_i\left(h_i + \frac{\mathrm{v}_i^2}{2} + \mathrm{g}\mathrm{z}_i\right) - \sum_e \dot{m}_e\left(h_e + \frac{\mathrm{v}_e^2}{2} + \mathrm{g}\mathrm{z}_e\right) \tag{2.24}$$

Equation 2.24 is an *accounting* rate balance for the energy of the control volume. It states that the time rate of accumulation of energy within the control volume equals the difference between the total rates of energy transfer in and out across the boundary. The mechanisms of energy transfer are heat and work, as for closed systems, and the energy accompanying the entering and exiting mass.

Control Volume Entropy Balance

Like mass and energy, entropy is an extensive property. And like mass and energy, entropy can be transferred into or out of a control volume by streams of matter. As this is the principal difference between the closed system and control volume forms, the control volume entropy rate balance is obtained by modifying Equation 2.17 to account for these entropy transfers. The result is

$$\underbrace{\frac{dS_{cv}}{dt}}_{\substack{\text{rate of}\\ \text{entropy}\\ \text{change}}} = \underbrace{\sum_j \frac{\dot{Q}_j}{T_j} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e}_{\substack{\text{rate of}\\ \text{entropy}\\ \text{transfer}}} + \underbrace{\dot{S}_{gen}}_{\substack{\text{rate of}\\ \text{entropy}\\ \text{generation}}} \tag{2.25}$$

where dS_{cv}/dt represents the time rate of change of entropy within the control volume. The terms $\dot{m}_i s_i$ and $\dot{m}_e s_e$ account, respectively, for rates of entropy *transfer* into and out of the control volume associated with mass flow. One-dimensional flow is assumed at locations where mass enters and exits. $\dot{Q}_j$ represents the time rate of heat transfer at the location on the boundary where the instantaneous temperature is T_j; and $\dot{Q}_j / T_j$ accounts for the associated rate of entropy *transfer.* $\dot{S}_{gen}$ denotes the time rate of entropy *generation* due to irreversibilities *within* the control volume. When a control volume comprises a number of components, $\dot{S}_{gen}$ is the sum of the rates of entropy generation of the components.

Control Volumes at Steady State

Engineering systems are often idealized as being at *steady state,* meaning that all properties are unchanging in time. For a control volume at steady state, the identity of the matter within the control volume change continuously, but the total amount of mass remains constant. At steady state, Equation 2.19 reduces to

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e \tag{2.26a}$$

The energy rate balance of Equation 2.24 becomes, at steady state,

$$0 = \dot{Q}_{cv} - \dot{W}_{cv} + \sum_i \dot{m}_i \left(h_i + \frac{\mathrm{v}_i^2}{2} + \mathrm{g}\mathrm{z}_i \right) - \sum_e \dot{m}_e \left(h_e + \frac{\mathrm{v}_e^2}{2} + \mathrm{g}\mathrm{z}_e \right) \tag{2.26b}$$

At steady state, the entropy rate balance of Equation 2.25 reads

$$0 = \sum_j \frac{\dot{Q}_j}{T_j} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \dot{S}_{gen} \tag{2.26c}$$

Mass and energy are conserved quantities, but entropy is not generally conserved. Equation 2.26a indicates that the total rate of mass flow into the control volume equals the total rate of mass flow out of the control volume. Similarly, Equation 2.26b states that the total rate of energy transfer into the control volume equals the total rate of energy transfer out of the control volume. However, Equation 2.26c shows that the rate at which entropy is transferred out *exceeds* the rate at which entropy enters, the difference being the rate of entropy generation within the control volume owing to irreversibilities.

Applications frequently involve control volumes having a single inlet and a single outlet, as, for example, the control volume of Figure 2.1 where heat transfer (if any) occurs at T_b: the temperature, or a suitable average temperature, on the boundary where heat transfer occurs. For this case the mass rate balance, Equation 2.26a, reduces to $\dot{m}_i = \dot{m}_e$. Denoting the common mass flow rate by $\dot{m}$, Equations 2.26b and 2.26c read, respectively,

$$0 = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}\left[\left(h_i - h_e \right) + \left(\frac{\mathrm{v}_i^2 - \mathrm{v}_e^2}{2} \right) + \mathrm{g}\left(\mathrm{z}_i - \mathrm{z}_e \right) \right] \tag{2.27a}$$

$$0 = \frac{\dot{Q}_{cv}}{T_b} + \dot{m}\left(s_i - s_e \right) + \dot{S}_{gen} \tag{2.28a}$$

When Equations 2.27a and 2.28a are applied to particular cases of interest, additional simplifications are usually made. The heat transfer term $\dot{Q}_{cv}$ is dropped when it is insignificant relative to other energy

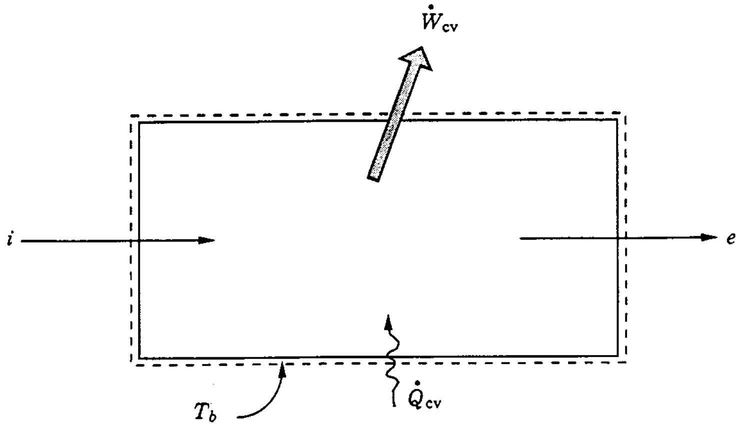

FIGURE 2.1 One-inlet, one-outlet control volume at steady state.

transfers across the boundary. This may be the result of one or more of the following: (1) the outer surface of the control volume is insulated; (2) the outer surface area is too small for there to be effective heat transfer; (3) the temperature difference between the control volume and its surroundings is small enough that the heat transfer can be ignored; (4) the gas or liquid passes through the control volume so quickly that there is not enough time for significant heat transfer to occur. The work term $\dot{W}_{cv}$ drops out of the energy rate balance when there are no rotating shafts, displacements of the boundary, electrical effects, or other work mechanisms associated with the control volume being considered. The changes in kinetic and potential energy of Equation 2.27a are frequently negligible relative to other terms in the equation.

The special forms of Equations 2.27a and 2.28a listed in Table 2.1 are obtained as follows: when there is no heat transfer, Equation 2.28a gives

$$s_e - s_i = \frac{\dot{S}_{gen}}{\dot{m}} \geq 0 \qquad (2.28b)$$

$$(\text{no heat transfer})$$

Accordingly, when irreversibilities are present within the control volume, the specific entropy increases as mass flows from inlet to outlet. In the ideal case in which no internal irreversibilities are present, mass passes through the control volume with no change in its entropy — that is, *isentropically.*

For no heat transfer, Equation 2.27a gives

$$\dot{W}_{cv} = \dot{m}\left[\left(h_i - h_e\right) + \left(\frac{\mathrm{v}_i^2 - \mathrm{v}_e^2}{2}\right) + \mathrm{g}\left(\mathrm{z}_i - \mathrm{z}_e\right)\right] \qquad (2.27b)$$

A special form that is applicable, at least approximately, to *compressors*, *pumps*, and *turbines* results from dropping the kinetic and potential energy terms of Equation 2.27b, leaving

$$\dot{W}_{cv} = \dot{m}\left(h_i - h_e\right) \qquad (2.27c)$$

$$(\textit{compressors, pumps, } \text{and } \textit{turbines})$$

TABLE 2.1 Energy and Entropy Balances for One-Inlet, One-Outlet Control Volumes at Steady State and No Heat Transfer

Energy balance

$$\dot{W}_{cv} = \dot{m}\left[\left(h_i - h_e\right) + \left(\frac{\mathrm{v}_i^2 - \mathrm{v}_e^2}{2}\right) + g\left(\mathrm{z}_i - \mathrm{z}_e\right)\right] \tag{2.27b}$$

Compressors, pumps, and turbines[a]

$$\dot{W}_{cv} = \dot{m}\left(h_i - h_e\right) \tag{2.27c}$$

Throttling

$$h_e \cong h_i \tag{2.27d}$$

Nozzles, diffusers[b]

$$\mathrm{v}_e = \sqrt{\mathrm{v}_i^2 + 2\left(h_i - h_e\right)} \tag{2.27f}$$

Entropy balance

$$s_e - s_i = \frac{\dot{S}_{gen}}{\dot{m}} \geq 0 \tag{2.28b}$$

---

[a] For an ideal gas with constant c_p, Equation 1′ of Table 2.7 allows Equation 2.27c to be written as

$$\dot{W}_{cv} = \dot{m}c_p\left(T_i - T_e\right) \tag{2.27c′}$$

The power developed in an *isentropic process* is obtained with Equation 5′ of Table 2.7 as

$$\dot{W}_{cv} = \dot{m}c_p T_i\left[1 - \left(p_e/p_i\right)^{(k-1)/k}\right] \quad (s = c) \tag{2.27c″}$$

where $c_p = kR/(k - 1)$.

[b] For an ideal gas with constant c_p, Equation 1′ of Table 2.7 allows Equation 2.27f to be written as

$$\mathrm{v}_e = \sqrt{\mathrm{v}_i^2 + 2c_p\left(T_i - T_e\right)} \tag{2.27f′}$$

The exit velocity for an *isentropic process* is obtained with Equation 5′ of Table 2.7 as

$$\mathrm{v}_e = \sqrt{\mathrm{v}_i^2 + 2c_p T_i\left[1 - \left(p_e/p_i\right)^{(k-1)/k}\right]} \quad (s = c) \tag{2.27f″}$$

where $c_p = kR/(k - 1)$.

In *throttling devices* a significant reduction in pressure is achieved simply by introducing a restriction into a line through which a gas or liquid flows. For such devices $\dot{W}_{cv} = 0$ and Equation 2.27c reduces further to read

$$h_e \cong h_i \quad (\textit{throttling process}) \tag{2.27d}$$

That is, upstream and downstream of the throttling device, the specific enthalpies are equal.

A *nozzle* is a flow passage of varying cross-sectional area in which the velocity of a gas or liquid increases in the direction of flow. In a *diffuser*, the gas or liquid decelerates in the direction of flow. For such devices, $\dot{W}_{cv} = 0$. The heat transfer and potential energy change are also generally negligible. Then Equation 2.27b reduces to

$$0 = h_i - h_e + \frac{\mathrm{v}_i^2 - \mathrm{v}_e^2}{2} \tag{2.27e}$$

Solving for the outlet velocity

$$\mathrm{v}_e = \sqrt{\mathrm{v}_i^2 + 2(h_i - h_e)} \qquad (2.27\mathrm{f})$$

$$(nozzle,\ diffuser)$$

Further discussion of the flow-through nozzles and diffusers is provided in Chapter 3.

The mass, energy, and entropy rate balances, Equations 2.26, can be applied to control volumes with multiple inlets and/or outlets, as, for example, cases involving heat-recovery steam generators, feedwater heaters, and counterflow and crossflow heat exchangers. Transient (or unsteady) analyses can be conducted with Equations 2.19, 2.24, and 2.25. Illustrations of all such applications are provided by Moran and Shapiro (1995).

Example 1

A turbine receives steam at 7 MPa, 440°C and exhausts at 0.2 MPa for subsequent process heating duty. If heat transfer and kinetic/potential energy effects are negligible, determine the steam mass flow rate, in kg/hr, for a turbine power output of 30 MW when (a) the steam quality at the turbine outlet is 95%, (b) the turbine expansion is internally reversible.

Solution. With the indicated idealizations, Equation 2.27c is appropriate. Solving, $\dot{m} = \dot{W}_{cv}/(h_i - h_e)$. Steam table data (Table A.5) at the inlet condition are h_i = 3261.7 kJ/kg, s_i = 6.6022 kJ/kg · K.

(a) At 0.2 MPa and $x = 0.95$, h_e = 2596.5 kJ/kg. Then

$$\dot{m} = \frac{30\ \mathrm{MW}}{(3261.7 - 2596.5)\ \mathrm{kJ/kg}}\left(\frac{10^3\ \mathrm{kJ/sec}}{1\ \mathrm{MW}}\right)\left(\frac{3600\ \mathrm{sec}}{1\ \mathrm{hr}}\right)$$

$$= 162{,}357\ \ \mathrm{kg/hr}$$

(b) For an internally reversible expansion, Equation 2.28b reduces to give $s_e = s_i$. For this case, h_e = 2499.6 kJ/kg (x = 0.906), and $\dot{m}$ = 141,714 kg/hr.

Example 2

Air at 500°F, 150 lbf/in.^{2}, and 10 ft/sec expands adiabatically through a nozzle and exits at 60°F, 15 lbf/in.^{2}. For a mass flow rate of 5 lb/sec determine the exit area, in in.^{2}. Repeat for an isentropic expansion to 15 lbf/in.^{2}. Model the air as an ideal gas (Section 2.3, Ideal Gas Model) with specific heat c_p = 0.24 Btu/lb · °R (k = 1.4).

Solution. The nozle exit area can be evaluated using Equation 2.20, together with the ideal gas equation, $v = RT/p$:

$$A_e = \frac{\dot{m}v_e}{\mathrm{v}_e} = \frac{\dot{m}(RT_e/p_e)}{\mathrm{v}_e}$$

The exit velocity required by this expression is obtained using Equation 2.27f′ of Table 2.1,

$$\mathrm{v}_e = \sqrt{\mathrm{v}_i^2 + 2c_p(T_i - T_e)}$$

$$= \sqrt{\left(\frac{10\ \mathrm{ft}}{s}\right)^2 + 2\left(0.24\frac{\mathrm{Btu}}{\mathrm{lb}\cdot\mathrm{R}}\right)\left(\frac{778.17\ \mathrm{ft}\cdot\mathrm{lbf}}{1\ \mathrm{Btu}}\right)(440°\mathrm{R})\left(\frac{32.174\ \mathrm{lb}\cdot\mathrm{ft/sec}^2}{1\ \mathrm{lbf}}\right)}$$

$$= 2299.5\ \mathrm{ft\ sec}$$

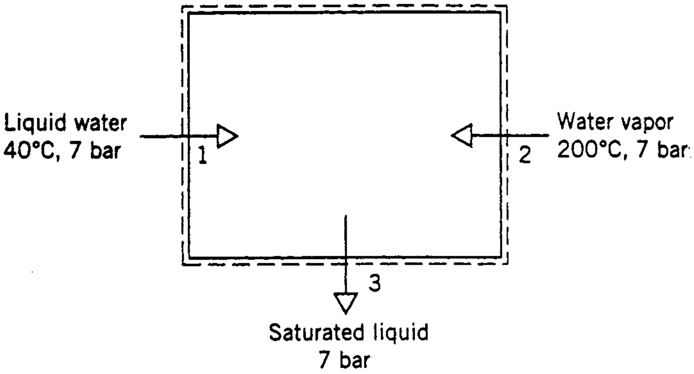

FIGURE 2.2 Open feedwater heater.

Finally, with $R = \bar{R}/\mathcal{M} = 53.33$ ft · lbf/lb · °R,

$$A_e = \frac{\left(5\dfrac{\text{lb}}{\text{sec}}\right)\left(53.3\dfrac{\text{ft}\cdot\text{lbf}}{\text{lb}\cdot{}^\circ\text{R}}\right)(520^\circ\text{R})}{\left(2299.5\dfrac{\text{ft}}{\text{sec}}\right)\left(15\dfrac{\text{lbf}}{\text{in.}^2}\right)} = 4.02\ \text{in.}^2$$

Using Equation 2.27f″ in Table 2.1 for the isentropic expansion,

$$\text{v}_e = \sqrt{(10)^2 + 2(0.24)(778.17)(960)(32.174)\left[1-\left(\frac{15}{150}\right)^{0.4/1.4}\right]}$$

$$= 2358.3\ \text{ft/sec}$$

Then $A_e = 3.92$ in.^{2}.

Example 3

Figure 2.2 provides steady-state operating data for an open feedwater heater. Ignoring heat transfer and kinetic/potential energy effects, determine the ratio of mass flow rates, $\dot{m}_1/\dot{m}_2$.

Solution. For this case Equations 2.26a and 2.26b reduce to read, respectively,

$$\dot{m}_1 + \dot{m}_2 = \dot{m}_3$$

$$0 = \dot{m}_1 h_1 + \dot{m}_2 h_2 - \dot{m}_3 h_3$$

Combining and solving for the ratio $\dot{m}_1/\dot{m}_2$,

$$\frac{\dot{m}_1}{\dot{m}_2} = \frac{h_2 - h_3}{h_3 - h_1}$$

Inserting steam table data, in kJ/kg, from Table A.5,

$$\frac{\dot{m}_1}{\dot{m}_2} = \frac{2844.8 - 697.2}{697.2 - 167.6} = 4.06$$

Internally Reversible Heat Transfer and Work

For one-inlet, one-outlet control volumes at steady state, the following expressions give the heat transfer rate and power in the absence of internal irreversibilities:

$$\left(\frac{\dot{Q}_{cv}}{\dot{m}}\right)_{\substack{int\\rev}} = \int_1^2 Tds \tag{2.29}$$

$$\left(\frac{\dot{W}_{cv}}{\dot{m}}\right)_{\substack{int\\rev}} = -\int_1^2 \mathrm{v}dp + \frac{\mathrm{V}_1^2 - \mathrm{V}_2^2}{2} + g(z_1 - z_2) \tag{2.30a}$$

(see, e.g., Moran and Shapiro, 1995).

If there is no significant change in kinetic or potential energy from inlet to outlet, Equation 2.30a reads

$$\left(\frac{\dot{W}_{cv}}{\dot{m}}\right)_{\substack{int\\rev}} = -\int_1^2 \mathrm{v}dp \qquad (\Delta ke = \Delta pe = 0) \tag{2.30b}$$

The specific volume remains approximately constant in many applications with liquids. Then Equation 30b becomes

$$\left(\frac{\dot{W}_{cv}}{\dot{m}}\right)_{\substack{int\\rev}} = -v(p_2 - p_1) \qquad (v = \text{constant}) \tag{2.30c}$$

When the states visited by a unit of mass flowing without irreversibilities from inlet to outlet are described by a continuous curve on a plot of temperature vs. specific entropy, Equation 2.29 implies that the area under the curve is the magnitude of the heat transfer per unit of mass flowing. When such an ideal process is described by a curve on a plot of pressure vs. specific volume, as shown in Figure 2.3, the magnitude of the integral $\int vdp$ of Equations 2.30a and 2.30b is represented by the area a-b-c-d *behind* the curve. The area a-b-c′-d′ *under* the curve is identified with the magnitude of the integral $\int pdv$ of Equation 2.10.

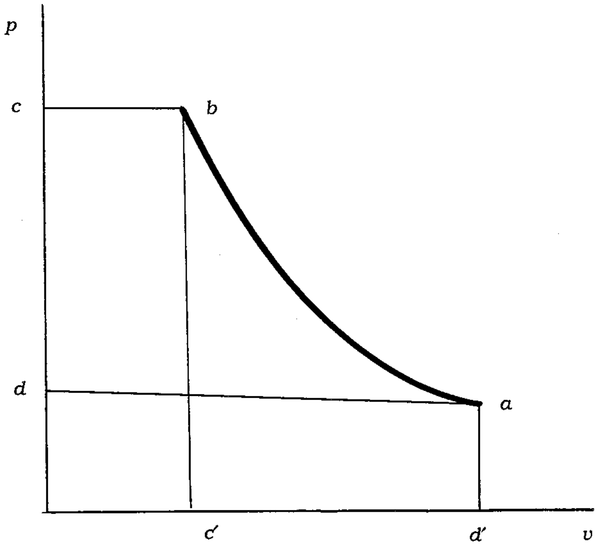

FIGURE 2.3 Internally reversible process on p–v coordinates.

2.3 Property Relations and Data

Pressure, temperature, volume, and mass can be found experimentally. The relationships between the specific heats c_v and c_p and temperature at relatively low pressure are also accessible experimentally, as are certain other property data. Specific internal energy, enthalpy, and entropy are among those properties that are not so readily obtained in the laboratory. Values for such properties are calculated using experimental data of properties that are more amenable to measurement, together with appropriate property relations derived using the principles of thermodynamics. In this section property relations and data sources are considered for *simple compressible systems*, which include a wide range of industrially important substances.

Property data are provided in the publications of the *National Institute of Standards and Technology* (formerly the U.S. Bureau of Standards), of professional groups such as the *American Society of Mechanical Engineering (ASME),* the *American Society of Heating. Refrigerating, and Air Conditioning Engineers (ASHRAE)*, and the *American Chemical Society*, and of corporate entities such as *Dupont* and *Dow Chemical.* Handbooks and property reference volumes such as included in the list of references for this chapter are readily accessed sources of data. Property data are also retrievable from various commercial online data bases. Computer software is increasingly available for this purpose as well.

Basic Relations for Pure Substances

An energy balance in differential form for a closed system undergoing an internally reversible process in the absence of overall system motion and the effect of gravity reads

$$dU = (\delta Q)_{\substack{int\\rev}} - (\delta W)_{\substack{int\\rev}}$$

From Equation 2.14b, $(\delta Q)_{\substack{int\\rev}} = TdS$. When consideration is limited to *simple compressible systems:* systems for which the only significant work in an internally reversible process is associated with volume change, $(\delta W)_{\substack{int\\rev}} = pdV$, the following equation is obtained:

$$dU = TdS - pdV \tag{2.31a}$$

Introducing enthalpy, $H = U + pV$, the Helmholtz function, $\Psi = U - TS$, and the Gibbs function, $G = H - TS$, three additional expressions are obtained:

$$dH = TdS + Vdp \tag{2.31b}$$

$$d\Psi = -pdV - SdT \tag{2.31c}$$

$$dG = Vdp - SdT \tag{2.31d}$$

Equations 2.31 can be expressed on a per-unit-mass basis as

$$du = Tds - pdv \tag{2.32a}$$

$$dh = Tds + vdp \tag{2.32b}$$

$$d\psi = -pdv - sdT \tag{2.32c}$$

$$dg = vdp - sdT \tag{2.32d}$$

Similar expressions can be written on a per-mole basis.

Maxwell Relations

Since only properties are involved, each of the four differential expressions given by Equations 2.32 is an *exact* differential exhibiting the general form $dz = M(x, y)dx + N(x, y)dy$, where the second mixed partial derivatives are equal: $(\partial M/\partial y) = (\partial N/\partial x)$. Underlying these exact differentials are, respectively, functions of the form $u(s, v)$, $h(s, p)$, $\psi(v, T)$, and $g(T, p)$. From such considerations the *Maxwell relations* given in Table 2.2 can be established.

Example 4

Derive the Maxwell relation following from Equation 2.32a.

TABLE 2.2 Relations from Exact Differentials

Function	*Differential*	*Coefficients*	*Maxwell*
General:			
$z = z(x, y)$	$dz = M(x, y)dx + N(x, y)dy$	$\left(\frac{\partial z}{\partial x}\right)_y = M$ $\left(\frac{\partial z}{\partial y}\right)_x = N$	$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$
Internal energy:			
$u(s, v)$	$du = Tds - pdv$	$\left(\frac{\partial u}{\partial s}\right)_v = T$ $\left(\frac{\partial u}{\partial v}\right)_s = -p$	$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$
Enthalpy:			
$h(s, p)$	$dh = Tds + vdp$	$\left(\frac{\partial h}{\partial s}\right)_p = T$ $\left(\frac{\partial h}{\partial p}\right)_s = v$	$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$
Helmholtz function:			
$\psi(v, T)$	$d\psi = -pdv - sdT$	$\left(\frac{\partial \psi}{\partial v}\right)_T = -p$ $\left(\frac{\partial \psi}{\partial T}\right)_v = -s$	$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$
Gibbs function:			
$g(T, p)$	$dg = vdp - sdT$	$\left(\frac{\partial g}{\partial p}\right)_T = v$ $\left(\frac{\partial g}{\partial T}\right)_p = -s$	$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$

Solution. The differential of the function $u = u(s, v)$ is

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$$

By comparison with Equation 2.32a,

$$T = \left(\frac{\partial u}{\partial s}\right)_v, \quad -p = \left(\frac{\partial u}{\partial v}\right)_s$$

In Equation 2.32a, T plays the role of M and $-p$ plays the role of N, so the equality of second mixed partial derivatives gives the Maxwell relation,

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

Since each of the properties T, p, v, and s appears on the right side of two of the eight coefficients of Table 2.2, four additional property relations can be obtained by equating such expressions:

$$\left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p, \quad \left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial \psi}{\partial v}\right)_T$$

$$\left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T, \quad \left(\frac{\partial \psi}{\partial T}\right)_v = \left(\frac{\partial g}{\partial T}\right)_p$$

These four relations are identified in Table 2.2 by brackets. As any three of Equations 2.32 can be obtained from the fourth simply by manipulation, the 16 property relations of Table 2.2 also can be regarded as following from this single differential expression. Several additional first-derivative property relations can be derived; see, e.g., Zemansky, 1972.

Specific Heats and Other Properties

Engineering thermodynamics uses a wide assortment of thermodynamic properties and relations among these properties. Table 2.3 lists several commonly encountered properties.

Among the entries of Table 2.3 are the specific heats c_v and c_p. These intensive properties are often required for thermodynamic analysis, and are defined as partial derivations of the functions $u(T, v)$ and $h(T, p)$, respectively,

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \tag{2.33}$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p \tag{2.34}$$

Since u and h can be expressed either on a unit mass basis or a per-mole basis, values of the specific heats can be similarly expressed. Table 2.4 summarizes relations involving c_v and c_p. The property k, the specific heat ratio, is

$$k = \frac{c_p}{c_v} \tag{2.35}$$

TABLE 2.3 Symbols and Definitions for Selected Properties

Property	Symbol	Definition	Property	Symbol	Definition
Pressure	p		Specific heat, constant volume	c_v	$(\partial u/\partial T)_v$
Temperature	T		Specific heat, constant pressure	c_p	$(\partial h/\partial T)_p$
Specific volume	v		Volume expansivity	β	$\frac{1}{v}(\partial v/\partial T)_p$
Specific internal energy	u		Isothermal compressivity	κ	$-\frac{1}{v}(\partial v/\partial p)_T$
Specific entropy	s		Isentropic compressibility	α	$-\frac{1}{v}(\partial v/\partial p)_s$
Specific enthalpy	h	$u + pv$	Isothermal bulk modulus	B	$-v(\partial p/\partial v)_T$
Specific Helmholtz function	ψ	$u - Ts$	Isentropic bulk modulus	B_s	$-v(\partial p/\partial v)_s$
Specific Gibbs function	g	$h - Ts$	Joule-Thomson coefficient	μ_J	$(\partial T/\partial p)_h$
Compressibility factor	Z	pv/RT	Joule coefficient	η	$(\partial T/\partial v)_u$
Specific heat ratio	k	c_p/c_v	Velocity of sound	c	$\sqrt{-v^2(\partial p/\partial v)_s}$

Values for c_v and c_p can be obtained via statistical mechanics using *spectroscopic* measurements. They can also be determined macroscopically through exacting property measurements. Specific heat data for common gases, liquids, and solids are provided by the handbooks and property reference volumes listed among the Chapter 2 references. Specific heats are also considered in Section 2.3 as a part of the discussions of the *incompressible model* and the *ideal gas model.* Figure 2.4 shows how c_p for water vapor varies as a function of temperature and pressure. Other gases exhibit similar behavior. The figure also gives the variation of c_p with temperature in the limit as pressure tends to zero (the ideal gas limit). In this limit c_p increases with increasing temperature, which is a characteristic exhibited by other gases as well

The following two equations are often convenient for establishing relations among properties:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1 \tag{2.36a}$$

$$\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -1 \tag{2.36b}$$

Their use is illustrated in Example 5.

Example 5

Obtain Equations 2 and 11 of Table 2.4 from Equation 1.

Solution. Identifying x, y, z with s, T, and v, respectively, Equation 2.36b reads

$$\left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial v}{\partial s}\right)_T \left(\frac{\partial s}{\partial T}\right)_v = -1$$

Applying Equation 2.36a to each of $(\partial T/\partial v)_s$ and $(\partial v/\partial s)_T$,

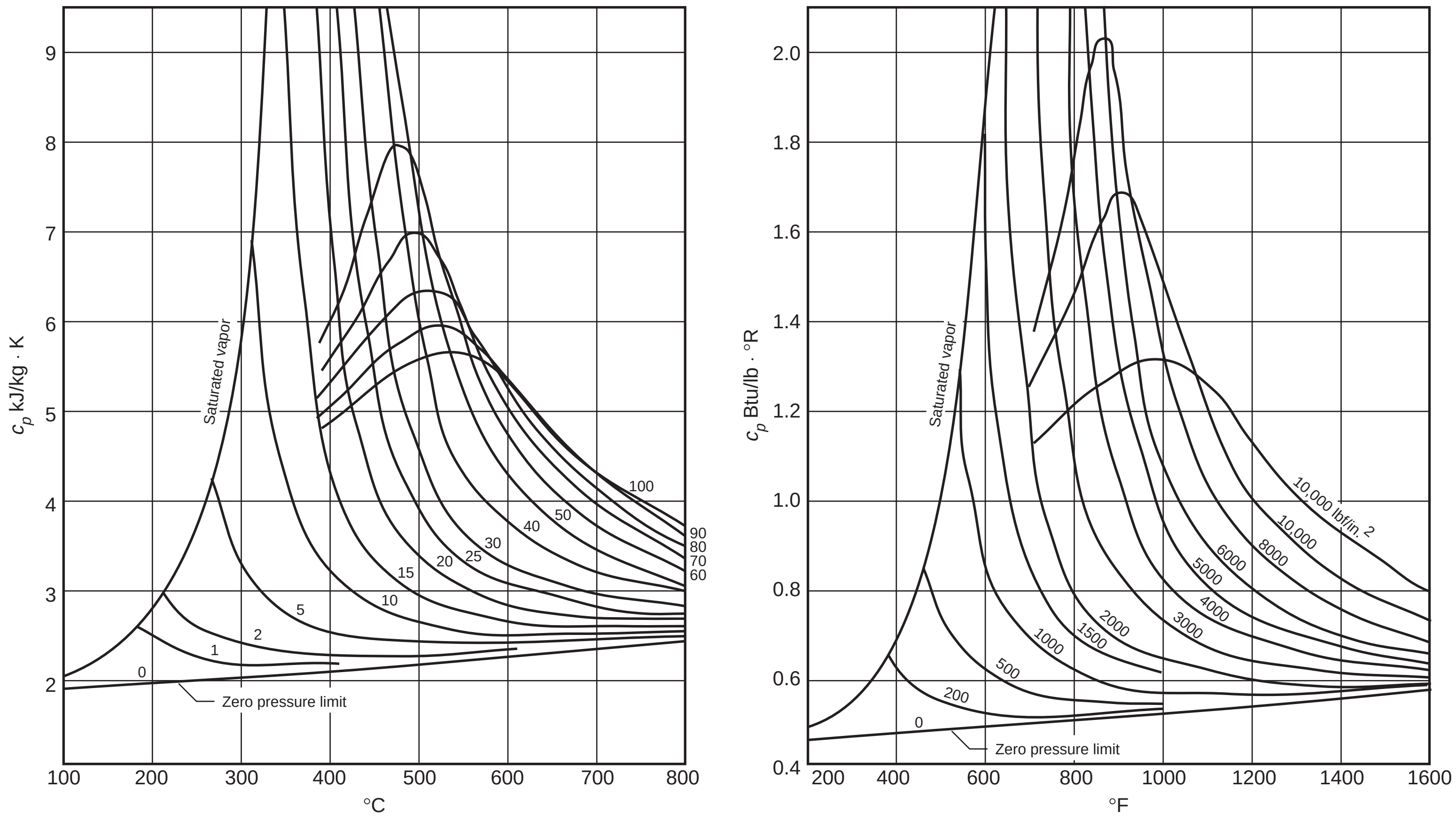

FIGURE 2.4 c_p of water vapor as a function of temperature and pressure. (Adapted from Keenan, J.H., Keyes, F.G., Hill, P.G., and Moore, J.G. 1969 and 1978. *Steam Tables — S.I. Units* (*English Units*). John Wiley & Sons, New York.)

TABLE 2.4 Specific Heat Relations[a]

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v \tag{1}$$

$$= -T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_s \tag{2}$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p \tag{3}$$

$$= T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_s \tag{4}$$

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p \tag{5}$$

$$= -T\left(\frac{\partial v}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial v}\right)_T \tag{6}$$

$$= \frac{Tv\beta^2}{\kappa} \tag{7}$$

$$c_p = \frac{1}{\mu_J}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] \tag{8}$$

$$c_v = -\frac{1}{\eta}\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] \tag{9}$$

$$k = \frac{c_p}{c_v} = \left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial v}\right)_s \tag*{10)}$$

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v \tag{11}$$

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p \tag{12}$$

[a] See, for example, Moran, M.J. and Shapiro, H.N. 1995. *Fundamentals of Engineering Thermodynamics*, 3rd ed. Wiley, New York, chap. 11.

$$\left(\frac{\partial s}{\partial T}\right)_v = -\frac{1}{(\partial T/\partial v)_s (\partial v/\partial s)_T} = -\left(\frac{\partial v}{\partial T}\right)_s \left(\frac{\partial s}{\partial v}\right)_T$$

Introducing the Maxwell relation from Table 2.2 corresponding to $\psi(T, v)$,

$$\left(\frac{\partial s}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_s \left(\frac{\partial p}{\partial T}\right)_v$$

With this, Equation 2 of Table 2.4 is obtained from Equation 1, which in turn is obtained in Example 6. Equation 11 of Table 2.4 can be obtained by differentiating Equation 1 with repect to specific volume at fixed temperature, and again using the Maxwell relation corresponding to ψ.

P-v-T Relations

Considerable pressure, specific volume, and temperature data have been accumulated for industrially important gases and liquids. These data can be represented in the form $p = f(v, T)$, called an *equation of state*. Equations of state can be expressed in tabular, graphical, and analytical forms.

P-v-T Surface

The graph of a function $p = f(v, T)$ is a surface in three-dimensional space. Figure 2.5 shows the *p-v-T* relationship for water. Figure 2.5b shows the projection of the surface onto the pressure-temperature plane, called the *phase diagram*. The projection onto the *p–v* plane is shown in Figure 2.5c.

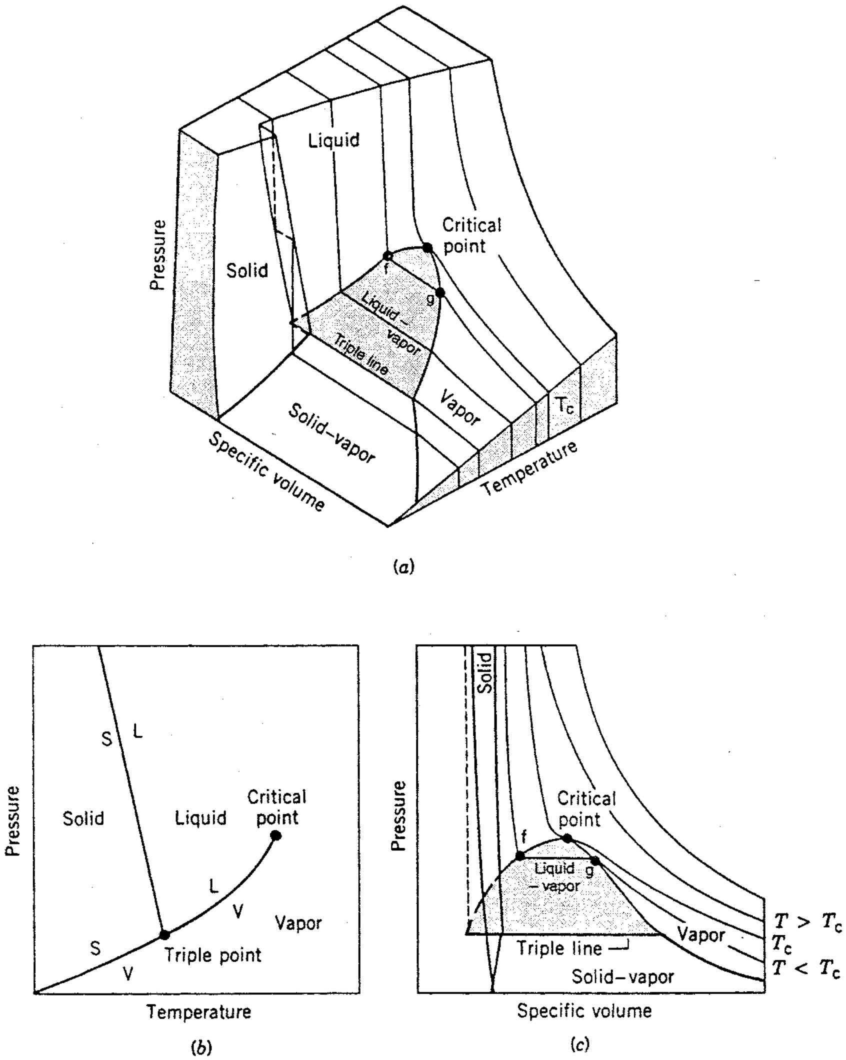

FIGURE 2.5 Pressure-specific volume-temperature surface and projections for water (not to scale).

Figure 2.5 has three regions labeled solid, liquid, and vapor where the substance exists only in a single phase. Between the single phase regions lie *two-phase* regions, where two phases coexist in equilibrium. The lines separating the single-phase regions from the two-phase regions are *saturation lines*. Any state represented by a point on a saturation line is a *saturation state*. The line separating the liquid phase and the two-phase liquid-vapor region is the saturated liquid line. The state denoted by f is a saturated liquid state. The saturated vapor line separates the vapor region and the two-phase liquid-vapor region. The state denoted by g is a saturated vapor state. The saturated liquid line and the saturated vapor line meet at the *critical point.* At the critical point, the pressure is the *critical pressure* p_c, and the temperature is the *critical temperature* T_c. Three phases can coexist in equilibrium along the line labeled *triple line.* The triple line projects onto a point on the phase diagram. The triple point of water is used in defining the Kelvin temperature scale (Section 2.1, Basic Concepts and Definitions; The Second Law of Thermodynamics, Entropy).

When a phase change occurs during constant pressure heating or cooling, the temperature remains constant as long as both phases are present. Accordingly, in the two-phase liquid-vapor region, a line of constant pressure is also a line of constant temperature. For a specified pressure, the corresponding temperature is called the *saturation temperature.* For a specified temperature, the corresponding pressure is called the *saturation pressure.* The region to the right of the saturated vapor line is known as the *superheated vapor region* because the vapor exists at a temperature greater than the saturation temperature for its pressure. The region to the left of the saturated liquid line is known as the *compressed liquid region* because the liquid is at a pressure higher than the saturation pressure for its temperature.

When a mixture of liquid and vapor coexists in equilibrium, the liquid phase is a saturated liquid and the vapor phase is a saturated vapor. The total volume of any such mixture is $V = V_f + V_g$; or, alternatively, $mv = m_f v_f + m_g v_g$, where m and v denote mass and specific volume, respectively. Dividing by the total mass of the mixture m and letting the *mass fraction* of the vapor in the mixture, m_g/m, be symbolized by x, called the *quality*, the apparent specific volume v of the mixture is

$$\begin{aligned} v &= (1-x)v_{\mathrm{f}} + xv_{\mathrm{g}} \\ &= v_{\mathrm{f}} + xv_{\mathrm{fg}} \end{aligned} \tag{2.37a}$$

where $v_{\mathrm{fg}} = v_{\mathrm{g}} - v_{\mathrm{f}}$. Expressions similar in form can be written for internal energy, enthalpy, and entropy:

$$\begin{aligned} u &= (1-x)u_{\mathrm{f}} + xu_{\mathrm{g}} \\ &= u_{\mathrm{f}} + xu_{\mathrm{fg}} \end{aligned} \tag{2.37b}$$

$$\begin{aligned} h &= (1-x)h_{\mathrm{f}} + xh_{\mathrm{g}} \\ &= h_{\mathrm{f}} + xh_{\mathrm{fg}} \end{aligned} \tag{2.37c}$$

$$\begin{aligned} s &= (1-x)s_{\mathrm{f}} + xs_{\mathrm{g}} \\ &= s_{\mathrm{f}} + xs_{\mathrm{fg}} \end{aligned} \tag{2.37d}$$

For the case of water, Figure 2.6 illustrates the phase change from solid to liquid (melting): *a-b-c*; from solid to vapor (sublimation): *a′-b′-c′*; and from liquid to vapor (vaporization): *a″-b″-c″*. During any such phase change the temperature and pressure remain constant and thus are not independent properties. The *Clapeyron equation* allows the change in enthalpy during a phase change at fixed temperature to be evaluated from *p-v-T* data pertaining to the phase change. For vaporization, the Clapeyron equation reads

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{h_{\mathrm{g}} - h_{\mathrm{f}}}{T\left(v_{\mathrm{g}} - v_{\mathrm{f}}\right)} \tag{2.38}$$

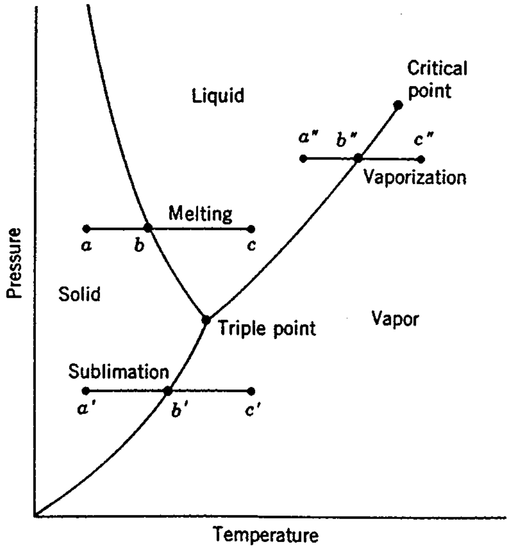

FIGURE 2.6 Phase diagram for water (not to scale).

where $(dp/dT)_{sat}$ is the slope of the saturation pressure-temperature curve at the point determined by the temperature held constant during the phase change. Expressions similar in form to Equation 2.38 can be written for sublimation and melting.

The Clapeyron equation shows that the slope of a saturation line on a phase diagram depends on the signs of the specific volume and enthalpy changes accompanying the phase change. In most cases, when a phase change takes place with an increase in specific enthalpy, the specific volume also increases, and $(dp/dT)_{sat}$ is positive. However, in the case of the melting of ice and a few other substances, the specific volume decreases on melting. The slope of the saturated solid-liquid curve for these few substances is negative, as illustrated for water in Figure 2.6.

Graphical Representations

The intensive states of a pure, simple compressible system can be represented graphically with any two independent intensive properties as the coordinates, excluding properties associated with motion and gravity. While any such pair may be used, there are several selections that are conventionally employed. These include the p-T and p-v diagrams of Figure 2.5, the T-s diagram of Figure 2.7, the h-s (Mollier) diagram of Figure 2.8, and the p-h diagram of Figure 2.9. The compressibility charts considered next use the compressibility factor as one of the coordinates.

Compressibility Charts

The p-v-T relation for a wide range of common gases is illustrated by the generalized compressibility chart of Figure 2.10. In this chart, the compressibility factor, Z, is plotted vs. the *reduced* pressure, p_R, *reduced* temperature, T_R, and *pseudoreduced* specific volume, v'_R, where

$$Z = \frac{p\bar{v}}{\bar{R}T} \tag{2.39}$$

and

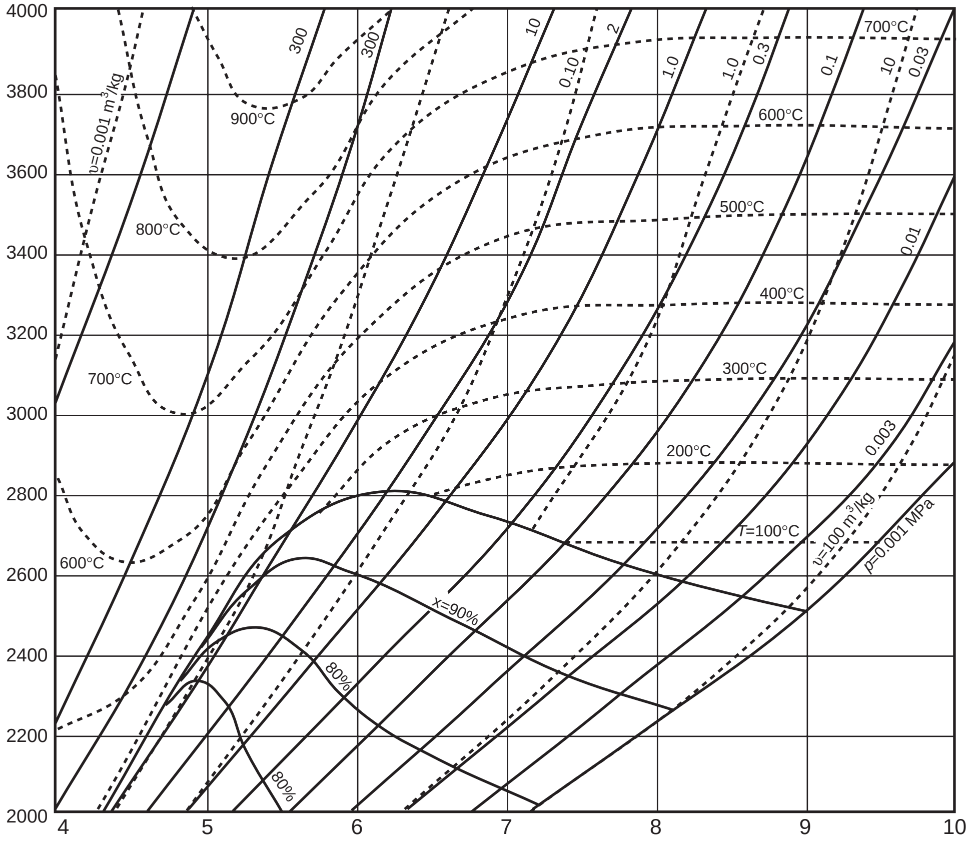

FIGURE 2.7 Temperature-entropy diagram for water. (*Source:* Jones, J.B. and Dugan, R.E. 1996. *Engineering Thermodynamics*, Prentice-Hall, Englewood Cliffs, NJ, based on data and formulations from Haar, L., Gallagher, J.S., and Kell, G.S. 1984. *NBS/NRC Steam Tables.* Hemisphere, Washington, D.C.)

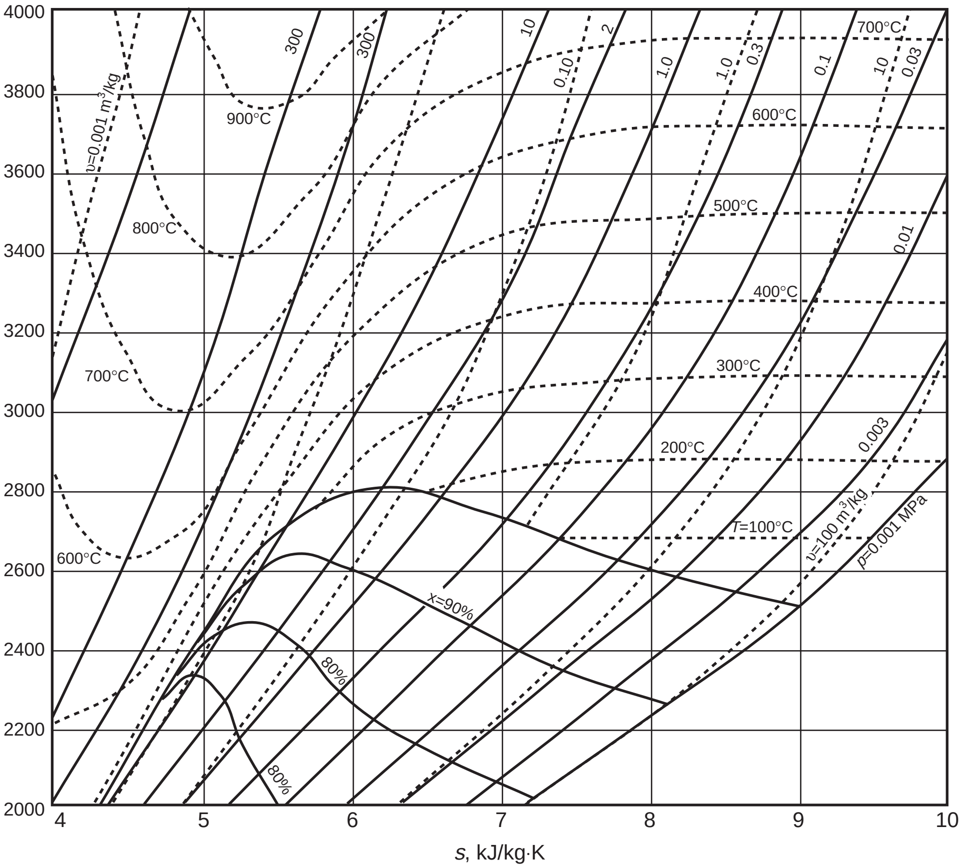

FIGURE 2.8 Enthalpy-entropy (Mollier) diagram for water. (*Source:* Jones, J.B. and Dugan, R.E. 1996. *Engineering Thermodynamics*. Prentice-Hall, Englewood Cliffs, NJ, based on data and formulations from Haar, L., Gallagher, J.S., and Kell, G.S. 1984. *NBS/NRC Steam Tables*. Hemisphere, Washington, D.C.)

$$p_R = \frac{p}{p_c}, \quad T_R = \frac{T}{T_c}, \quad v'_R = \frac{\bar{v}}{\left(\bar{R}T_c/p_c\right)} \tag{2.40}$$

In these expressions, $\bar{R}$ is the universal gas constant and p_c and T_c denote the critical pressure and temperature, respectively. Values of p_c and T_c are given for several substances in Table A.9. The reduced isotherms of Figure 2.10 represent the best curves fitted to the data of several gases. For the 30 gases used in developing the chart, the deviation of observed values from those of the chart is at most on the order of 5% and for most ranges is much less.*

Figure 2.10 gives a common value of about 0.27 for the compressibility factor at the critical point. As the critical compressibility factor for different substances actually varies from 0.23 to 0.33, the chart is inaccurate in the vicinity of the critical point. This source of inaccuracy can be removed by restricting the correlation to substances having essentially the same Z_c values. which is equivalent to including the critical compressibility factor as an independent variable: $Z = f(T_R, p_R, Z_c)$. To achieve greater accuracy

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* To determine Z for hydrogen, helium, and neon above a T_R of 5, the reduced temperature and pressure should be calculated using $T_R = T/(T_c + 8)$ and $P_R = p/(p_c + 8)$, where temperatures are in K and pressures are in atm.

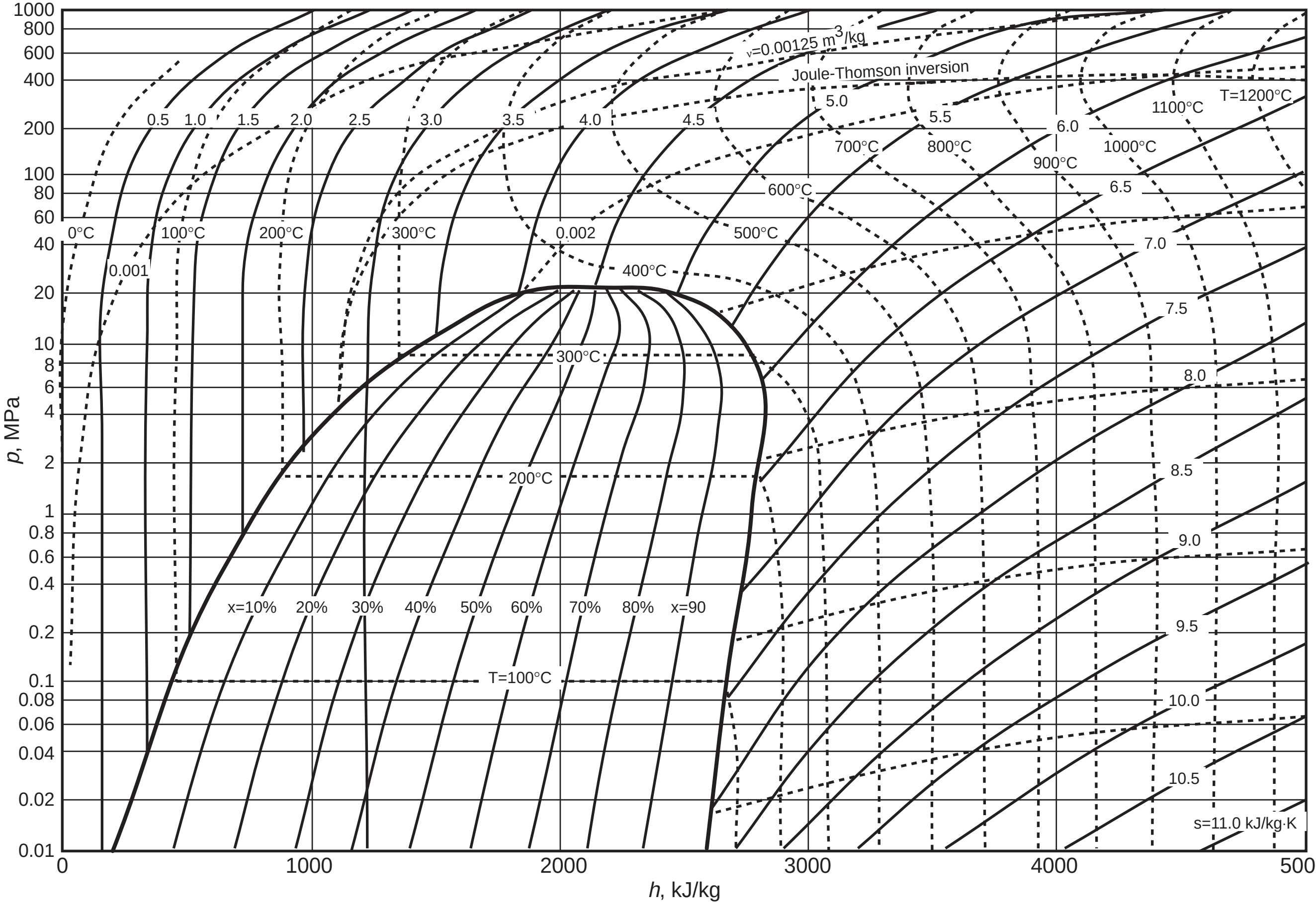


FIGURE 2.9 Pressure-enthalpy diagram for water. (*Source:* Jones, J.B. and Dugan, R.E. 1996. *Engineering Thermodynamics*. Prentice-Hall, Englewood Cliffs, NJ, based on data and formulations from Haar, L., Gallagher, J.S., and Kell, G.S. 1984. *NBS/NRC Steam Tables*. Hemisphere, Washington, D.C.)

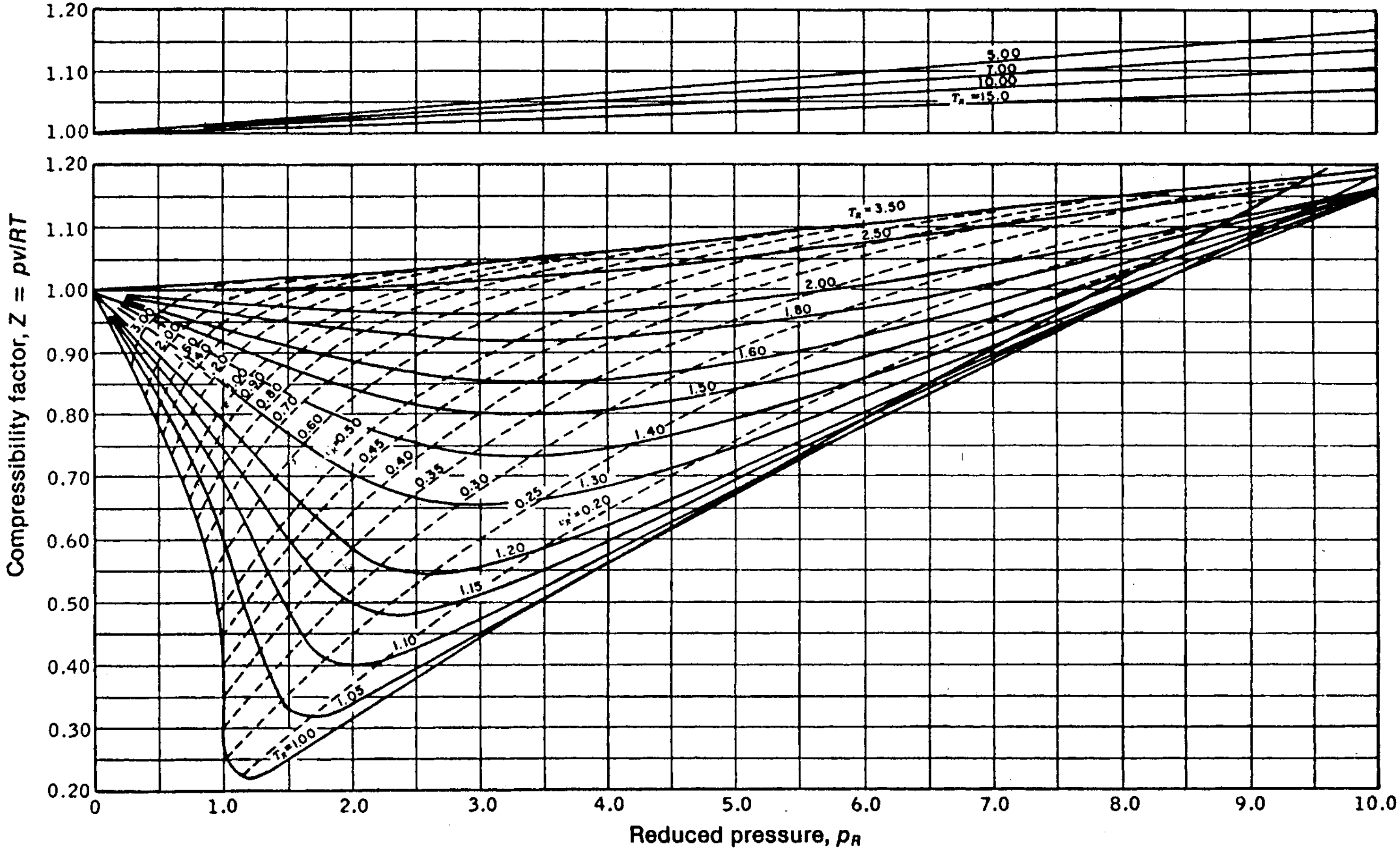


FIGURE 2.10 Generalized compressibility chart ($T_R = T/T_C$, $p_R = p/p_C$, $v'_R = \bar{v}p_C/RT_C$) for $p_R \leq 10$. (*Source:* Obert, E.F. 1960 *Concepts of Thermodynamics*. McGraw-Hill, New York.)

variables other than Z_c have been proposed as a third parameter — for example, the *acentric factor* (see, e.g., Reid and Sherwood, 1966).

Generalized compressibility data are also available in tabular form (see, e.g., Reid and Sherwood, 1966) and in equation form (see, e.g., Reynolds, 1979). The use of generalized data in any form (graphical, tabular, or equation) allows p, v, and T for gases to be evaluated simply and with reasonable accuracy. When accuracy is an essential consideration, generalized compressibility data should not be used as a substitute for p-v-T data for a given substance as provided by computer software, a table, or an equation of state.

Equations of State

Considering the isotherms of Figure 2.10, it is plausible that the variation of the compressibility factor might be expressed as an equation, at least for certain intervals of p and T. Two expressions can be written that enjoy a theoretical basis. One gives the compressibility factor as an infinite series expansion in pressure,

$$Z = 1 + \hat{B}(T)p + \hat{C}(T)p^2 + \hat{D}(T)p^3 + \dots$$

and the other is a series in $1/\bar{v}$,

$$Z = 1 + \frac{B(T)}{\bar{v}} + \frac{C(T)}{\bar{v}^2} + \frac{D(T)}{\bar{v}^3} + \dots$$

These expressions are known as *virial expansions*, and the coefficients $\hat{B}, \hat{C}\ \hat{D}, \dots$ and $B, C, D \dots$ are called *virial coefficients.* In principle, the virial coefficients can be calculated using expressions from statistical mechanics derived from consideration of the force fields around the molecules. Thus far only the first few coefficients have been calculated and only for gases consisting of relatively simple molecules. The coefficients also can be found, in principle, by fitting p-v-T data in particular realms of interest. Only the first few coefficients can be found accurately this way, however, and the result is a *truncated* equation valid only at certain states.

Over 100 equations of state have been developed in an attempt to portray accurately the p-v-T behavior of substances and yet avoid the complexities inherent in a full virial series. In general, these equations exhibit little in the way of fundamental physical significance and are mainly empirical in character. Most are developed for gases, but some describe the p-v-T behavior of the liquid phase, at least qualitatively. Every equation of state is restricted to particular states. The realm of applicability is often indicated by giving an interval of pressure, or density, where the equation can be expected to represent the p-v-T behavior faithfully. When it is not stated, the realm of applicability often may be approximated by expressing the equation in terms of the compressibility factor Z and the reduced properties, and superimposing the result on a generalized compressibility chart or comparing with compressibility data from the literature.

Equations of state can be classified by the number of adjustable constants they involve. The Redlich-Kwong equation is considered by many to be the best of the two-constant equations of state. It gives pressure as a function of temperature and specific volume and thus is *explicit* in pressure:

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}(\bar{v} + b)T^{1/2}} \tag{2.41}$$

This equation is primarily empirical in nature, with no rigorous justification in terms of molecular arguments. Values for the Redlich-Kwong constants for several substances are provided in Table A.9. Modified forms of the equation have been proposed with the aim of achieving better accuracy.

Although the two-constant Redlich-Kwong equation performs better than some equations of state having several adjustable constants, two-constant equations tend to be limited in accuracy as pressure (or density) increases. Increased accuracy normally requires a greater number of adjustable constants. For example, the Benedict-Webb-Rubin equation, which involves eight adjustable constants, has been successful in predicting the *p-v-T* behavior of *light hydrocarbons.* The Benedict-Webb-Rubin equation is also explicit in pressure,

$$p = \frac{\bar{R}T}{\bar{v}} + \left(B\bar{R}T - A - \frac{C}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{\left(b\bar{R}T - a\right)}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2} \left(1 + \frac{\gamma}{\bar{v}^2} \right) \exp\left(-\frac{\gamma}{\bar{v}^2} \right) \tag{2.42}$$

Values of the Benedict-Webb-Rubin constants for various gases are provided in the literature (see, e.g., Cooper and Goldfrank, 1967). A modification of the Benedict-Webb-Rubin equation involving 12 constants is discussed by Lee and Kessler, 1975. Many multiconstant equations can be found in the engineering literature, and with the advent of high speed computers, equations having 50 or more constants have been developed for representing the *p-v-T* behavior of different substances.

Gas Mixtures

Since an unlimited variety of mixtures can be formed from a given set of pure components by varying the relative amounts present, the properties of mixtures are reported only in special cases such as air. Means are available for predicting the properties of mixtures, however. Most techniques for predicting mixture properties are empirical in character and are not derived from fundamental physical principles. The realm of validity of any particular technique can be established by comparing predicted property values with empirical data. In this section, methods for evaluating the *p-v-T* relations for pure components are adapted to obtain plausible estimates for gas mixtures. The case of ideal gas mixtures is discussed in Section 2.3, Ideal Gas Model. In Section 2.3, Multicomponent Systems, some general aspects of property evaluation for multicomponent systems are presented.

The total number of moles of mixture, n, *is* the sum of the number of moles of the components, n_i:

$$n = n_1 + n_2 + \dots n_j = \sum_{i=1}^{j} n_i \tag{2.43}$$

The *relative* amounts of the components present can be described in terms of *mole fractions.* The mole fraction y_i of component i is $y_i = n_i/n$. The sum of the mole fractions of all components present is equal to unity. The apparent molecular weight $\mathcal{M}$ is the mole fraction average of the component molecular weights, such that

$$\mathcal{M} = \sum_{i=1}^{j} y_i \mathcal{M}_i \tag{2.44}$$

The *relative* amounts of the components present also can be described in terms of *mass fractions:* m_i/m, where m_i is the mass of component i and m is the total mass of mixture.

The *p-v-T* relation for a gas mixture can be estimated by applying an equation of state to the overall mixture. The constants appearing in the equation of state are *mixture values* determined with empirical combining rules developed for the equation. For example, mixture values of the constants a and b for use in the Redlich-Kwong equation are obtained using relations of the form

$$a = \left(\sum_{i=1}^{j} y_i a_i^{1/2} \right)^2, \quad b = \sum_{i=1}^{j} y_i b_i \tag{2.45}$$

where a_i and b_i are the values of the constants for component *i*. Combination rules for obtaining mixture values for the constants in other equations of state are also found in the literature.

Another approach is to regard the mixture as if it were a single pure component having critical properties calculated by one of several mixture rules. *Kay's rule is* perhaps the simplest of these, requiring only the determination of a mole fraction averaged critical temperature T_c and critical pressure p_c:

$$T_c = \sum_{i=1}^{j} y_i T_{c,i}, \quad p_c = \sum_{i=1}^{j} y_i p_{c,i} \tag{2.46}$$

where $T_{c,i}$ and $p_{c,i}$ are the critical temperature and critical pressure of component *i*, respectively. Using T_c and p_c, the mixture compressibility factor Z is obtained as for a single pure component. The unkown quantity from among the pressure p, volume V, temperature T, and total number of moles n of the gas mixture can then be obtained by solving $Z = pV/n\bar{R}T$.

Additional means for predicting the *p-v-T* relation of a mixture are provided by empirical mixture rules. Several are found in the engineering literature. According to the *additive pressure rule*, the pressure of a gas mixture is expressible as a sum of pressures exerted by the individual components:

$$p = p_1 + p_2 + p_3 \ldots \Big]_{T,V} \tag{2.47a}$$

where the pressures p_1, p_2, etc. are evaluated by considering the respective components to be at the volume V and temperature T of the mixture. The additive pressure rule can be expressed alternatively as

$$Z = \sum_{i=1}^{j} y_i Z_i \Bigg]_{T,V} \tag{2.47b}$$

where Z is the compressibility factor of the mixture and the compressibility factors Z_i are determined assuming that component *i* occupies the entire volume of the mixture at the temperature T.

The *additive volume rule* postulates that the volume V of a gas mixture is expressible as the sum of volumes occupied by the individual components:

$$V = V_1 + V_2 + V_3 \ldots \Big]_{p,T} \tag{2.48a}$$

where the volumes V_1, V_2, etc. are evaluated by considering the respective components to be at the pressure p and temperature T of the mixture. The additive volume rule can be expressed alternatively as

$$Z = \sum_{i=1}^{j} y_i Z_i \Bigg]_{p,T} \tag{2.48b}$$

where the compressibility factors Z_i are determined assuming that component *i* exists at the pressure p and temperature T of the mixture.

Evaluating Δh, Δu, and Δs

Using appropriate specific heat and *p-v-T* data, the changes in specific enthalpy, internal energy, and entropy can be determined between states of single-phase regions. Table 2.5 provides expressions for such property changes in terms of particular choices of the independent variables: temperature and pressure, and temperature and specific volume.

Taking Equation 1 of Table 2.5 as a representative case, the change in specific enthalpy between states 1 and 2 can be determined using the three steps shown in the accompanying property diagram. This requires knowledge of the variation of c_p with temperature at a fixed pressure p', and the variation of $[v - T(\partial v/\partial T)_p]$ with pressure at temperatures T_1 and T_2:

1-a: Since temperature is constant at T_1, the first integral of Equation 1 in Table 2.5 vanishes, and

$$h_a - h_1 = \int_{p_1}^{p'} \left[v - T(\partial v/\partial T)_p\right] dp$$

a-b: Since pressure is constant at p', the second integral of Equation 1 vanishes, and

$$h_b - h_a = \int_{T_1}^{T_2} c_p(T, p') dT$$

b-2: Since temperature is constant at T_2, the first integral of Equation 1 vanishes, and

$$h_2 - h_b = \int_{p'}^{p_2} \left[v - T(\partial v/\partial T)_p\right] dp$$

Adding these expressions, the result is $h_2 - h_1$. The required integrals may be performed numerically or analytically. The analytical approach is expedited when an equation of state explicit in specific volume is known.

Similar considerations apply to Equations 2 to 4 of Table 2.5. To evaluate $u_2 - u_1$ with Equation 3, for example, requires the variation of c_v with temperature at a fixed specific volume v', and the variation of $[T(\partial p/\partial T)_v - p]$ with specific volume at temperatures T_1 and T_2. An analytical approach to performing the integrals is expedited when an equation of state explicit in pressure is known.

As changes in specific enthalpy and internal energy are related through $h = u + pv$ by

$$h_2 - h_1 = (u_2 - u_1) + (p_2 v_2 - p_1 v_1) \tag{2.49}$$

only one of $h_2 - h_1$ and $u_2 - u_1$ need be found by integration. The other can be evaluated from Equation 2.49. The one found by integration depends on the information available: $h_2 - h_1$ would be found when an equation of state explicit in v and c_p as a function of temperature at some fixed pressure is known, $u_2 - u_1$ would be found when an equation of state explicit in p and c_v as a function of temperature at some specific volume is known.

Example 6

Obtain Equation 1 of Table 2.4 and Equations 3 and 4 of Table 2.5.

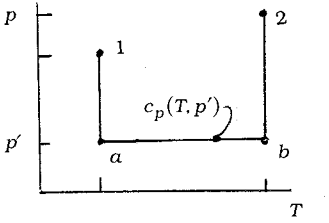
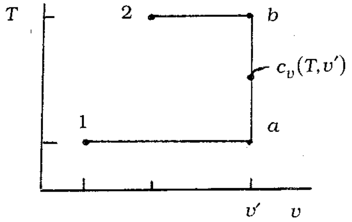
Solution. With Equation 2.33 and the Maxwell relation corresponding to $\psi(T, v)$ from Table 2.2, Equations 3′ and 4′ of Table 2.5 become, respectively,

$$du = c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial T}\right)_v dv$$

Introducing these expressions for du and ds in Equation 2.32a, and collecting terms,

TABLE 2.5 Δh, Δu, Δs Expressions

Independent properties:	temperature and pressure		temperature and specific volume	
Preferred data:	$v(T,p)$, $c_p(T,p)$		$p(T,v)$, $c_v(T,v)$	
Property diagram:				
Property expressions:	$h(T,p)$:		$u(T,v)$:	
	$dh = \underbrace{\left(\frac{\partial h}{\partial T}\right)_p}_{c_p} dT + \underbrace{\left(\frac{\partial h}{\partial p}\right)_T}_{\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]} dp$	(1′)	$du = \underbrace{\left(\frac{\partial u}{\partial T}\right)_v}_{c_v} dT + \underbrace{\left(\frac{\partial u}{\partial v}\right)_T}_{\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]} dv$	(3′)
	$\Delta h = \int c_p dT + \int \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$	(1)	$\Delta u = \int c_v dT + \int \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv$	(3)
	$s(T,p)$:		$s(T,v)$:	
	$ds = \underbrace{\left(\frac{\partial s}{\partial T}\right)_p}_{\frac{c_p}{T}} dT + \underbrace{\left(\frac{\partial s}{\partial p}\right)_T}_{-\left(\frac{\partial v}{\partial T}\right)_p} dp$	(2′)	$ds = \underbrace{\left(\frac{\partial s}{\partial T}\right)_v}_{\frac{c_v}{T}} dT + \underbrace{\left(\frac{\partial s}{\partial v}\right)_T}_{\left(\frac{\partial p}{\partial T}\right)_v} dv$	(4′)
	$\Delta s = \int \frac{c_p}{T} dT - \int \left(\frac{\partial v}{\partial T}\right)_p dp$	(2)	$\Delta s = \int \frac{c_v}{T} dT + \int \left(\frac{\partial p}{\partial T}\right)_v dv$	(4)

$$\left[T\left(\frac{\partial s}{\partial T}\right)_v - c_v\right]dT = \left[\left(\frac{\partial u}{\partial v}\right)_T + p - T\left(\frac{\partial p}{\partial T}\right)_v\right]dv$$

Since T and v are independent, the coefficients of dT and dv must vanish, giving, respectively,

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

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

The first of these corresponds to Equation 1 of Table 2.4 and Equation 4 of Table 2.5. The second of the above expressions establishes Equation 3 of Table 2.5. With similar considerations, Equation 3 of Table 2.4 and Equations 1 and 2 of Table 2.5 may be obtained.

Fundamental Thermodynamic Functions

A fundamental thermodynamic function is one that provides a complete description of the thermodynamic state. The functions $u(s, v)$, $h(s, p)$, $\psi(T, v)$, and $g(T, p)$ listed in Table 2.2 are fundamental thermodynamic functions.

In principle, all properties of interest can be determined from a fundamental thermodynamic function by differentiation and combination. Taking the function $\psi(T, v)$ as a representative case, the properties v and T, being the independent variables, are specified to fix the state. The pressure p and specific entropy s at this state can be determined by differentiation of $\psi(T, v)$, as shown in Table 2.2. By definition, $\psi = u - Ts$, so specific internal energy is obtained as

$$u = \psi + Ts$$

with u, p, and v known, the specific enthalpy can be found from the definition $h = u + pv$. Similarly, the specific Gibbs function is found from the definition $g = h - Ts$. The specific heat c_v can be determined by further differentiation $c_v = (\partial u/\partial T)_v$.

The development of a fundamental function requires the selection of a functional form in terms of the appropriate pair of independent properties and a set of adjustable coefficients that may number 50 or more. The functional form is specified on the basis of both theoretical and practical considerations. The coefficients of the fundamental function are determined by requiring that a set of selected property values and/or observed conditions be statisfied in a least-squares sense. This generally involves property data requiring the assumed functional form to be differentiated one or more times, for example *p*-*v*-*T* and specific heat data. When all coefficients have been evaluated, the function is tested for accuracy by using it to evaluate properties for which accepted values are known such as *velocity of sound* and *Joule-Thomson* data. Once a suitable fundamental function is established, extreme accuracy in and consistency among the thermodynamic properties are possible. The properties of water tabulated by Keenan et al. (1969) and by Haar et al. (1984) have been calculated from representations of the Helmholtz function.

Thermodynamic Data Retrieval

Tabular presentations of pressure, specific volume, and temperature are available for practically important gases and liquids. The tables normally include other properties useful for thermodynamic analyses, such as internal energy, enthalpy, and entropy. The various *steam tables* included in the references of this chapter provide examples. Computer software for retrieving the properties of a wide range of substances is also available, as, for example, the ASME Steam Tables (1993) and Bornakke and Sonntag (1996).

Increasingly, textbooks come with computer disks providing thermodynamic property data for water, certain refrigerants, and several gases modeled as ideal gases — see, e.g., Moran and Shapiro (1996).

The sample *steam table* data presented in Table 2.6 are representative of data available for substances commonly encountered in mechanical engineering practice. Table A.5 and Figures 2.7 to 2.9 provide *steam table* data for a greater range of states. The form of the tables and figures, and how they are used are assumed to be familiar. In particular, the use of *linear interpolation* with such tables is assumed known.

Specific internal energy, enthalpy, and entropy data are determined relative to arbitrary datums and such datums vary from substance to substance. Referring to Table 2.6a, the datum state for the specific internal energy and specific entropy of water is seen to correspond to saturated liquid water at 0.01°C (32.02°F), the triple point temperature. The value of each of these properties is set to zero at this state. If calculations are performed involving only differences in a particular specific property, the datum cancels. When there are changes in chemical composition during the process, special care should be exercised. The approach followed when composition changes due to chemical reaction is considered in Section 2.4.

Liquid water data (see Table 2.6d) suggests that at fixed temperature the variation of specific volume, internal energy, and entropy with pressure is slight. The variation of specific enthalpy with pressure at fixed temperature is somewhat greater because pressure is explicit in the definition of enthalpy. This behavior for v, u, s, and h is exhibited generally by liquid data and provides the basis for the following set of equations for estimating property data at liquid states from saturated liquid data:

$$v(T,p) \approx v_{\mathrm{f}}(T) \tag{2.50a}$$

$$u(T,p) \approx u_{\mathrm{f}}(T) \tag{2.50b}$$

$$h(T,p) \approx h_f(T) + \underline{v_{\mathrm{f}}\left[p - p_{sat}(T)\right]} \tag{2.50c}$$

$$s(T,p) \approx s_{\mathrm{f}}(T) \tag{2.50d}$$

As before, the subscript f denotes the saturated liquid state at the temperature T, and p_{sat} *is* the corresponding saturation pressure. The underlined term of Equation 2.50c is often negligible, giving $h(T, p) \approx h_{\mathrm{f}}(\mathrm{T})$, which is used in Example 3 to evaluate h_1.

In the absence of saturated liquid data, or as an alternative to such data, the *incompressible model* can be employed:

$$\text{Incompressible model:} \begin{cases} v = \text{constant} \\ u = u(T) \end{cases} \tag{2.51}$$

This model is also applicable to solids. Since internal energy varies only with temperature, the specific heat c_v is also a function of only temperature: $c_v(T) = du/dT$. Although specific volume is constant, enthalpy varies with both temperature and pressure, such that

$$h(T,p) = u(T) + pv \tag{2.52}$$

Differentiation of Equation 2.52 with respect to temperature at fixed pressure gives $c_p = c_v$. The common specific heat is often shown simply as c. Specific heat and density data for several liquids and solids are

TABLE 2.6 Sample Steam Table Data

(a) Properties of Saturated Water (Liquid-Vapor): Temperature Table

		Specific Volume (m^3/kg)		Internal Energy (kJ/kg)		Enthalpy (kJ/kg)			Entropy (kJ/kg · K)	
Temp (°C)	Pressure (bar)	Saturated Liquid ($v_f \times 10^3$)	Saturated Vapor (v_g)	Saturated Liquid (u_f)	Saturated Vapor (u_g)	Saturated Liquid (h_f)	Evap. (h_{fg})	Saturated Vapor (h_g)	Saturated Liquid (s_f)	Saturated Vapor (s_g)
.01	0.00611	1.0002	206.136	0.00	2375.3	0.01	2501.3	2501.4	0.0000	9.1562
4	0.00813	1.0001	157.232	16.77	2380.9	16.78	2491.9	2508.7	0.0610	9.0514
5	0.00872	1.0001	147.120	20.97	2382.3	20.98	2489.6	2510.6	0.0761	9.0257
6	0.00935	1.0001	137.734	25.19	2383.6	25.20	2487.2	2512.4	0.0912	9.0003
8	0.01072	1.0002	120.917	33.59	2386.4	33.60	2482.5	2516.1	0.1212	8.9501

(b) Properties of Saturated Water (Liquid-Vapor): Pressure Table

		Specific Volume (m^3/kg)		Internal Energy (kJ/kg)		Enthalpy (kJ/kg)			Entropy (kJ/kg · K)	
Pressure (bar)	Temp (°C)	Saturated Liquid ($v_f \times 10^3$)	Saturated Vapor (v_g)	Saturated Liquid (u_f)	Saturated Vapor (u_g)	Saturated Liquid (h_f)	Evap. (h_{fg})	Saturated Vapor (h_g)	Saturated Liquid (s_f)	Saturated Vapor (s_g)
0.04	28.96	1.0040	34.800	121.45	2415.2	121.46	2432.9	2554.4	0.4226	8.4746
0.06	36.16	1.0064	23.739	151.53	2425.0	151.53	2415.9	2567.4	0.5210	8.3304
0.08	41.51	1.0084	18.103	173.87	2432.2	173.88	2403.1	2577.0	0.5926	8.2287
0.10	45.81	1.0102	14.674	191.82	2437.9	191.83	2392.8	2584.7	0.6493	8.1502
0.20	60.06	1.0172	7.649	251.38	2456.7	251.40	2358.3	2609.7	0.8320	7.9085

TABLE 2.6 Sample Steam Table Data (continued)

(c) Properties of Superheated Water Vapor

T(°C)	v(m^3/kg)	u(kJ/kg)	h(kJ/kg)	s(kJ/kg · K)	v(m^3/kg)	u(kJ/kg)	h(kJ/kg)	s(kJ/kg · K)
	p = 0.06 bar = 0.006 MPa (T_{sat} 36.16°C)				p = 0.35 bar = 0.035 MPa (T_{sat} = 72.69°C)			
Sat.	23.739	2425.0	2567.4	8.3304	4.526	2473.0	2631.4	7.7158
80	27.132	2487.3	2650.1	8.5804	4.625	2483.7	2645.6	7.7564
120	30.219	2544.7	2726.0	8.7840	5.163	2542.4	2723.1	7.9644
160	33.302	2602.7	2802.5	8.9693	5.696	2601.2	2800.6	8.1519
200	36.383	2661.4	2879.7	9.1398	6.228	2660.4	2878.4	8.3237

(d) Properties of Compressed Liquid Water

T(°C)	$v \times 10^3$ (m^3/kg)	u(kJ/kg)	h(kJ/kg)	s(kJ/kg · K)	$v \times 10^3$ (m^3/kg)	u(kJ/kg)	h(kJ/kg)	s(kJ/kg · K)
	p = 25 bar = 2.5 MPa (T_{sat} 223.99°C)				p = 50 bar = 5.0 MPa (T_{sat} = 263.99°C)			
20	1.0006	83.80	86.30	0.2961	0.9995	83.65	88.65	0.2956
80	1.0280	334.29	336.86	1.0737	1.0268	333.72	338.85	1.0720
140	1.0784	587.82	590.52	1.7369	1.0768	586.76	592.15	1.7343
200	1.1555	849.9	852.8	2.3294	1.1530	848.1	853.9	2.3255
Sat.	1.1973	959.1	962.1	2.5546	1.2859	1147.8	1154.2	2.9202

Source: Moran, M.J. and Shapiro, H.N. 1995. *Fundamentals of Engineering Thermodynamics*, 3rd ed. Wiley, New York, as extracted from Keenan, J. H., Keyes, F.G., Hill, P.G., and Moore, J.G. 1969. *Steam Tables*. Wiley, New York.

provided in Tables B.2, C.1, and C.2. As the variation of c with temperature is slight, c is frequently taken as constant.

When the incompressible model is applied. Equation 2.49 takes the form

$$\begin{aligned} h_2 - h_1 &= \int_{T_1}^{T_2} c(T)\,dT + v(p_2 - p_1) \\ &= c_{ave}(T_2 - T_1) + v(p_2 - p_1) \end{aligned} \tag{2.53}$$

Also, as Equation 2.32a reduces to $du = Tds$, and $du = c(T)dT$, the change in specific entropy is

$$\begin{aligned} \Delta s &= \int_{T_1}^{T_2} \frac{c(T)}{T}\,dT \\ &= c_{ave} \ln \frac{T_2}{T_1} \end{aligned} \tag{2.54}$$

Ideal Gas Model

Inspection of the generalized compressibility chart, Figure 2.10, shows that when p_R is small, and for many states when T_R is large, the value of the compressibility factor Z is close to 1. In other words, for pressures that are low relative to p_c, and for many states with temperatures high relative to T_c, the compressibility factor approaches a value of 1. Within the indicated limits, it may be assumed with reasonable accuracy that $Z = 1$ — that is,

$$p\bar{v} = \bar{R}T \quad \text{or} \quad pv = RT \tag{2.55a}$$

where $R = \bar{R}/\mathcal{M}$ is the *specific* gas constant. Other forms of this expression in common use are

$$pV = n\bar{R}T, \qquad pV = mRT \tag{2.55b}$$

Referring to Equation 3′ of Table 2.5, it can be concluded that $(\partial u/\partial v)_T$ vanishes identically for a gas whose equation of state is *exactly* given by Equation 2.55, and thus the specific internal energy depends only on temperature. This conclusion is supported by experimental observations beginning with the work of Joule, who showed that the internal energy of air at low density depends primarily on temperature.

These considerations allow for an *ideal gas model* of each real gas: (1) the equation of state is given by Equation 2.55 and (2) the internal energy and enthalpy are functions of temperature alone. The real gas approaches the model in the limit of low reduced pressure. At other states the actual behavior may depart substantially from the predictions of the model. Accordingly, caution should be exercised when invoking the ideal gas model lest significant error is introduced.

Specific heat data for gases can be obtained by direct measurement. When extrapolated to zero pressure, ideal gas-specific heats result. Ideal gas-specific heats also can be calculated using molecular models of matter together with data from spectroscopic measurements. Table A.9 provides ideal gas-specific heat data for a number of substances. The following ideal gas-specific heat relations are frequently useful:

$$c_p(T) = c_v(T) + R \tag{2.56a}$$

$$c_p = \frac{kR}{k-1}, \qquad c_v = \frac{R}{k-1} \tag{2.56b}$$

where $k = c_p/c_v$.

With the ideal gas model, Equations 1 to 4 of Table 2.5 give Equations 1 to 4 of Table 2.7, respectively. Equation 2 of Table 2.7 can be expressed alternatively using $s°(T)$ defined by

$$s°(T) \equiv \int_0^T \frac{c_p(T)}{T} dT \tag{2.57}$$

as

$$s(T_2, p_2) - s(T_1, p_1) = s°(T_2) - s°(T_1) - R \ln \frac{p_2}{p_1} \tag{2.58}$$

Expressions similar in form to Equations 2.56 to 2.68 can be written on a molar basis.

TABLE 2.7 Ideal Gas Expressions for Δ*h*, Δ*u*, and Δ*s*

Variable Specific Heats		Constant Specific Heats	
$h(T_2) - h(T_1) = \int_{T_1}^{T_2} c_p(T) dT$	(1)	$h(T_2) - h(T_1) = c_p(T_2 - T_1)$	(1′)
$s(T_2, p_2) - s(T_1, p_1) = \int_{T_1}^{T_2} \frac{c_p(T)}{T} dT - R \ln \frac{p_2}{p_1}$	(2)	$s(T_2, p_2) - s(T_1, p_1) = c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}$	(2′)
$u(T_2) - u(T_1) = \int_{T_1}^{T_2} c_v(T) dT$	(3)	$u(T_2) - u(T_1) = c_v(T_2 - T_1)$	(3′)
$s(T_2, v_2) - s(T_1, v_1) = \int_{T_1}^{T_2} \frac{c_v(T)}{T} dT + R \ln \frac{v_2}{v_1}$	(4)	$s(T_2, v_2) - s(T_1, v_1) = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$	(4′)
$s_2 = s_1$		$s_2 = s_1$	
$\frac{p_r(T_2)}{p_r(T_1)} = \frac{p_2}{p_1}$	(5)	$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(k-1)/k}$	(5′)
$\frac{v_r(T_2)}{v_r(T_1)} = \frac{v_2}{v_1}$	(6)	$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1}$	(6′)

For processes of an ideal gas between states having the same specific entropy, $s_2 = s_1$, Equation 2.58 gives

$$\frac{p_2}{p_1} = \frac{\exp\left[s°(T_2)/R\right]}{\exp\left[s°(T_1)/R\right]}$$

or with $p_r = \exp[s°(T)/R]$

$$\frac{p_2}{p_1} = \frac{p_r(T_2)}{p_r(T_1)} \qquad (s_2 = s_1) \tag{2.59a}$$

A relation between the specific volume and temperatures for two states of an ideal gas having the same specific entropy can also be developed:

$$\frac{v_2}{v_1} = \frac{v_r(T_2)}{v_r(T_1)} \qquad (s_2 = s_1) \tag{2.59b}$$

Equations 2.59 are listed in Table 2.7 as Equations 5 and 6, respectively.

Table A.8 provides a tabular display of h, u, $s°$, p_r, and v_r vs. temperature for air as an ideal gas. Tabulations of $\bar{h}$, $\bar{u}$, and $\bar{s}°$ for several other common gases are provided in Table A.2. Property retrieval software also provides such data; see, e.g., Moran and Shapiro (1996). The use of data from Table A.8 for the nozzle of Example 2 is illustrated in Example 7.

When the ideal gas-specific heats are assumed constant, Equations 1 to 6 of Table 2.7 become Equations 1′ to 6′, respectively. The specific heat c_p is taken as constant in Example 2.

Example 7

Using data from Table A.8, evaluate the exit velocity for the nozzle of Example 2 and compare with the exit velocity for an isentropic expansion to 15 lbf/in.^{2}.

Solution. The exit velocity is given by Equation 2.27f

$$\mathrm{v}_e = \sqrt{\mathrm{v}_i^2 + 2\left(h_i - h_e\right)}$$

At 960 and 520°R, Table A.8 gives, respectively, h_i = 231.06 Btu/lb and h_e = 124.27 Btu/lb. Then

$$\mathrm{v}_e = \sqrt{\left(\frac{10\text{ ft}}{s}\right)^2 + 2(231.06 - 124.27)\left(\frac{\text{Btu}}{\text{lb}}\right)\left(\frac{778.17\text{ ft}\cdot\text{lbf}}{1\text{ Btu}}\right)\left(\frac{32.174\text{ lb}\cdot\text{ft/sec}^2}{1\text{ lbf}}\right)}$$

$$= 2312.5 \text{ ft sec}$$

Using Equation 2.59a and p_r data from Table A.8, the specific enthalpy at the exit for an isentropic expansion is found as follows:

$$p_r\left(T_e\right) = p_r\left(T_i\right)\frac{p_e}{p_i} = 10.61\left(\frac{15}{150}\right) = 1.061$$

Interpolating with p_r data, h_e = 119.54 Btu/lb. With this, the exit velocity is 2363.1 ft/sec. The actual exit velocity is about 2% less than the velocity for an isentropic expansion, the maximum theoretical value. In this particular application, there is good agreement in each case between velocities calculated using Table A.8 data and, as in Example 2, assuming c_p constant. Such agreement cannot be expected generally, however. See, for example, the Brayton cycle data of Table 2.15.

Polytropic Processes

An internally reversible process described by the expression pv^n = constant is called a *polytropic process* and n *is* the *polytropic exponent.* Although this expression can be applied with real gas data, it most generally appears in practice together with the use of the ideal gas model. Table 2.8 provides several expressions applicable to polytropic processes and the special forms they take when the ideal gas model is assumed. The expressions for $\int pdv$ and $\int vdp$ have application to work evaluations with Equations 2.10 and 2.30, respectively. In some applications it may be appropriate to determine n by fitting pressure-specific volume data.

Example 8 illustrates both the polytropic process and the reduction in the compressor work achievable by cooling a gas as it is compressed.

Example 8

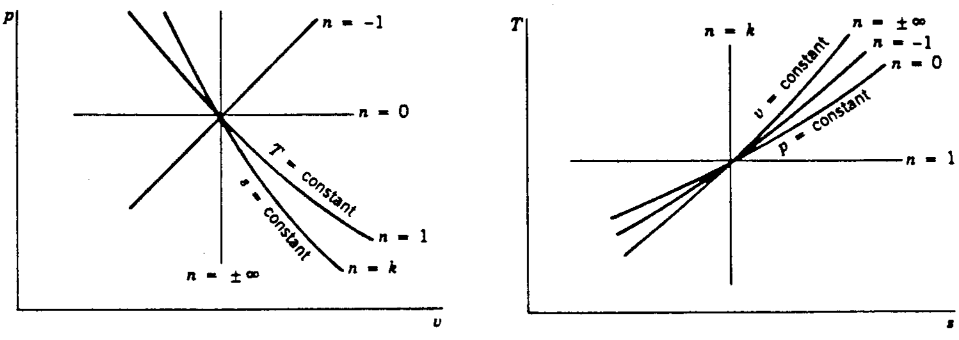
A compressor operates at steady state with air entering at 1 bar, 20°C and exiting at 5 bar. (a) If the air undergoes a polytropic process with n = 1.3, determine the work and heat transfer, each in kJ/kg of air flowing. Repeat for (b) an isothermal compression and (c) an isentropic compression.

TABLE 2.8 Polytropic Processes: pv^n = Constant[a]

General		Ideal Gas[b]	
$\frac{p_2}{p_1}=\left(\frac{v_1}{v_2}\right)^n$	(1)	$\frac{p_2}{p_1}=\left(\frac{v_1}{v_2}\right)^n=\left(\frac{T_2}{T_1}\right)^{n/(n-1)}$	(1′)
$n = 0$: constant pressure $n = \pm\infty$: constant specific volume		$n = 0$: constant pressure $n = \pm\infty$: constant specific volume $n = 1$: constant temperature $n = k$: constant specific entropy when k is constant	
$n = 1$		$n = 1$	
$\int_1^2 pdv = p_1v_1 \ln\frac{v_2}{v_1}$	(2)	$\int_1^2 pdv = RT\ln\frac{v_2}{v_1}$	(2′)
$-\int_1^2 vdp = -p_1v_1 \ln\frac{p_2}{p_1}$	(3)	$-\int_1^2 vdp = -RT\ln\frac{p_2}{p_1}$	(3′)
$n \neq 1$		$n \neq 1$	
$\int_1^2 pdv = \frac{p_2v_2 - p_1v_1}{1-n}$ $= \frac{p_1v_1}{n-1}\left[1-\left(\frac{p_2}{p_1}\right)^{(n-1)/n}\right]$	(4)	$\int_1^2 pdv = \frac{R(T_2 - T_1)}{1-n}$ $= \frac{RT_1}{n-1}\left[1-\left(\frac{p_2}{p_1}\right)^{(n-1)/n}\right]$	(4′)
$-\int_1^2 vdp = \frac{n}{1-n}(p_2v_2 - p_1v_1)$ $= \frac{np_1v_1}{n-1}\left[1-\left(\frac{p_2}{p_1}\right)^{(n-1)/n}\right]$	(5)	$-\int_1^2 vdp = \frac{nR}{1-n}(T_2 - T_1)$ $= \frac{nRT_1}{n-1}\left[1-\left(\frac{p_2}{p_1}\right)^{(n-1)/n}\right]$	(5′)

[a] For polytropic processes of closed systems where volume change is the only work mode, Equations 2, 4, and 2′, 4′ are applicable with Equation 2.10 to evaluate the work. When each unit of mass passing through a one-inlet, one-exit control volume at steady state undergoes a polytropic process, Equations 3, 5, and 3′, 5′ are applicable with Equations 2.30a and 2.30b to evaluate the power. Also note that generally, $-\int_1^2 vdp = n\int_1^2 pdv$.

[b]



Solution. Using Equation 5′ of Table 2.8 together with Equation 2.30b,

$$\frac{\dot{W}_{cv}}{\dot{m}} = \frac{nRT_1}{n-1}\left[1-\left(\frac{p_2}{p_1}\right)^{(n-1)/n}\right]$$

$$= \left(\frac{1.3}{0.3}\right)\left(\frac{8.314}{28.97}\frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right)(293\text{ K})\left[1-(5)^{0.3/1.3}\right]$$

$$= -163.9\ \frac{\text{kJ}}{\text{kg}}$$

(The area behind process 1-2 of Figure 2.11, area 1-2-a-b, represents the magnitude of the work required, per unit mass of air flowing.) Also, Equation 1′ of Table 2.8 gives T_2 = 425 K.

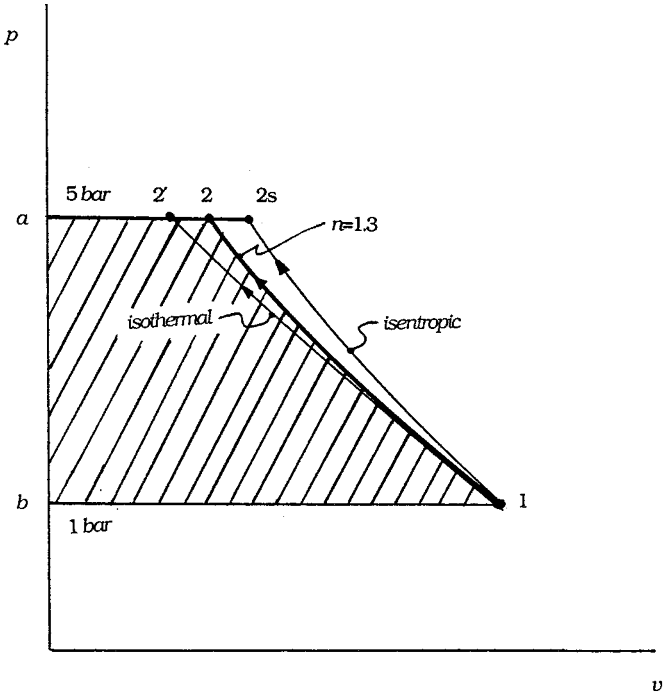


FIGURE 2.11 Internally reversible compression processes.

An energy rate balance at steady state and enthalpy data from Table A.8 gives

$$\frac{\dot{Q}_{cv}}{\dot{m}} = \frac{\dot{W}_{cv}}{\dot{m}} + h_2 - h_1$$

$$= -163.9 + (426.3 - 293.2) = -30.8\frac{\text{kJ}}{\text{kg}}$$

(b) Using Equation 3′ of Table 2.8 together with Equation 2.30b,

$$\frac{\dot{W}_{cv}}{\dot{m}} = -RT\ln\frac{p_2}{p_1}$$

$$= -\left(\frac{8.314}{28.97}\right)(293)\ln 5$$

$$= -135.3\frac{\text{kJ}}{\text{kg}}$$

Area 1-2′-*a*-*b* on Figure 2.11 represents the magnitude of the work required, per unit of mass of air flowing. An energy balance reduces to give $\dot{Q}_{cv}/\dot{m} = \dot{W}_{cv}/\dot{m}$ = –135.3 kJ/kg. (c) For an isentropic compression, $\dot{Q}_{cv} = 0$ and an energy rate balance reduces to give $\dot{W}_{cv}/\dot{m}$ = $-(h_{2s} - h_1)$, where 2*s* denotes the exit state. With Equation 2.59a and p_r data, h_{2s} = 464.8 kJ/kg (T_{2s} = 463K). Then $\dot{W}_{cv}/\dot{m}$ = –(464.8 – 293.2) = –171.6 kJ/kg. Area 1-2s-*a*-*b* on Figure 2.11 represents the magnitude of the work required, per unit of mass of air flowing.

Ideal Gas Mixtures

When applied to an ideal gas mixture, the additive pressure rule (Section 2.3, *p*-*v*-*T* Relations) is known as the *Dalton model*. According to this model, each gas in the mixture acts as if it exists separately at the volume and temperature of the mixture. Applying the ideal gas equation of state to the mixture as a whole and to each component *i*, $pV = n\bar{R}T$, $p_iV = n_i\bar{R}T$, where p_i, the *partial pressure* of component *i*, is the pressure that component *i* would exert if n_i moles occupied the full volume *V* at the temperature *T*. Forming a ratio, the partial pressure of component *i* is

$$p_i = \frac{n_i}{n}p = y_i p \tag{2.60}$$

where y_i is the mole fraction of component *i*. The sum of the partial pressures equals the mixture pressure.

The internal energy, enthalpy, and entropy of the mixture can be determined as the sum of the respective properties of the component gases, provided that the contribution from each gas is evaluated at the condition at which the gas exists in the mixture. On a *molar* basis,

$$U = \sum_{i=1}^{j} n_i\bar{u}_i \quad \text{or} \quad \bar{u} = \sum_{i=1}^{j} y_i\bar{u}_i \tag{2.61a}$$

$$H = \sum_{i=1}^{j} n_i\bar{h}_i \quad \text{or} \quad \bar{h} = \sum_{i=1}^{j} y_i\bar{h}_i \tag{2.61b}$$

$$S = \sum_{i=1}^{j} n_i\bar{s}_i \quad \text{or} \quad \bar{s} = \sum_{i=1}^{j} y_i\bar{s}_i \tag{2.61c}$$

The specific heats $\bar{c}_v$ and $\bar{c}_p$ for an ideal gas mixture in terms of the corresponding specific heats of the components are expressed similarly:

$$\bar{c}_v = \sum_{i=1}^{j} y_i\bar{c}_{vi} \tag{2.61d}$$

$$\bar{c}_p = \sum_{i=1}^{j} y_i \bar{c}_{pi} \tag{2.61e}$$

When working on a *mass* basis, expressions similar in form to Equations 2.61 can be written using *mass* and *mass fractions* in place of *moles* and *mole fractions*, respectively, and using u, h, s, c_p, and c_v in place of $\bar{u}, \bar{h}, \bar{s}, \bar{c}_p,$ and $\bar{c}_V,$ respectively.

The internal energy and enthalpy of an ideal gas depend only on temperature, and thus the $\bar{u}_i$ and $\bar{h}_i$ terms appearing in Equations 2.61 are evaluated at the temperature of the mixture. Since entropy depends on *two* independent properties, the $\bar{s}_i$ terms are evaluated either at the temperature and the partial pressure p_i of component i, or at the temperature and volume of the mixture. In the former case

$$\begin{aligned} S &= \sum_{i=1}^{j} n_i \bar{s}_i (T, p_i) \\ &= \sum_{i=1}^{j} n_i \bar{s}_i (T, x_i p) \end{aligned} \tag{2.62}$$

Inserting the expressions for H and S given by Equations 2.61b and 2.61c into the Gibbs function, $G = H - TS$,

$$\begin{aligned} G &= \sum_{i=1}^{j} n_i \bar{h}_i (T) - T \sum_{i=1}^{j} n_i \bar{s}_i (T, p_i) \\ &= \sum_{i=1}^{j} n_i \bar{g}_i (T, p_i) \end{aligned} \tag{2.63}$$

where the molar-specific Gibbs function of component i is $g_i(T, p_i) = h_i(T) - Ts_i(T, p_i)$. The Gibbs function of i can be expressed alternatively as

$$\begin{aligned} \bar{g}_i (T, p_i) &= \bar{g}_i (T, p') + \bar{R} T \ln\left(p_i / p'\right) \\ &= \bar{g}_i (T, p') + \bar{R} T \ln\left(x_i p / p'\right) \end{aligned} \tag{2.64}$$

were p' is some specified pressure. Equation 2.64 is obtained by integrating Equation 2.32d at fixed temperature T from pressure p' to p_i.

Moist Air

An ideal gas mixture of particular interest for many practical applications is *moist air.* Moist air refers to a mixture of dry air and water vapor in which the dry air is treated as if it were a pure component. Ideal gas mixture principles usually apply to moist air. In particular, the *Dalton model is* applicable, and so the mixture pressure p is the sum of the partial pressures p_a and p_v of the dry air and water vapor, respectively.

Saturated air is a mixture of dry air and saturated water vapor. For saturated air, the partial pressure of the water vapor equals $p_{sat}(T)$, which is the saturation pressure of water corresponding to the dry-bulb (mixture) temperature T. The makeup of moist air can be described in terms of the *humidity ratio* (*specific humidity*) and the *relative humidity.* The bulb of a *wet-bulb thermometer* is covered with a wick saturated with liquid water, and the *wet-bulb* temperature of an air-water vapor mixture is the temperature indicated by such a thermometer exposed to the mixture.

When a sample of moist air is cooled at constant pressure, the temperature at which the sample becomes saturated is called the *dew point temperature.* Cooling below the dew point temperature results in the condensation of some of the water vapor initially present. When cooled to a final equilibrium state at a temperature below the dew point temperature, the original sample would consist of a gas phase of dry air and saturated water vapor in equilibrium with a liquid water phase.

Psychrometric charts are plotted with various moist air parameters, including the dry-bulb and wet-bulb temperatures, the humidity ratio, and the relative humidity, usually for a specified value of the mixture pressure such as 1 atm. Further discussion of moist air and related psychrometric principles and applications is provided in Chapter 9.

Generalized Charts for Enthalpy, Entropy, and Fugacity

The changes in enthalpy and entropy between two states can be determined in principle by correcting the respective property change determined using the ideal gas model. The corrections can be obtained, at least approximately, by inspection of the generalized enthalpy correction and entropy correction charts, Figures 2.12 and 2.13, respectively. Such data are also available in tabular form (see, e.g., Reid and Sherwood, 1966) and calculable using a generalized equation for the compressibility factor (Reynolds, 1979). Using the superscript * to identify ideal gas property values, the changes in specific enthalpy and specific entropy between states 1 and 2 are

$$\bar{h}_2 - \bar{h}_1 = \underline{\bar{h}_2^* - \bar{h}_1^*} - \underline{\bar{R}T_c\left[\left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c}\right)_2 - \left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c}\right)_1\right]} \tag{2.65a}$$

$$\bar{s}_2 - \bar{s}_1 = \underline{\bar{s}_2^* - \bar{s}_1^*} - \underline{\bar{R}\left[\left(\frac{\bar{s}^* - \bar{s}}{\bar{R}}\right)_2 - \left(\frac{\bar{s}^* - \bar{s}}{\bar{R}}\right)_1\right]} \tag{2.65b}$$

The first underlined term on the right side of each expression represents the respective property change assuming ideal gas behavior. The second underlined term is the correction that must be applied to the ideal gas value to obtain the actual value. The quantities $(\bar{h}^* - \bar{h})/\bar{R}T_c$ *and* $(\bar{s}^* - \bar{s})/\bar{R}$ at state 1 would be read from the respective correction chart or table or calculated, using the reduced temperature T_{R1} and reduced pressure p_{R1} corresponding to the temperature T_1 and pressure p_1 at state 1, respectively. Similarly, $(\bar{h}^* - \bar{h})/\bar{R}T_c$ *and* $(\bar{s}^* - \bar{s})/\bar{R}$ at state 2 would be obtained using T_{R2} and p_{R2}. Mixture values for T_c and p_c determined by applying Kay's rule or some other mixture rule also can be used to enter the generalized enthalpy correction and entropy correction charts.

Figure 2.14 gives the *fugacity* coefficient, *f/p*, as a function of reduced pressure and reduced temperature. The fugacity *f* plays a similar role in determining the specific Gibbs function for a real gas as pressure plays for the ideal gas. To develop this, consider the variation of the specific Gibbs function with pressure at fixed temperature (from Table 2.2)

$$\left.\frac{\partial g}{\partial p}\right)_T = v$$

For an ideal gas, integration at fixed temperature gives

$$g^* = RT \ln p + C(T)$$

where $C(T)$ is a function of integration. To evaluate g for a real gas, fugacity replaces pressure,

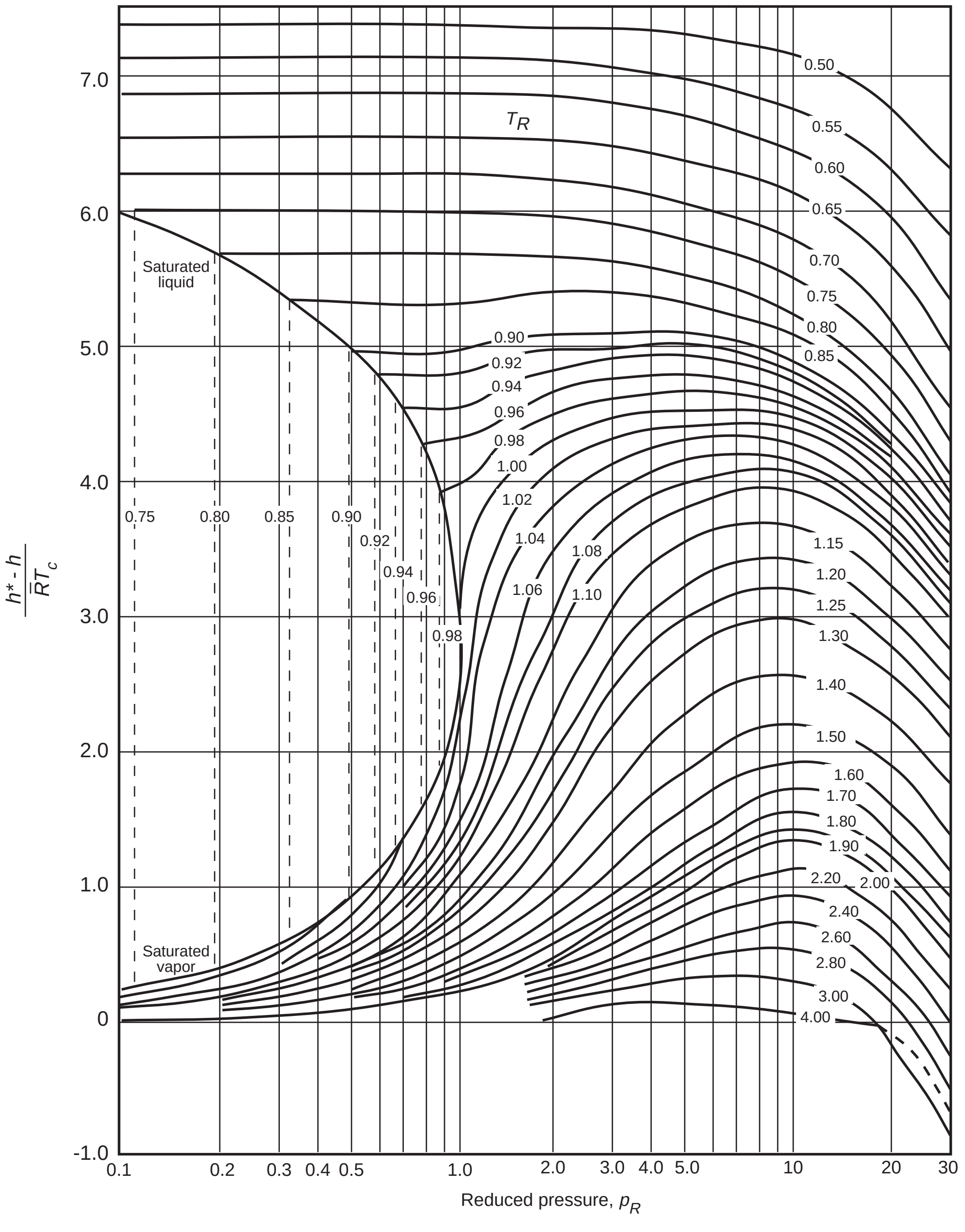


FIGURE 2.12 Generalized enthalpy correction chart. (*Source:* Adapted from Van Wylen, G. J. and Sonntag, R. E. 1986. *Fundamentals of Classical Thermodynamics*, 3rd ed., English/SI. Wiley, New York.)

$$g = RT \ln f + C(T)$$

In terms of the fugacity coefficient the departure of the real gas value from the ideal gas value at fixed temperature is then

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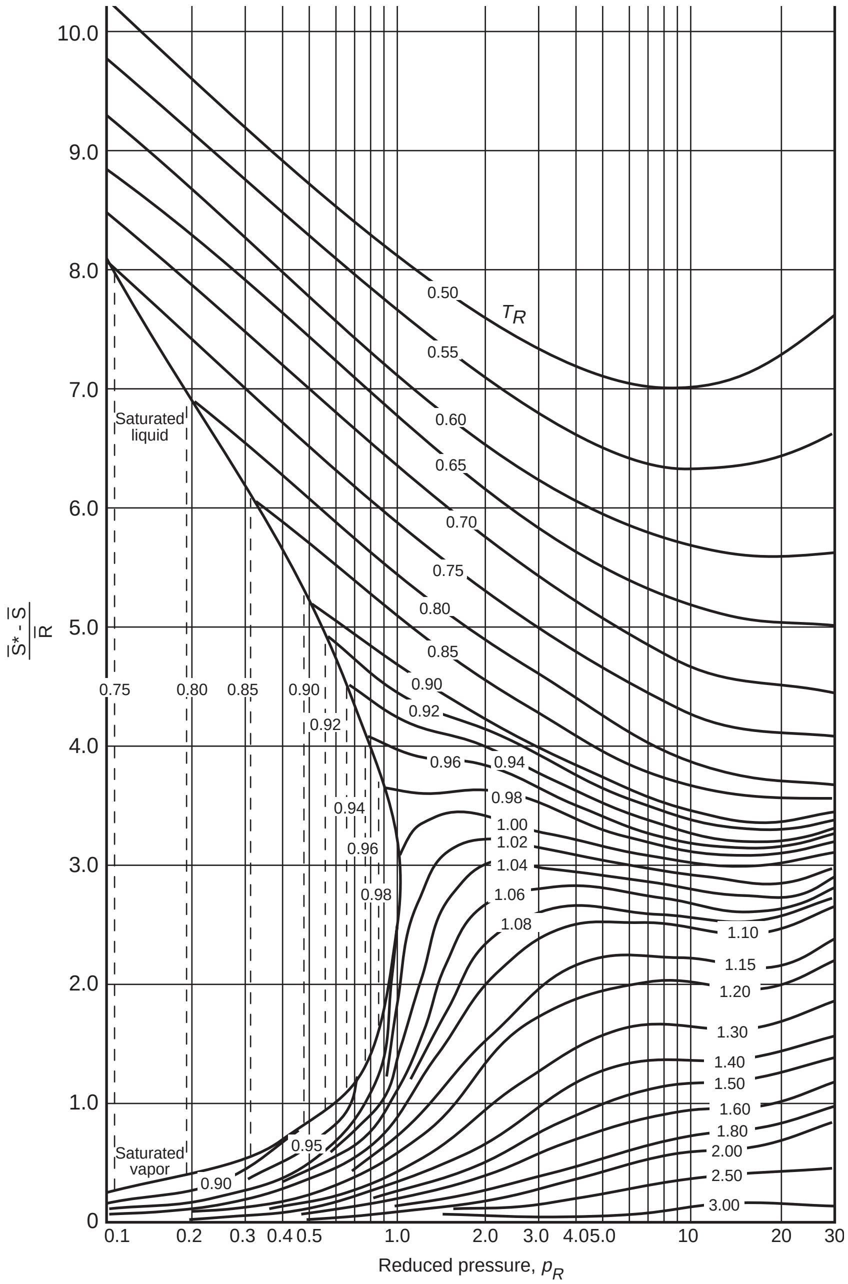


FIGURE 2.13 Generalized entropy correction chart. (*Source:* Adapted from Van Wylen, G. J. and Sonntag, R. E. 1986. *Fundamentals of Classical Thermodynamics*, 3rd ed., English/SI. Wiley, New York.)

$$g - g^* = RT \ln \frac{f}{p} \tag{2.66}$$

As pressure is reduced at fixed temperature, *f/p* tends to unity, and the specific Gibbs function is given by the ideal gas value.

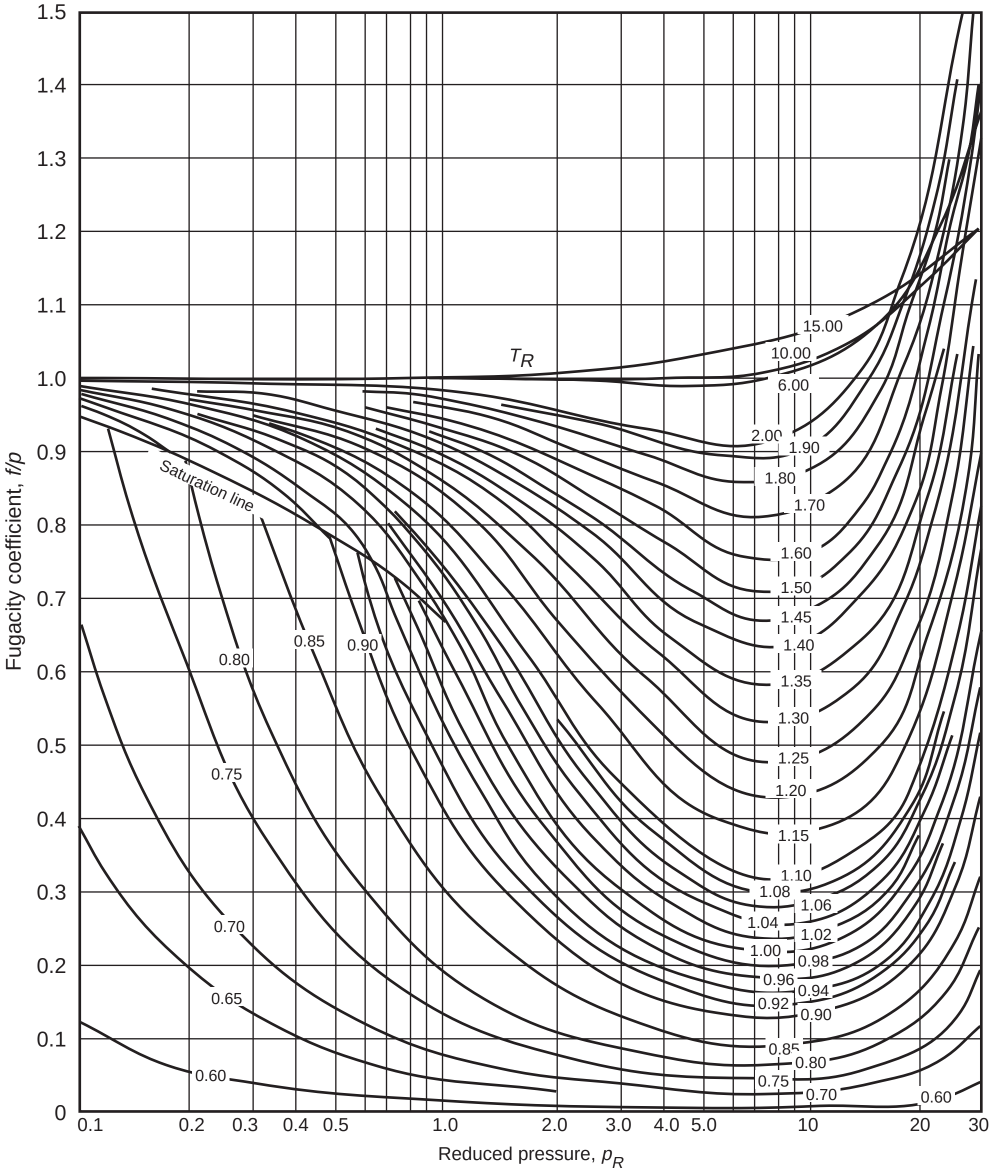


FIGURE 2.14 Generalized fugacity coefficient chart. (*Source:* Van Wylen, G. J. and Sonntag, R. E. 1986. *Fundamentals of Classical Thermodynamics*, 3rd ed., English/SI. Wiley, New York.)

Multicomponent Systems

In this section are presented some general aspects of the properties of multicomponent systems consisting of nonreacting mixtures. For a single phase *multicomponent* system consisting of j components, an extensive property X may be regarded as a function of temperature, pressure, and the number of moles of each component present in the mixture: $X = X(T, p, n_1, n_2, \ldots n_j)$. Since X is mathematically *homogeneous of degree one* in the n's, the function is expressible as

$$X = \sum_{i=1}^{j} n_i \bar{X}_i \tag{2.67}$$

where the *partial molar property* $\bar{X}_i$ is by definition

$$\bar{X}_i = \left.\frac{\partial X}{\partial n_i}\right)_{T,p,n_\ell} \tag{2.68}$$

and the subscript n_ℓ denotes that all n's except n_i are held fixed during differentiation. As $\bar{X}_i$ depends in general on temperature, pressure, and mixture composition: $\bar{X}_i(T, p, n_1, n_2, \dots n_j)$, the partial molal property $\bar{X}_i$ is an intensive property of the mixture and not simply a property of the i*th* component.

Selecting the extensive property X to be volume, internal energy, enthalpy, entropy, and the Gibbs function, respectively, gives

$$\begin{aligned} V &= \sum_{i=1}^{j} n_i \bar{V}_i, & U &= \sum_{i=1}^{j} n_i \bar{U}_i \\ H &= \sum_{i=1}^{j} n_i \bar{H}_i, & S &= \sum_{i=1}^{j} n_i \bar{S}_i \\ G &= \sum_{i=1}^{j} n_i \bar{G}_i \end{aligned} \tag{2.69}$$

where $\bar{V}_i, \bar{U}_i, \bar{H}_i, \bar{S}_i,$ and $\bar{G}_i$ denote the respective partial molal properties.

When pure components, each initially at the same temperature and pressure, are mixed, the changes in volume, internal energy, enthalpy, and entropy on mixing are given by

$$\Delta V_{\text{mixing}} = \sum_{i=1}^{j} n_i \left(\bar{V}_i - \bar{v}_i\right) \tag{2.70a}$$

$$\Delta U_{\text{mixing}} = \sum_{i=1}^{j} n_i \left(\bar{U}_i - \bar{u}_i\right) \tag{2.70b}$$

$$\Delta H_{\text{mixing}} = \sum_{i=1}^{j} n_i \left(\bar{H}_i - \bar{h}_i\right) \tag{2.70c}$$

$$\Delta S_{\text{mixing}} = \sum_{i=1}^{j} n_i \left(\bar{S}_i - \bar{s}_i\right) \tag{2.70d}$$

where $\bar{v}_i, \bar{u}_i, \bar{h}_i,$ and $\bar{s}_i$ denote the molar-specific volume, internal energy, enthalpy, and entropy of pure component i.

Chemical Potential

The partial molal Gibbs function of the *i*th component of a multicomponent system is the *chemical potential*, μ_i,

$$\mu_i = \overline{G}_i = \left.\frac{\partial G}{\partial n_i}\right)_{T,p,n_\ell} \tag{2.71}$$

Like temperature and pressure, the chemical potential, μ_i is an *intensive* property.

When written in terms of chemical potentials, Equation 2.67 for the Gibbs function reads

$$G = \sum_{i=1}^{j} n_i \mu_i \tag{2.72}$$

For a *single component sysrem,* Equation 2.72 reduces to $G = n\mu$; that is, the chemical potential equals the molar Gibbs function. For an ideal gas mixture, comparison of Equations 2.63 and 2.72 suggests $\mu_i = \bar{g}_i\,(T, p_i)$; that is, the chemical potential of component i in an ideal gas mixture equals its Gibbs function per mole of gas i evaluated at the mixture temperature and the partial pressure of the ith gas of the mixture.

The chemical potential is a measure of the *escaping tendency* of a substance in a multiphase system: a substance tends to move from the phase having the higher chemical potential for that substance to the phase having a lower chemical potential. A necessary condition for *phase equilibrium is* that the chemical potential of each component has the same value in every phase.

The *Gibbs phase rule* gives the number F of independent intensive properties that may be arbitrarily specified to fix the intensive state of a system at equilibrium consisting of N nonreacting components present in P phases: $F = 2 + N - P$. F is called the *degrees of freedom* (or the *variance*). For water as a single component, for example, $N = 1$ and $F = 3 - P$.

- For a single phase, $P = 1$ and $F = 2$: two intensive properties can be varied independently, say temperature *and* pressure, while maintaining a single phase.
- For two phases, $P = 2$ and $F = 1$: only one intensive property can be varied independently if two phases are maintained — for example, temperature *or* pressure.
- For three phases, $P = 3$ and $F = 0$: there are no degrees of freedom; each intensive property of each phase is fixed. For a system consisting of ice, liquid water, and water vapor at equilibrium, there is a unique temperature: 0.01°C (32.02°F) and a unique pressure: 0.6113 kPa (0.006 atm).

The phase rule does not address the relative amounts that may be present in the various phases.

With $G = H - TS$ and $H = U + pV$, Equation 2.72 can be expressed as

$$U = TS - pV + \sum_{i=1}^{j} n_i \mu_i \tag{2.73}$$

from which can be derived

$$dU = TdS - pdV + \sum_{i=1}^{j} \mu_i dn_i \tag{2.74}$$

When the mixture composition is constant, Equation 2.74 reduces to Equation 2.31a.

Ideal Solution

The *Lewis-Randall rule* states that the fugacity $\bar{f}_i$ of each component i in an *ideal solution* is the product of its mole fraction and the fugacity of the pure component, f_i, at the same temperature, pressure, and state of aggregation (gas, liquid, or solid) as the mixture:

$$\bar{f}_i = y_i f_i \qquad \text{(Lewis-Randall rule)} \tag{2.75}$$

The following characteristics are exhibited by an ideal solution: $\overline{V}_i = \bar{v}_i, \overline{U}_i = \bar{u}_i, \overline{H}_i = \bar{h}_i$. With these, Equations 2.70a, b, and c show that there is no change in volume, internal energy, or enthalpy on mixing pure components to form an ideal solution. The *adiabatic* mixing of different pure components would result in an increase in entropy, however, because such a process is irreversible.

The volume of an ideal solution is

$$V = \sum_{i=1}^{j} n_i \bar{v}_i = \sum_{i=1}^{j} V_i \qquad \text{(ideal solution)} \tag{2.76}$$

where V_i is the volume that pure component i would occupy when at the temperature and pressure of the mixture. Comparing Equations 2.48a and 2.76, the *additive volume rule* is seen to be exact for ideal solutions. The internal energy and enthalpy of an ideal solution are

$$U = \sum_{i=1}^{j} n_i \bar{u}_i, \quad H = \sum_{i=1}^{j} n_i \bar{h}_i \qquad \text{(ideal solution)} \tag{2.77}$$

where $\bar{u}_i$ and $\bar{h}_i$ denote, respectively, the molar internal energy and enthalpy of pure component i at the temperature and pressure of the mixture. Many gaseous mixtures at low to moderate pressures are adequately modeled by the Lewis Randall rule. The ideal gas mixtures considered in Section 2.3, Ideal Gas Model, is an important special case. Some liquid solutions also can be modeled with the Lewis-Randall rule.

2.4 Combustion

The thermodynamic analysis of reactive systems is primarily an extension of principles presented in Sections 2.1 to 2.3. It is necessary, though, to modify the methods used to evaluate specific enthalpy and entropy.

Reaction Equations

In combustion reactions, rapid oxidation of combustible elements of the fuel results in energy release as combustion products are formed. The three major combustible chemical elements in most common fuels are carbon, hydrogen, and sulfur. Although sulfur is usually a relatively unimportant contributor to the energy released, it can be a significant cause of pollution and corrosion.

The emphasis in this section is on hydrocarbon fuels, which contain hydrogen, carbon, sulfur, and possibly other chemical substances. Hydrocarbon fuels may be liquids, gases, or solids such as coal. Liquid hydrocarbon fuels are commonly derived from crude oil through distillation and cracking processes. Examples are gasoline, diesel fuel, kerosene, and other types of fuel oils. The compositions of liquid fuels are commonly given in terms of mass fractions. For simplicity in combustion calculations, gasoline is often considered to be octane, C_8H_{18}, and diesel fuel is considered to be dodecane, $C_{12}H_{26}$. Gaseous hydrocarbon fuels are obtained from natural gas wells or are produced in certain chemical processes. Natural gas normally consists of several different hydrocarbons, with the major constituent being methane, CH_4. The compositions of gaseous fuels are commonly given in terms of mole fractions. Both gaseous and liquid hydrocarbon fuels can be synthesized from coal, oil shale, and tar sands. The composition of coal varies considerably with the location from which it is mined. For combustion calculations, the makeup of coal is usually expressed as an *ultimate analysis* giving the composition on a mass basis in terms of the relative amounts of chemical elements (carbon, sulfur, hydrogen, nitrogen, oxygen) and ash. Coal combustion is considered further in Chapter 8, Energy Conversion.

A fuel is said to have burned *completely* if all of the carbon present in the fuel is burned to carbon dioxide, all of the hydrogen is burned to water, and all of the sulfur is burned to sulfur dioxide. In practice, these conditions are usually not fulfilled and combustion is *incomplete.* The presence of carbon monoxide (CO) in the products indicates incomplete combustion. The products of combustion of *actual* combustion reactions and the relative amounts of the products can be determined with certainty only by experimental means. Among several devices for the experimental determination of the composition of products of combustion are the *Orsat analyzer*, *gas chromatograph*, *infrared analyzer*, and *flame ionization detector.* Data from these devices can be used to determine the makeup of the gaseous products of combustion. Analyses are frequently reported on a "dry" basis: mole fractions are determined for all gaseous products as if no water vapor were present. Some experimental procedures give an analysis including the water vapor, however.

Since water is formed when hydrocarbon fuels are burned, the mole fraction of water vapor in the gaseous products of combustion can be significant. If the gaseous products of combustion are cooled at constant mixture pressure, the *dew point temperature* (Section 2.3, Ideal Gas Model) is reached when water vapor begins to condense. Corrosion of duct work, mufflers, and other metal parts can occur when water vapor in the combustion products condenses.

Oxygen is required in every combustion reaction. Pure oxygen is used only in special applications such as cutting and welding. In most combustion applications, air provides the needed oxygen. Idealizations are often used in combustion calculations involving air: (1) all components of air other than oxygen (O_2) *ar*e lumped with nitrogen (N_2). On a molar basis air is then considered to be 21% oxygen and 79% nitrogen. With this idealization the molar ratio of the nitrogen to the oxygen in combustion air is 3.76; (2) the water vapor present in air may be considered in writing the combustion equation or ignored. In the latter case the combustion air is regarded as *dry*; (3) additional simplicity results by regarding the nitrogen present in the combustion air as inert. However, if high-enough temperatures are attained, nitrogen can form compounds, often termed NO_X, such as nitric oxide and nitrogen dioxide.

Even trace amounts of oxides of nitrogen appearing in the exhaust of internal combustion engines can be a source of air pollution.

The minimum amount of air that supplies sufficient oxygen for the complete combustion of all the combustible chemical elements is the *theoretical*, or *stoichiometic*, amount of air. In practice, the amount of air actually supplied may be greater than or less than the theoretical amount, depending on the application. The amount of air is commonly expressed as the *percent of theoretical air* or the *percent excess* (or *percent deficiency*) of air. The *air-fuel ratio* and its reciprocal *the fuel-air ratio*, each of which can be expressed on a mass or molar basis, are other ways that fuel-air mixtures are described. Another is the *equivalence ratio:* the ratio of the actual fuel-air ratio to the fuel-air ratio for complete combustion with the theoretical amount of air. The reactants form a *lean* mixture when the equivalence ratio is less than unity and a *rich* mixture when the ratio is greater than unity.

Example 9

Methane, CH_4, is burned with dry air. The molar analysis of the products on a dry basis is CO_2, 9.7%; CO, 0.5%; O_2, 2.95%; and N_2, 86.85%. Determine (a) the air-fuel ratio on both a molar and a mass basis, (b) the percent of theoretical air, (c) the equivalence ratio, and (d) the dew point temperature of the products, in °F, if the pressure is 1 atm.

Solution.

(a) The solution is conveniently conducted on the basis of 100 lbmol of dry products. The chemical equation then reads

$$a\mathrm{CH_4} + b(\mathrm{O_2} + 3.76\mathrm{N_2}) \rightarrow 9.7\mathrm{CO_2} + 0.5\mathrm{CO} + 2.95\mathrm{O_2} + 86.85\mathrm{N_2} + c\mathrm{H_2O}$$

where N_2 is regarded as inert. Water is included in the products together with the assumed 100 lbmol of dry products. Balancing the carbon, hydrogen, and oxygen, the reaction equation is

$$10.2\mathrm{CH_4} + 23.1(\mathrm{O_2} + 3.76\mathrm{N_2}) \rightarrow 9.7\mathrm{CO_2} + 0.5\mathrm{CO} + 2.95\mathrm{O_2} + 86.85\mathrm{N_2} + 20.4\mathrm{H_2O}$$

The nitrogen also balances, as can be verified. This checks the accuracy of both the given product analysis and the calculations conducted to determine the unknown coefficients. Exact closure cannot be expected with measured data, however. On a molar basis, the air-fuel ratio is

$$\overline{\mathrm{AF}} = \frac{23.1(4.76)}{10.2} = 10.78 \frac{\mathrm{lbmol(air)}}{\mathrm{lbmol(fuel)}}$$

On a mass basis

$$\mathrm{AF} = (10.78)\left(\frac{28.97}{16.04}\right) = 19.47 \frac{\mathrm{lb(air)}}{\mathrm{lb(fuel)}}$$

(b) The balanced chemical equation for the complete combustion of methane with the *theoretical* amount of air is

$$\mathrm{CH_4} + 2(\mathrm{O_2} + 3.76\mathrm{N_2}) \rightarrow \mathrm{CO_2} + 2\mathrm{H_2O} + 7.52\mathrm{N_2}$$

The theoretical air-fuel ratio on a molar basis is

$$\left(\overline{\mathrm{AF}}\right)_{theo} = \frac{2(4.76)}{1} = 9.52 \frac{\mathrm{lbmol(air)}}{\mathrm{lbmol(fuel)}}$$

The percent theoretical air is then

$$\% \text{ theoretical air} = \frac{(\overline{\text{AF}})}{(\overline{\text{AF}})_{theo}}$$

$$= \frac{10.78}{9.52} = 1.13(113\%)$$

(c) Equivalence ratio = $(\overline{FA})/(\overline{FA})_{theo}$ = 9.52/10.78 = 0.88. The reactants form a lean mixture.

(d) To determine the dew point temperature requires the partial pressure p_v of the water vapor. The mole fraction of the water vapor is

$$y_v = \frac{20.4}{100 + 20.4} = 0.169$$

Since p = 1 atm, p_v = 0.169 atm = 2.48 lbf/in.^{2}. With p_{sat} = 2.48 lbf/in.^{2}, the corresponding saturation temperature from the steam tables is 134°F. This is the dew point temperature.

Property Data for Reactive Systems

Tables of thermodynamic properties such as the steam tables provide values for the specific enthalpy and entropy relative to some arbitrary datum state where the enthalpy (or alternatively the internal energy) and entropy are set to zero. When a chemical reaction occurs, however, reactants disappear and products are formed, and it is generally no longer possible to evaluate $\Delta\bar{h}$ and $\Delta\bar{s}$ so that these arbitrary datums cancel. Accordingly, special means are required to assign specific enthalpy and entropy for application to reacting systems.

Property data suited for the analysis of reactive systems are available from several sources. The encyclopedic *JANAF Thermochemical Tables* is commonly used. Data for a wide range of substances are retrievable from Knacke et al. (1991), which provides both tabular data and analytical expressions readily programmable for use with personal computers of the specific heat, enthalpy, entropy, and Gibbs function. Textbooks on engineering thermodynamics also provide selected data, as, for example, Moran and Shapiro (1995).

Enthalpy of Formation

An enthalpy datum for reacting systems can be established by assigning arbitrarily a value of zero to the enthalpy of the *stable elements* at a *standard reference state* where the temperature is T_{ref} = 298.15 K (25°C) and the pressure is p_{ref}, which may be 1 bar or 1 atm depending on the data source. The term stable simply means that the particular element is chemically stable. For example, at the standard state the stable forms of hydrogen, oxygen, and nitrogen are H_2, O_2, and N_2 and not the monatomic H, O, and N.

The molar enthalpy of a *compound* at the standard state equals its *enthalpy of formation*, symbolized here by $\bar{h}_f^\circ$. The enthalpy of formation is the energy released or absorbed when the compound is formed from its elements, the compound and elements all being at T_{ref} and p_{ref}. The enthalpy of formation may be determined by application of procedures from statistical thermodynamics using observed spectroscopic data. The enthalpy of formation also can be found in principle by measuring the heat transfer in a reaction in which the compound is formed from the elements. In this chapter, the superscript ° is used to denote p_{ref}. For the case of the enthalpy of formation, the reference temperature T_{ref} is also intended by this symbol. Table 2.9 gives the values of the enthalpy of formation of various substances at 298 K and 1 atm.

The molar enthalpy of a substance at a state other than the standard state is found by adding the molar enthalpy change $\Delta\bar{h}$ between the standard state and the state of interest to the molar enthalpy of formation:

TABLE 2.9 Enthalpy of Formation, Gibbs Function of Formation, and Absolute Entropy of Various Substances at 298 K and 1 atm

$\bar{h}_f^\circ$ and $\bar{g}_f^\circ$ (kJ/kmol), $\bar{s}^\circ$ (kJ/kmol•K)

Substance	Formula	$\bar{h}_f^\circ$	$\bar{g}_f^\circ$	$\bar{s}^\circ$
Carbon	C(s)	0	0	5.74
Hydrogen	H_2(g)	0	0	130.57
Nitrogen	N_2(g)	0	0	191.50
Oxygen	O_2(g)	0	0	205.03
Carbon monoxide	CO(g)	–110,530	–137,150	197.54
Carbon dioxide	CO_2(g)	–393,520	–394,380	213.69
Water	H_2O(g)	–241,820	–228,590	188.72
	H_2O(l)	–285,830	–237,180	69.95
Hydrogen peroxide	H_2O_2(g)	–136,310	–105,600	232.63
Ammonia	NH_3(g)	–46,190	–16,590	192.33
Oxygen	O(g)	249,170	231,770	160.95
Hydrogen	H(g)	218,000	203,290	114.61
Nitrogen	N(g)	472,680	455,510	153.19
Hydroxyl	OH(g)	39,460	34,280	183.75
Methane	CH_4(g)	–74,850	–50,790	186.16
Acetylene	C_2H_2(g)	226,730	209,170	200.85
Ethylene	C_2H_4(g)	52,280	68,120	219.83
Ethane	C_2H_6(g)	–84,680	–32,890	229.49
Propylene	C_3H_6(g)	20,410	62,720	266.94
Propane	C_3H_8(g)	–103,850	–23,490	269.91
Butane	C_4H_{10}(g)	–126,150	–15,710	310.03
Pentane	C_5H_{12}(g)	–146,440	–8,200	348.40
Octane	C_8H_{18}(g)	–208,450	17,320	463.67
	C_8H_{18}(l)	–249,910	6,610	360.79
Benzene	C_6H_6(8)	82,930	129,660	269.20
Methyl alcohol	CH_3OH(g)	–200,890	–162,140	239.70
	CH_3OH(I)	–238,810	–166,290	126.80
Ethyl alcohol	C_2H_5OH(g)	–235,310	–168,570	282.59
	C_2H_5OH(I)	–277,690	174,890	160.70

Source: Adapted from Wark, K. 1983. *Thermodynamics*, 4th ed. McGraw-Hill, New York, as based on JANAF Thermochemical Tables, NSRDS-NBS-37, 1971; *Selected Values of Chemical Thermodynamic Properties*, NBS Tech. Note 270-3, 1968; and *API Research Project 44*, Carnegie Press, 1953.

$$\bar{h}(T,p) = \bar{h}_f^\circ + \left[\bar{h}(T,p) - \bar{h}\left(T_{ref}, p_{ref}\right)\right] = \bar{h}_f^\circ + \Delta\bar{h} \tag{2.78}$$

That is, the enthalpy of a substance is composed of $\bar{h}_f^\circ$, associated with the formation of the substance from its elements, and $\Delta\bar{h}$, associated with a change of state at constant composition. An arbitrarily chosen datum can be used to determine $\Delta\bar{h}$, since it is a *difference* at constant composition. Accordingly, $\Delta\bar{h}$ can be evaluated from sources such as the steam tables and the ideal gas tables.

The *enthalpy of combustion*, $\bar{h}_{RP}$, is the difference between the enthalpy of the products and the enthalpy of the reactants, each on a per-mole-of-fuel basis, when complete combustion occurs and both reactants and products are at the same temperature and pressure. For hydrocarbon fuels the enthalpy of combustion is negative in value since chemical internal energy is liberated in the reaction. The *heating value* of a fuel is a positive number equal to the magnitude of the enthalpy of combustion. Two heating values are recognized: the *higher* heating value and the *lower* heating value. The higher heating value is obtained when all the water formed by combustion is a liquid; the lower heating value is obtained when all the water formed by combustion is a vapor. The higher heating value exceeds the lower heating value by the energy that would be required to vaporize the liquid water formed at the specified temperature. Heating values are typically reported at a temperature of 25°C (77°F) and a pressure of 1 bar (or 1 atm). These values also depend on whether the fuel is a liquid or a gas. A sampling is provided on a unit-mass-of-fuel basis in Table 2.10.

TABLE 2.10 Heating Values in kJ/kg of Selected Hydrocarbons at 25°C

		Higher Value[a]		Lower Value[b]	
Hydrocarbon	**Formula**	**Liquid Fuel**	**Gas. Fuel**	**Liquid Fuel**	**Gas. Fuel**
Methane	CH_4	—	55,496	—	50,010
Ethane	C_2H_6	—	51,875	—	47,484
Propane	C_3H_8	49,973	50,343	45,982	46,352
n-Butane	C_4H_{10}	49,130	49,500	45,344	45,714
n-Octane	C_8H_{18}	47,893	48,256	44,425	44,788
n-Dodecane	$C_{12}H_{26}$	47,470	47,828	44,109	44,467
Methanol	CH_3OH	22,657	23,840	19,910	21,093
Ethanol	C_3H_5OH	29,676	30,596	26,811	27,731

[a] H_2O liquid in the products.

[b] H_2O vapor in the products.

In the absence of work $\dot{W}_{cv}$ and appreciable kinetic and potential energy effects, the energy liberated on combustion is transferred from a reactor at steady state in two ways: the energy accompanying the exiting combustion products and by heat transfer. The temperature that would be achieved by the products in the limit of adiabatic operation is the *adiabatic flame* or *adiabatic combustion* temperature.

For a specified fuel and specified temperature and pressure of the reactants, the *maximum* adiabatic flame temperature is realized for complete combustion with the theoretical amount of air. Example 10 provides an illustration. The measured value of the temperature of the combustion products may be several hundred degrees below the calculated maxunum adiabatic flame temperature, however, for several reasons including the following: (1) heat loss can be reduced but not eliminated; (2) once adequate oxygen has been provided to permit complete combustion, bringing in more air dilutes the combustion products, lowering the temperature; (3) incomplete combustion tends to reduce the temperature of the products, and combustion is seldom complete; (4) as result of the high temperatures achieved, some of the combustion products may dissociate. Endothermic dissociation reactions also lower the product temperature.

Absolute Entropy

A common datum for assigning entropy values to substances involved in chemical reactions is realized through the *third law* of thermodynamics, which is based on experimental observations obtained primarily from studies of chemical reactions at low temperatures and specific heat measurements at temperatures approaching absolute zero. The third law states that the entropy of a pure crystalline substance is zero at the absolute zero of temperature, 0 K or 0°R. Substances not having a pure crystalline structure have a nonzero value of entropy at absolute zero.

The third law provides a datum relative to which the entropy of each substance participating in a reaction can be evaluated. The entropy relative to this datum is called the *absolute* entropy. The change in entropy of a substance between absolute zero and any given state can be determined from measurements of energy transfers and specific heat data or from procedures based on statistical thermodynamics and observed molecular data. Table 2.9 and Tables A.2 and A.8 provide absolute entropy data for various substances. In these tables, p_{ref} =1 atm.

When the absolute entropy is known at pressure p_{ref} and temperature T, the absolute entropy at the same temperature and *any* pressure p can be found from

$$\bar{s}(T,p) = \bar{s}\left(T, p_{ref}\right) + \left[\bar{s}(T,p) - \bar{s}\left(T, p_{ref}\right)\right] \tag{2.79}$$

For an ideal gas, the second term on the right side of Equation 2.79 can be evaluated by using Equation 2.58, giving

$$\bar{s}(T,p) = \bar{s}^\circ(T) - \bar{R}\ln\frac{p}{p_{ref}} \qquad \text{(ideal gas)} \tag{2.80}$$

In this expression, $\bar{s}^\circ(T)$ denotes the absolute entropy at temperature T and pressure p_{ref}.

The entropy of the ith component of an *ideal gas mixture* is evaluated at the mixture temperature T and the *partial* pressure p_i: $\bar{s}_i(T, p_i)$. For the ith component, Equation 2.80 takes the form

$$\begin{aligned} \bar{s}_i\left(T, p_i\right) &= \bar{s}_i^\circ(T) - \bar{R}\ln\frac{p_i}{p_{ref}} \\ &= \bar{s}_i^\circ(T) - \bar{R}\ln\frac{y_i p}{p_{ref}} \qquad \text{(ideal gas)} \end{aligned} \tag{2.81}$$

where $\bar{s}_i^\circ(T)$ is the absolute entropy of component i at temperature T and p_{ref}.

Example 10

Liquid octane at 25°C, 1 atm enters a well insulated reactor and reacts with dry air entering at the same temperature and pressure. For steady-state operation and negligible effects of kinetic and potential energy, determine the temperature of the combustion products for complete combustion with the theoretical amount of air, and (b) the rates of entropy generation and exergy destruction, each per kmol of fuel.

Solution. For combustion of liquid octane with the theoretical amount of air, the chemical equation is

$$\mathrm{C_8H_{18}(l) + 12.5O_2 + 47N_2 \rightarrow 8CO_2 + 9H_2O(g) + 47N_2}$$

(a) At steady state, the control volume energy rate balance reduces to read

$$0 = \cancelto{0}{\frac{\dot{Q}_{cv}}{\dot{n}_F}} - \cancelto{0}{\frac{\dot{W}_{cv}}{\dot{n}_F}} + \sum_R n_i\left(\bar{h}_f^\circ + \Delta\bar{h}\right)_i - \sum_P n_e\left(\bar{h}_f^\circ + \Delta\bar{h}\right)_e$$

where R denotes reactants, P denotes products, and the symbols for enthalpy have the same significance as in Equation 2.78. Since the reactants enter at 25°C, the corresponding $(\Delta\bar{h})_i$ terms vanish, and the energy rate equation becomes

$$\sum_P n_e\left(\Delta\bar{h}\right)_e = \sum_R n_i\bar{h}_{fi}^\circ - \sum_P n_e\bar{h}_{fe}^\circ$$

Introducing coefficients from the reaction equation, this takes the form

$$\begin{aligned} 8\left(\Delta\bar{h}\right)_{\mathrm{CO_2}} + 9\left(\Delta\bar{h}\right)_{\mathrm{H_2O(g)}} + 47\left(\Delta\bar{h}\right)_{\mathrm{N_2}} &= \left[\left(\bar{h}_f^\circ\right)_{\mathrm{C_8H_{18}(l)}} + 12.5\left(\bar{h}_f^\circ\right)_{\mathrm{O_2}} + 47\left(\bar{h}_f^\circ\right)_{\mathrm{N_2}}\right] \\ &\quad - \left[8\left(\bar{h}_f^\circ\right)_{\mathrm{CO_2}} + 9\left(\bar{h}_f^\circ\right)_{\mathrm{H_2O(g)}} + 47\left(\Delta\bar{h}_f^\circ\right)_{\mathrm{N_2}}\right] \end{aligned}$$

Using data from Table 2.9 to evaluate the right side,

$$8\left(\Delta\bar{h}\right)_{\mathrm{CO_2}} + 9\left(\Delta\bar{h}\right)_{\mathrm{H_2O(g)}} + 47\left(\Delta\bar{h}\right)_{\mathrm{N_2}} = 5{,}074{,}630 \ \mathrm{kJ/kmol\ (fuel)}$$

Each $\Delta\bar{h}$ term on the left side of this equation depends on the temperature of the products, T_p, which can be solved for iteratively as T_p = 2395 K.

(b) The entropy rate balance on a per-mole-of-fuel basis takes the form

$$0 = \cancelto{0}{\sum_j \frac{\dot{Q}_j/T_j}{\dot{n}_F}} + \bar{s}_F + \left(12.5\bar{s}_{\mathrm{O_2}} + 47\bar{s}_{\mathrm{N_2}}\right) - \left(8\bar{s}_{\mathrm{CO_2}} + 9\bar{s}_{\mathrm{H_2O(g)}} + 47\bar{s}_{\mathrm{N_2}}\right) + \frac{\dot{S}_{gen}}{\dot{n}_F}$$

or on rearrangement,

$$\frac{\dot{S}_{gen}}{\dot{n}_F} = \left(8\bar{s}_{\mathrm{CO_2}} + 9\bar{s}_{\mathrm{H_2O(g)}} + 47\bar{s}_{\mathrm{N_2}}\right) - \bar{s}_F - \left(12.5\bar{s}_{\mathrm{O_2}} + 47\bar{s}_{\mathrm{N_2}}\right)$$

The absolute entropy of liquid octane from Table 2.9 is 360.79 kJ/mol · K. The oxygen and nitrogen in the combustion air enter the reactor as components of an ideal gas mixture at T_{ref}, p_{ref}. With Equation 2.81, where $p = p_{ref}$, and absolute entropy data from Table 2.9,

$$\begin{aligned}
\bar{s}_{\mathrm{O_2}} &= \bar{s}^{\circ}_{\mathrm{O_2}}\left(T_{ref}\right) - \bar{R}\ln y_{\mathrm{O_2}} \\
&= 205.03 - 8.314\ln 0.21 = 218.01 \ \mathrm{kJ/kmol\cdot K} \\
\bar{s}_{\mathrm{N_2}} &= \bar{s}^{\circ}_{\mathrm{N_2}}\left(T_{ref}\right) - \bar{R}\ln y_{\mathrm{N_2}} \\
&= 191.5 - 8.314\ln 0.79 = 193.46 \ \mathrm{kJ/kmol\cdot K}
\end{aligned}$$

The product gas exits as a gas mixture at 1 atm, 2395 K with the following composition: $y_{\mathrm{CO_2}}$ = 8/64 = 0.125, $y_{\mathrm{H_2O(g)}}$ = 9/64 = 0.1406, $y_{\mathrm{N_2}}$ = 47/64 = 0.7344. With Equation 2.81, where p = p_{ref}, *and* absolute entropy data at 2395 K from Table A.2,

$$\begin{aligned}
\bar{s}_{\mathrm{CO_2}} &= 320.173 - 8.314\ln 0.125 = 337.46 \ \mathrm{kJ/kmol\cdot K} \\
\bar{s}_{\mathrm{H_2O}} &= 273.986 - 8.314\ln 0.1406 = 290.30 \ \mathrm{kJ/kmol\cdot K} \\
\bar{s}_{\mathrm{N_2}} &= 258.503 - 8.314\ln 0.7344 = 261.07 \ \mathrm{kJ/kmol\cdot K}
\end{aligned}$$

Inserting values, the rate of entropy generation is

$$\begin{aligned}
\frac{\dot{S}_{gen}}{\dot{n}_F} &= 8(337.46) + 9(290.30) + 47(261.07) - 360.79 - 12.5(218.01) - 47(193.46) \\
&= 5404 \ \mathrm{kJ/kmol\cdot K}
\end{aligned}$$

Using Equation 2.87 and assuming T_0 = 298 K, the rate of exergy destruction is $\dot{E}_D/\dot{n}_F$ = 1.61 × 10^6 kJ/kmol.

Gibbs Function of Formation

Paralleling the approach used for enthalpy, a value of zero is assigned to the Gibbs function of each stable element at the standard state. The *Gibbs function of formation* of a compound equals the change in the Gibbs function for the reaction in which the compound is formed from its elements. Table 2.9 provides Gibbs function of formation data of various substances at 298 K and 1 atm.

The Gibbs function at a state other than the standard state is found by adding to the Gibbs function of formation the change in the specific Gibbs function $\Delta\bar{g}$ between the standard state and the state of interest:

$$\bar{g}(T,p) = \bar{g}_f^\circ + \left[\bar{g}(T,p) - \bar{g}\left(T_{ref}, p_{ref}\right)\right] = \bar{g}_f^\circ + \Delta\bar{g} \tag{2.82a}$$

where

$$\Delta\bar{g} = \left[\bar{h}(T,p) - \bar{h}\left(T_{ref}, p_{ref}\right)\right] - \left[T\bar{s}(T,p) - T_{ref}\bar{s}\left(T_{ref}, p_{ref}\right)\right] \tag{2.82b}$$

The Gibbs function of component *i* in an ideal gas mixture is evaluated at the partial pressure of component *i* and the mixture temperature.

As an application, the maximum theoretical work that can be developed, per mole of fuel consumed, is evaluated for the control volume of Figure 2.15, where the fuel and oxygen each enter in separate streams and carbon dioxide and water each exit separately. All entering and exiting streams are at the same temperature *T* and pressure *p*. The reaction is complete:

$$C_aH_b + \left(a + \frac{b}{4}\right)\mathrm{O}_2 \rightarrow a\mathrm{CO}_2 + \frac{b}{2}\mathrm{H}_2\mathrm{O}$$

This control volume is similar to idealized devices such as a reversible fuel *cell* or a *van't Hoff equilibrium box*.

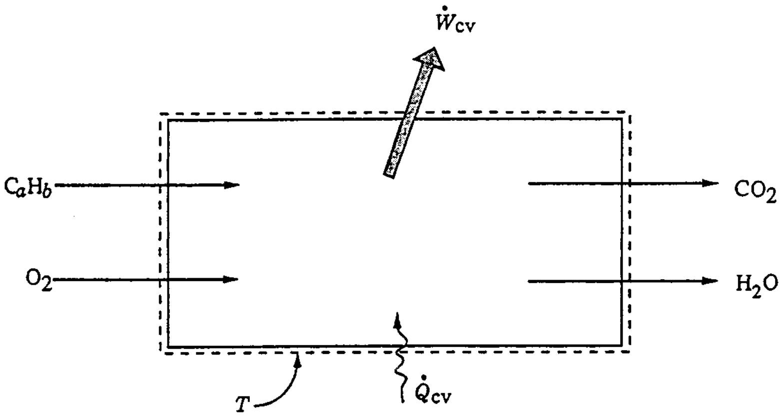


FIGURE 2.15 Device for evaluating maximum work.

For steady-state operation, the energy rate balance reduces to give

$$\frac{\dot{W}_{cv}}{\dot{n}_F} = \frac{\dot{Q}_{cv}}{\dot{n}_F} + \bar{h}_F + \left(a + \frac{b}{4}\right)\bar{h}_{\mathrm{O}_2} - a\bar{h}_{\mathrm{CO}_2} - \frac{b}{2}\bar{h}_{\mathrm{H}_2\mathrm{O}}$$

---

where $\dot{n}_F$ denotes the molar flow rate of the fuel. Kinetic and potential energy effects are regarded as negligible. If heat transfer occurs only at the temperature *T*, an entropy balance for the control volume takes the form

$$0 = \frac{\dot{Q}_{cv}/\dot{n}_F}{T} + \bar{s}_F + \left(a + \frac{b}{4}\right)\bar{s}_{O_2} - a\bar{s}_{CO_2} - \frac{b}{2}\bar{s}_{H_2O} + \frac{\dot{S}_{gen}}{\dot{n}_F}$$

Eliminating the heat transfer term from these expressions, an expression for the maximum theoretical value of the work developed per mole of fuel is obtained when the entropy generation term is set to zero:

$$\left(\frac{\dot{W}_{cv}}{\dot{n}_F}\right)_{\substack{int\\rev}} = \left[\bar{h}_F + \left(a + \frac{b}{4}\right)\bar{h}_{O_2} - a\bar{h}_{CO_2} - \frac{b}{2}\bar{h}_{H_2O}\right](T,p) - T\left[\bar{s}_F + \left(a + \frac{b}{4}\right)\bar{s}_{O_2} - a\bar{s}_{CO_2} - \frac{b}{2}\bar{s}_{H_2O}\right](T,p)$$

This can be written alternatively in terms of the enthalpy of combustion as

$$\left(\frac{\dot{W}_{cv}}{\dot{n}_F}\right)_{\substack{int\\rev}} = -\bar{h}_{RP}(T,p) - T\left[\bar{s}_F + \left(a + \frac{b}{4}\right)\bar{s}_{O_2} - a\bar{s}_{CO_2} - \frac{b}{2}\bar{s}_{H_2O}\right](T,p) \tag{2.83a}$$

or in terms of Gibbs functions as

$$\left(\frac{\dot{W}_{cv}}{\dot{n}_F}\right)_{\substack{int\\rev}} = \left[\bar{g}_F + \left(a + \frac{b}{4}\right)\bar{g}_{O_2} - a\bar{g}_{CO_2} - \frac{b}{2}\bar{g}_{H_2O}\right](T,p) \tag{2.83b}$$

Equation 2.83b is used in the solution to Example 11.

Example 11

Hydrogen (H_2) and oxygen (O_2), each at 25°C, 1 atm, enter a fuel cell operating at steady state, and liquid water exits at the same temperature and pressure. The hydrogen flow rate is 2×10^{-4} kmol/sec and the fuel cell operates isothermally at 25°C. Determine the maximum theoretical power the cell can develop, in kW.

Solution. The overall cell reaction is $H_2 + 1/2\ O_2 \rightarrow H_2O(\ell)$, and Equations 2.83 are applicable. Selecting Equation 2.83b, and using Gibbs function data from Table 2.9,

$$\left(\frac{\dot{W}_{cv}}{\dot{n}_F}\right)_{\substack{int\\rev}} = \left(\bar{g}_{H_2} + \frac{1}{2}\bar{g}_{O_2} - \bar{g}_{H_2O(\ell)}\right)(25°\text{C, 1 atm})$$

$$= 0 + \frac{1}{2}(0) - (-237{,}180) = 237{,}180 \text{ kJ/kmol}$$

Then

$$\left(\dot{W}_{cv}\right)_{\substack{int\\rev}} = \left(237{,}180 \frac{\text{kJ}}{\text{kmol}}\right)\left(2 \times 10^{-4} \frac{\text{kmol}}{\text{s}}\right)\left(\frac{\text{kW}}{1\text{kJ/s}}\right) = 47.4 \text{ kW}$$

Reaction Equilibrium

Let the objective be to determine the equilibrium composition of a system consisting of five gases A, B, C, D, and E, at a temperature T and pressure p, subject to a chemical reaction of the form

$$v_A A + v_B B \leftrightarrow v_C C + v_D D$$

where the v's are stoichiometric coefficients. Component E is assumed to be inert and thus does not appear in the reaction equation. The equation suggests that at equilibrium the tendency of A and B to form C and D is just balanced by the tendency of C and D to form A and B.

At equilibrium, the temperature and pressure would be uniform throughout the system. Additionally, the *equation of reaction equilibrium* must be satisfied:

$$v_A \mu_A + v_B \mu_B = v_C \mu_C + v_D \mu_D \tag{2.84a}$$

where the μ's are the chemical potentials (Section 2.3, Multicomponent Systems) of A, B, C, and D in the equilibrium mixture. In principle, the composition that would be present at equilibrium for a given temperature and pressure can be determined by solving this equation.

For ideal gas mixtures, the solution procedure is simplified by using the *equilibrium constant* $K(T)$ and the following equation:

$$\begin{aligned} K(T) &= \frac{y_C^{v_C} y_D^{v_D}}{y_A^{v_A} y_B^{v_B}} \left(\frac{p}{p_{ref}} \right)^{v_C + v_D - v_A - v_B} \\ &= \frac{n_C^{v_C} n_D^{v_D}}{n_A^{v_A} n_B^{v_B}} \left(\frac{p/p_{ref}}{n} \right)^{v_C + v_D - v_A - v_B} \end{aligned} \tag{2.84b}$$

where y_A, y_B, y_C, and y_D denote the mole fractions of A, B, C, and D in the equilibrium mixture and $n = n_A + n_B + n_C + n_D + n_E$, where the n's denote the molar amounts of the gases in the mixture. Tabulations of $K(T)$ for each of several reactions of the form Equation 2.84a are provided in Table 2.11. An application of Equation 2.84b is provided in Example 12.

Example 12

One kmol of CO reacts with the theoretical amount of dry air to form an equilibrium mixture of CO_2, CO, O_2, and N_2 at 2500 K, 1 atm. Determine the amount of CO in the equilibrium mixture, in kmol.

Solution. The reaction of CO with the theoretical amount of dry air to form CO_2, CO, O_2, and N_2 is

$$\text{CO} + \frac{1}{2}\text{O}_2 + 1.88\text{N}_2 \rightarrow z\text{CO} + \frac{z}{2}\text{O}_2 + (1-z)\text{CO}_2 + 1.88\text{N}_2$$

where z is the amount of CO, in kmol, present in the equilibrium mixture. The total number of moles n is

$$n = z + \frac{z}{2} + (1-z) + 1.88 = \frac{5.76 + z}{2}$$

At equilibrium $CO_2 \leftrightarrow CO + 1/2\ O_2$; and Equation 2.84b takes the form

$$K = \frac{z(z/2)^{1/2}}{1-z} \left[\frac{p/p_{ref}}{(5.76+z)/2} \right]^{1/2}$$

where $p/p_{ref} = 1$. At 2500 K, Table 2.11 gives $K = 0.0363$. Solving iteratively, $z = 0.175$.

TABLE 2.11 Logarithms to the Base 10 of the Equilibrium Constant *K*

	$\log_{10} K$								
Temp (K)	$H_2 \Leftrightarrow 2H$	$O_2 \Leftrightarrow 2O$	$N_2 \Leftrightarrow 2N$	$^1/_2O_2 + ^1/_2N_2 \Leftrightarrow NO$	$H_2O \Leftrightarrow H_2 + ^1/_2O_2$	$H_2O \Leftrightarrow OH + ^1/_2H_2$	$CO_2 \Leftrightarrow CO + ^1/_2 O_2$	$CO_2 + H_2 \Leftrightarrow CO + H_2O$	**Temp (°R)**
298	–71.224	–81.208	–159.600	–15.171	–40.048	–46.054	–45.066	–5.018	537
500	–40.316	–45.880	–92.672	–8.783	–22.886	–26.130	–25.025	–2.139	900
1000	–17.292	–19.614	–43.056	–4.062	–10.062	–11.280	–10.221	–0.159	1800
1200	–13.414	–15.208	–34.754	–3.275	–7.899	–8.811	–7.764	+0.135	2160
1400	–10.630	–12.054	–28.812	–2.712	–6.347	–7.021	–6.014	+0.333	2520
1600	–8.532	–9.684	–24.350	–2.290	–5.180	–5.677	–4.706	+0.474	2880
1700	–7.666	–8.706	–22.512	–2.116	–4.699	–5.124	–4.169	+0.530	3060
1800	–6.896	–7.836	–20.874	–1.962	–4.270	–4.613	–3.693	+0.577	3240
1900	–6.204	–7.058	–19.410	–1.823	–3.886	–4.190	–3.267	+0.619	3420
2000	–5.580	–6.356	–18.092	–1.699	–3.540	–3.776	–2.884	+0.656	3600
2100	–5.016	–5.720	–16.898	–1.586	–3.227	–3.434	–2.539	+0.688	3780
2200	–4.502	–5.142	–15.810	–1.484	–2.942	–3.091	–2.226	+0.716	3960
2300	–4.032	–4.614	–14.818	–1.391	–2.682	–2.809	–1.940	+0.742	4140
2400	–3.600	–4.130	–13.908	–1.305	–2.443	–2.520	–1.679	+0.764	4320
2500	–3.202	–3.684	–13.070	–1.227	–2.224	–2.270	–1.440	+0.784	4500
2600	–2.836	–3.272	–12.298	–1.154	–2.021	–2.038	–1.219	+0.802	4680
2700	–2.494	–2.892	–11.580	–1.087	–1.833	–1.823	–1.015	+0.818	4860
2800	–2.178	–2.536	–10.914	–1.025	–1.658	–1.624	–0.825	+0.833	5040
2900	–1.882	–2.206	–10.294	–0.967	–1.495	–1.438	–0.649	+0.846	5220
3000	–1.606	–1.898	–9.716	–0.913	–1.343	–1.265	–0.485	+0.858	5400
3100	–1.348	–1.610	–9.174	–0.863	–1.201	–1.103	–0.332	+0.869	5580
3200	–1.106	–1.340	–8.664	–0.815	–1.067	–0.951	–0.189	+0.878	5760
3300	–0.878	–1.086	–8.186	–0.771	–0.942	–0.809	–0.054	+0.888	5940
3400	–0.664	–0.846	–7.736	–0.729	–0.824	–0.674	+0.071	+0.895	6120
3500	–0.462	–0.620	–7.312	–0.690	–0.712	–0.547	+0.190	+0.902	6300

Source: Based on data from the JANAF Thermochemical Tables, NSRDS-NBS-37, 1971.

2.5 Exergy Analysis

The method of *exergy analysis* (*availability analysis*) presented in this section enables the location, cause, and true magnitude of energy resource waste and loss to be determined. Such information can be used in the design of new energy-efficient systems and for improving the performance of existing systems. Exergy analysis also provides insights that elude a purely first-law approach. For example, on the basis of first-law reasoning alone, the condenser of a power plant may be mistakenly identified as the component primarily responsible for the plant's seemingly low overall performance. An exergy analysis correctly reveals not only that the condenser loss is relatively unimportant (see the last two rows of the Rankine cycle values of Table 2.15), but also that the steam generator is the principal site of thermodynamic inefficiency owing to combustion and heat transfer irreversibilities within it.

When exergy concepts are combined with principles of engineering economy, the result is known as *thermoeconomics.* Thermoeconomics allows the real cost sources at the component level to be identified: capital investment costs, operating and maintenance costs, and the costs associated with the destruction and loss of exergy. Optimization of thermal systems can be achieved by a careful consideration of such cost sources. From this perspective thermoeconomics *is exergy-aided cost minimization.*

Discussions of exergy analysis and thermoeconomics are provided by Bejan et al. (1996), Moran (1989), and Moran and Shapiro (1995). In this section salient aspects are presented.

Defining Exergy

An opportunity for doing work exists whenever two systems at different states are placed in communication because, in principle, work can be developed as the two are allowed to come into equilibrium. When one of the two systems is a suitably idealized system called an *environment* and the other is some system of interest, *exergy* is the maximum theoretical useful work (shaft work or electrical work) obtainable as the systems interact to equilibrium, heat transfer occurring with the environment only. (Alternatively, exergy is the minimum theoretical useful work required to form a quantity of matter from substances present in the environment and to bring the matter to a specified state.) Exergy is a measure of the *departure* of the state of the system from that of the environment, and is therefore an attribute of the system and environment together. Once the environment is specified, however, a value can be assigned to exergy in terms of property values for the system only, so exergy can be regarded as an extensive property of the system.

Exergy can be destroyed and generally is not conserved. A limiting case is when exergy would be completely destroyed, as would occur if a system were to come into equilibrium with the environment *spontaneously* with no provision to obtain work. The capability to develop work that existed initially would be completely wasted in the spontaneous process. Moreover, since no work needs to be done to effect such a spontaneous change, the value of exergy can never be negative.

Environment

Models with various levels of specificity are employed for describing the environment used to evaluate exergy. Models of the environment typically refer to some portion of a system's surroundings, the intensive properties of each phase of which are uniform and do not change significantly as a result of any process under consideration. The environment is regarded as composed of common substances existing in abundance within the Earth's atmosphere, oceans, and crust. The substances are in their stable forms as they exist naturally, and there is no possibility of developing work from interactions — physical or chemical — between parts of the environment. Although the intensive properties of the environment are assumed to be unchanging, the extensive properties can change as a result of interactions with other systems. Kinetic and potential energies are evaluated relative to coordinates in the environment, all parts of which are considered to be at rest with respect to one another.

For computational ease, the temperature T_0 and pressure p_0 of the environment are often taken as standard-state values, such as 1 atm and 25°C (77°F). However, these properties may be specified differently depending on the application. T_0 and p_0 might be taken as the average ambient temperature and pressure, respectively, for the location at which the system under consideration operates. Or, if the system uses atmospheric air, T_0 might be specified as the average air temperature. If both air and water from the natural surroundings are used, T_0 would be specified as the lower of the average temperatures for air and water.

Dead States

When a system is in equilibrium with the environment, the state of the system is called the *dead state*. At the dead state, the conditions of mechanical, thermal, and chemical equilibrium between the system and the environment are satisfied: the pressure, temperature, and chemical potentials of the system equal those of the environment, respectively. In addition, the system has no motion or elevation relative to coordinates in the environment. Under these conditions, there is no possibility of a spontaneous change within the system or the environment, nor can there be an interaction between them. The value of exergy is zero.

Another type of equilibrium between the system and environment can be identified. This is a restricted form of equilibrium where only the conditions of mechanical and thermal equilibrium must be satisfied. This state of the system is called the *restricted dead state*. At the restricted dead state, the fixed quantity of matter under consideration is imagined to be sealed in an envelope impervious to mass flow, at zero velocity and elevation relative to coordinates in the environment, and at the temperature T_0 and pressure p_0.

Exergy Balances

Exergy can be transferred by three means: exergy transfer associated with work, exergy transfer associated with heat transfer, and exergy transfer associated with the matter entering and exiting a control volume. All such exergy transfers are evaluated relative to the environment used to define exergy. Exergy is also destroyed by irreversibilities within the system or control volume.

Exergy balances can be written in various forms, depending on whether a closed system or control volume is under consideration and whether steady-state or transient operation is of interest. Owing to its importance for a wide range of applications, an exergy rate balance for control volumes at steady state is presented next.

Control Volume Exergy Rate Balance

At steady state, the control volume exergy rate balance takes the form

$$0 = \underbrace{\sum_j \dot{E}_{q,j} - \dot{W}_{cv} + \sum_i \dot{E}_i - \sum_e \dot{E}_e}_{\text{rates of exergy transfer}} - \underbrace{\dot{E}_D}_{\text{rate of exergy destruction}} \tag{2.85a}$$

or

$$0 = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j - \dot{W}_{cv} + \sum_i \dot{m}_i e_i - \sum_e \dot{m}_e e_e - \dot{E}_D \tag{2.85b}$$

$\dot{W}_{cv}$ has the same significance as in Equation 2.22: the work rate excluding the flow work. $\dot{Q}_j$ is the time rate of heat transfer at the location on the boundary of the control volume where the instantaneous temperature is T_j. The associated rate of exergy transfer is

$$\dot{E}_{q,j} = \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j \tag{2.86}$$

As for other control volume rate balances, the subscripts *i* and *e* denote inlets and outlets, respectively. The exergy transfer rates at control volume inlets and outlets are denoted, respectively, as $\dot{E}_i = \dot{m}_i e_i$ and $\dot{E}_e = \dot{m}_e e_e$. Finally, $\dot{E}_D$ accounts for the time rate of exergy destruction due to irreversibilities within the control volume. The exergy destruction rate is related to the entropy generation rate by

$$\dot{E}_D = T_0 \dot{S}_{gen} \tag{2.87}$$

The specific exergy transfer terms e_i and e_e are expressible in terms of four components: physical exergy e^{PH}, kinetic exergy e^{KN}, potential exergy e^{PT}, and chemical exergy e^{CH}:

$$e = e^{PH} + e^{KN} + e^{PT} + e^{CH} \tag{2.88}$$

The first three components are evaluated as follows:

$$e^{PH} = \left(h - h_0\right) - T_0\left(s - s_0\right) \tag{2.89a}$$

$$e^{KN} = \frac{1}{2}\mathrm{v}^2 \tag{2.89b}$$

$$e^{PT} = gz \tag{2.89c}$$

In Equation 2.89a, h_0 and s_0 denote, respectively, the specific enthalpy and specific entropy at the restricted dead state. In Equations 2.89b and 2.89c, v and z denote velocity and elevation relative to coordinates in the environment, respectively. The chemical exergy e^{CH} is considered next.

Chemical Exergy

To evaluate the chemical exergy, the exergy component associated with the departure of the chemical composition of a system from that of the environment, the substances comprising the system are referred to the properties of a suitably selected set of environmental substances. For this purpose, alternative models of the environment have been developed. For discussion, see, for example, Moran (1989) and Kotas (1995).

Exergy analysis is facilitated, however, by employing a *standard environment* and a corresponding table of *standard chemical exergies*. Standard chemical exergies are based on standard values of the environmental temperature T_0 and pressure p_0 — for example, 298.15 K (25°C) and 1 atm, respectively. A standard environment is also regarded as consisting of a set of reference substances with standard concentrations reflecting as closely as possible the chemical makeup of the natural environment. The reference substances generally fall into three groups: gaseous components of the atmosphere, solid substances from the lithosphere, and ionic and noninonic substances from the oceans. The chemical exergy data of Table 2.12 correspond to two alternative standard exergy reference environments, called here model I and model II, that have gained acceptance for engineering evaluations.

Although the use of standard chemical exergies greatly facilitates the application of exergy principles, the term *standard* is somewhat misleading since there is no one specification of the environment that suffices for all applications. Still, chemical exergies calculated relative to alternative specifications of the environment are generally in good agreement. For a broad range of engineering applications the simplicity and ease of use of standard chemical exergies generally outweigh any slight lack of accuracy that might result. In particular, the effect of slight variations in the values of T_0 and p_0 about the values used to determine the standard chemical exergies reported in Table 2.12 can be neglected.

The literature of exergy analysis provides several expressions allowing the chemical exergy to be evaluated in particular cases of interest. The molar chemical exergy of a gas mixture, for example, can be evaluated from

$$\bar{e}^{CH} = \sum_{i=1}^{j} y_i \bar{e}_i^{CH} + \bar{R}T_0 \sum_{i=1}^{j} y_i \ln y_i \tag{2.90}$$

where $\bar{e}_i^{CH}$ is the molar chemical exergy of the *i*th component.

Example 13

Ignoring the kinetic and potential exergies, determine the exergy rate, in kJ/kg, associated with each of the following streams of matter:

(a) Saturated water vapor at 20 bar.
(b) Methane at 5 bar, 25°C.

Let T_0 = 298 K, p_0 = 1.013 bar (1 atm).

Solution. Equation 2.88 reduces to read

$$e = (h - h_0) - T_0(s - s_0) + e^{CH}$$

(a) From Table A.5, h = 2799.5 kJ/kg, s = 6.3409 kJ/kg · K. At T_0 = 298 K (25°C), water would be a liquid; thus with Equations 2.50c and 2.50d, $h_0 \approx$ 104.9 kJ/kg, $s_0 \approx$ 0.3674 kJ/kg · K. Table 2.12 (model I) gives e^{CH} = 45/18.02 = 2.5 kJ/kg. Then

$$\begin{aligned} e &= (2799.5 - 104.9) - 298(6.3409 - 0.3674) + 2.5 \\ &= 914.5 + 2.5 = 917.0 \ \text{kJ/kg} \end{aligned}$$

Here the specific exergy is determined predominately by the physical component.

(b) Assuming the ideal gas model for methane, $h - h_0 = 0$. Also, Equation 2.58 reduces to give $s - s_0 = -R\ln p/p_0$. Then, Equation 2.88 reads

$$e = RT_0 \ln p/p_0 + e^{CH}$$

With e^{CH} = 824,350/16.04 = 51,393.4 kJ/kg from Table 2.12 (model I),

$$\begin{aligned} e &= \left(\frac{8.314}{16.04}\frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right)(298\ \text{K})\ln\frac{5}{1.013} + 51{,}393.4\frac{\text{kJ}}{\text{kg}} \\ &= 246.6 + 51{,}393.4 \\ &= 51{,}640 \ \text{kJ/kg} \end{aligned}$$

Here the specific exergy is determined predominately by the chemical component.

TABLE 2.12 Standard Molar Chemical Exergy, e^{CH} (kJ/kmol), of Various Substances at 298 K and p_0

Substance	Formula	Model I[a]	Model II[b]
Nitrogen	N_2(g)	640	720
Oxygen	O_2(g)	3,950	3,970
Carbon dioxide	CO_2(g)	14,175	19,870
Water	H_2O(g)	8,635	9,500
	H_2O(l)	45	900
Carbon (graphite)	C(s)	404,590	410,260
Hydrogen	H_2(g)	235,250	236,100
Sulfur	S(s)	598,160	609,600
Carbon monoxide	CO(g)	269,410	275,100
Sulfur dioxide	SO_2(g)	301,940	313,400
Nitrogen monoxide	NO(g)	88,850	88,900
Nitrogen dioxide	NO_2(g)	55,565	55,600
Hydrogen sulfide	H_2S(g)	799,890	812,000
Ammonia	NH_3(g)	336,685	337,900
Methane	CH_4(g)	824,350	831,650
Ethane	C_2H_6(g)	1,482,035	1,495,840
Methanol	CH_3OH(g)	715,070	722,300
	CH_3OH(l)	710,745	718,000
Ethyl alcohol	C_2H_5OH(g)	1,348,330	1,363,900
	C_2H_5OH(l)	1,342,085	1,357,700

[a] Ahrendts, J. 1977. Die Exergie Chemisch Reaktionsfähiger Systeme, *VDI-Forschungsheft*. VDI-Verlag, Dusseldorf, 579. Also see Reference States, *Energy — The International Journal*, 5: 667–677, 1980. In Model I, p_0 = 1.019 atm. This model attempts to impose a criterion that the reference environment be in equilibrium. The reference substances are determined assuming restricted chemical equilibrium for nitric acid and nitrates and unrestricted thermodynamic equilibrium for all other chemical components of the atmosphere, the oceans, and a portion of the Earth's crust. The chemical composition of the gas phase of this model approximates the composition of the natural atmosphere.

[b] Szargut, J., Morris, D. R., and Steward, F. R. 1988. *Energy Analysis of Thermal, Chemical, and Metallurgical Processes*. Hemisphere, New York. In Model II, p_0 = 1.0 atm. In developing this model a reference substance is selected for each chemical element from among substances that contain the element being considered and that are abundantly present in the natural environment, even though the substances are not in completely mutual stable equilibrium. An underlying rationale for this approach is that substances found abundantly in nature have little economic value. On an overall basis, the chemical composition of the exergy reference environment of Model II is closer than Model I to the composition of the natural environment, but the equilibrium criterion is not always satisfied.

The small difference between p_0 = 1.013 bar and the value of p_0 for model I has been ignored.

Exergetic Efficiency

The exergetic efficiency (second law efficiency, effectiveness, or rational efficiency) provides a true measure of the performance of a system from the thermodynamic viewpoint. To define the exergetic efficiency both a *product* and a *fuel* for the system being analyzed are identified. The product represents the desired result of the system (power, steam, some combination of power and steam, etc.). Accordingly, the definition of the product must be consistent with the purpose of purchasing and using the system.

The fuel represents the resources expended to generate the product and is not necessarily restricted to being an actual fuel such as a natural gas, oil, or coal. Both the product and the fuel are expressed in terms of exergy.

For a control volume at steady state whose exergy rate balance reads

$$\dot{E}_F = \dot{E}_P + \dot{E}_D + \dot{E}_L$$

the exergetic efficiency is

$$\varepsilon = \frac{\dot{E}_P}{\dot{E}_F} = 1 - \frac{\dot{E}_D + \dot{E}_L}{\dot{E}_F} \tag{2.91}$$

where the rates at which the fuel is supplied and the product is generated are $\dot{E}_F$ and $\dot{E}_P$, respectively. $\dot{E}_D$ and $\dot{E}_L$ denote the rates of exergy destruction and exergy loss, respectively. Exergy is destroyed by irreversibilities within the control volume, and exergy is lost from the control volume via stray heat transfer, material streams vented to the surroundings, and so on. The exergetic efficiency shows the percentage of the fuel exergy provided to a control volume that is found in the product exergy. Moreover, the difference between 100% and the value of the exergetic efficiency, expressed as a percent, is the percentage of the fuel exergy wasted in this control volume as exergy destruction and exergy loss.

To apply Equation 2.91, decisions are required concerning what are considered as the fuel and the product. Table 2.13 provides illustrations for several common components. Similar considerations are used to write exergetic efficiencies for systems consisting of several such components, as, for example, a power plant.

Exergetic efficiencies can be used to assess the thermodynamic performance of a component, plant, or industry relative to the performance of *similar* components, plants, or industries. By this means the performance of a gas turbine, for instance, can be gauged relative to the typical present-day performance level of gas turbines. A comparison of exergetic efficiencies for *dissimilar* devices — gas turbines and heat exchangers, for example — is generally not significant, however.

The exergetic efficiency is generally more meaningful, objective, and useful than other efficiencies based on the first or second law of thermodynamics, including the thermal efficiency of a power plant, the isentropic efficiency of a compressor or turbine, and the effectiveness of a heat exchanger. The thermal efficiency of a cogeneration system, for instance, is misleading because it treats both work and heat transfer as having equal thermodynamic value. The isentropic turbine efficiency (Equation 2.95a) does not consider that the working fluid at the outlet of the turbine has a higher temperature (and consequently a higher exergy that may be used in the next component) in the actual process than in the isentropic process. The heat exchanger effectiveness fails, for example, to identify the exergy destruction associated with the pressure drops of the heat exchanger working fluids.

Example 14

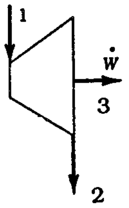
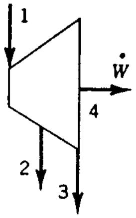
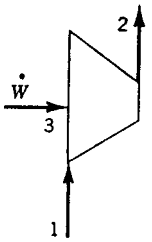
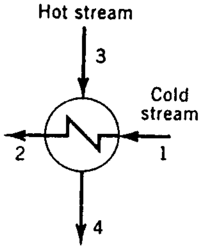
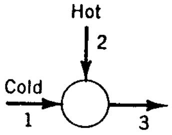
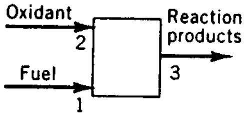
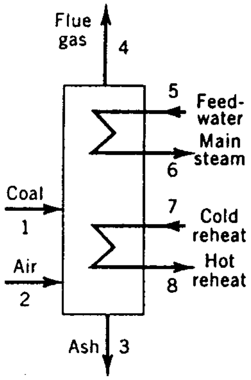
Evaluate the exergetic efficiency of the turbine in part (a) of Example 1 for T_0 = 298 K.

Solution. The exergetic efficiency from Table 2.13 is

$$\varepsilon = \frac{\dot{W}}{\dot{E}_1 - \dot{E}_2} = \frac{\dot{W}}{\dot{m}\left(e_1 - e_2\right)}$$

Using Equations 2.88 and 2.89a, and noting that the chemical exergy at 1 and 2 cancels,

TABLE 2.13 The Exergetic Efficiency for Selected Components at Steady State[a]

	Turbine or Expander	Extraction Turbine	Compressor, Pump, or Fan	Heat Exchanger[b]	Mixing Unit	Gasifier or Combustion Chamber	Boiler
Component							
$\dot{E}_P$	$\dot{W}$	$\dot{W}$	$\dot{E}_2 - \dot{E}_1$	$\dot{E}_2 - \dot{E}_1$	$\dot{E}_3$	$\dot{E}_3$	$\left(\dot{E}_6 - \dot{E}_5\right) + \left(\dot{E}_8 - \dot{E}_7\right)$
$\dot{E}_F$	$\dot{E}_1 - \dot{E}_2$	$\dot{E}_1 - \dot{E}_2 - \dot{E}_3$	$\dot{W}$	$\dot{E}_3 - \dot{E}_4$	$\dot{E}_1 + \dot{E}_2$	$\dot{E}_1 + \dot{E}_2$	$\left(\dot{E}_1 + \dot{E}_2\right) + \left(\dot{E}_3 + \dot{E}_4\right)$
ε	$\dfrac{\dot{W}}{\dot{E}_1 - \dot{E}_2}$	$\dfrac{\dot{W}}{\dot{E}_1 - \dot{E}_2 - \dot{E}_3}$	$\dfrac{\dot{E}_2 - \dot{E}_1}{\dot{W}}$	$\dfrac{\dot{E}_2 - \dot{E}_1}{\dot{E}_3 - \dot{E}_4}$	$\dfrac{\dot{E}_3}{\dot{E}_1 + \dot{E}_2}$	$\dfrac{\dot{E}_3}{\dot{E}_1 + \dot{E}_2}$	$\dfrac{\left(\dot{E}_6 - \dot{E}_5\right) + \left(\dot{E}_8 - \dot{E}_7\right)}{\left(\dot{E}_1 + \dot{E}_2\right) - \left(\dot{E}_3 + \dot{E}_4\right)}$

[a] For discussion, see Bejan et al. (1996).

[b] This definition assumes that the purpose of the heat exchanger is to heat the cold stream ($T_1 \geq T_0$). If the purpose of the heat exchanger is to provide cooling ($T_3 \geq T_0$), then the following relations should be used: $\dot{E}_P = \dot{E}_4 - \dot{E}_3$ and $\dot{E}_F = \dot{E}_1 - \dot{E}_2$.

$$\varepsilon = \frac{\dot{W}}{\dot{m}\left[\left(h_1 - h_2\right) - T_0\left(s_1 - s_2\right)\right]}$$

Since $\dot{W} = \dot{m}(h_1 - h_2)$,

$$\varepsilon = \frac{\dot{W}}{\dot{W} + \dot{m}T_0\left(s_2 - s_1\right)}$$

Finally, using data from Example 1 and $s_2 = 6.8473$ kJ/kg · K,

$$\varepsilon = \frac{30\text{ MW}}{30\text{ MW} + \left(\frac{162{,}357}{3600}\frac{\text{kg}}{\text{s}}\right)(298\text{ K})(6.8473 - 6.6022)\left(\frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right)\left(\frac{1\text{ MW}}{10^3\text{ kJ/sec}}\right)}$$

$$= \frac{30\text{ MW}}{(30 + 3.29)\text{MW}} = 0.9(90\%)$$

Exergy Costing

Since exergy measures the true thermodynamic values of the work, heat, and other interactions between the system and its surroundings as well as the effect of irreversibilities within the system, exergy is a rational basis for assigning costs. This aspect of thermoeconomics is called *exergy costing.*

Referring to Figure 2.16 showing a steam turbine-electric generator at steady state, the total cost to produce the electricity and exiting steam equals the cost of the entering steam plus the cost of owning and operating the device. This is expressed by the *cost rate balance* for the turbine-generator:

$$\dot{C}_e + \dot{C}_2 = \dot{C}_1 + \dot{Z} \tag{2.92a}$$

where $\dot{C}_e$ is the cost rate associated with the electricity, $\dot{C}_1$ and $\dot{C}_2$ are the cost rates associated with the entering steam and exiting steam, respectively, and $\dot{Z}$ accounts for the cost rate associated with owning and operating the system, each *annualized* in $ per year.

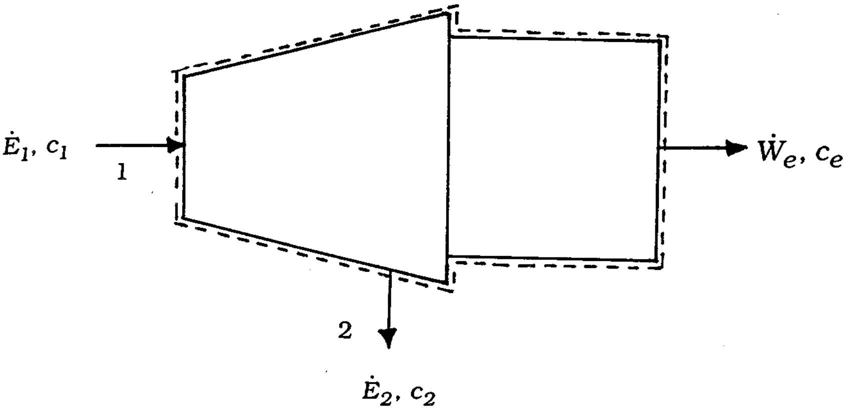


FIGURE 2.16 Steam turbine/electric generator used to discuss exergy costing.

With exergy costing, the cost rates $\dot{C}_1, \dot{C}_2,$ and $\dot{C}_e$ are evaluated in terms of the associated rate of exergy transfer and a *unit cost.* Equation 2.92a then appears as

$$c_e \dot{W}_e + c_2 \dot{E}_2 = c_1 \dot{E}_1 + \dot{Z} \tag{2.92b}$$

The coefficients c_1, c_2, and c_e in Equation 2.92b denote the *average* cost per unit of exergy for the associated exergy rate. The unit cost c_1 of the entering steam would be obtained from exergy costing applied to the components upstream of the turbine. Assigning the same unit cost to the exiting steam: $c_2 = c_1$ on the basis that the purpose of the turbine-generator is to generate electricity and thus all costs associated with owning and operating the system should be charged to the power, Equation 2.92b becomes

$$c_e \dot{W}_e = c_1 \left(\dot{E}_1 - \dot{E}_2 \right) + \dot{Z} \tag{2.92c}$$

The first term on the right side accounts for the cost of the net exergy used and the second term accounts for cost of the system itself. Introducing the exergetic efficiency from Table 2.13, the unit cost of the electricity is

$$c_e = \frac{c_1}{\varepsilon} + \frac{\dot{Z}}{\dot{W}_e} \tag{2.93}$$

This equation shows, for example, that the unit cost of electricity would increase if the exergetic efficiency were to decrease owing to a deterioration of the turbine with use.

Example 15

A turbine-generator with an exergetic efficiency of 90% develops 7×10^7 kW · hr of electricity annually. The annual cost of owning and operating the system is $\$2.5 \times 10^5$. If the average unit cost of the steam entering the system is \$0.0165 per kW · hr of exergy, evaluate the unit cost of the electricity.

Solution. Substituting values into Equation 2.93,

$$c_e = \frac{\$0.0165/\text{kW} \cdot \text{h}}{0.9} + \frac{\$2.5 \times 10^5/\text{year}}{7 \times 10^7 \ \text{kW} \cdot \text{h/year}}$$

$$= 0.0183 + 0.0036 = \$0.0219/\text{kW} \cdot \text{h}$$

2.6 Vapor and Gas Power Cycles

Vapor and gas power systems develop electrical or mechanical power from energy sources of chemical, solar, or nuclear origin. In *vapor* power systems the *working fluid*, normally water, undergoes a phase change from liquid to vapor, and conversely. In *gas* power systems, the working fluid remains a gas throughout, although the composition normally varies owing to the introduction of a fuel and subsequent combustion. The present section introduces vapor and gas power systems. Further discussion is provided in Chapter 8. Refrigeration systems are considered in Chapter 9.

The processes taking place in power systems are sufficiently complicated that idealizations are typically employed to develop tractable thermodynamic models. The *air standard analysis* of gas power systems considered later in the present section is a noteworthy example. Depending on the degree of idealization, such models may provide only qualitative information about the performance of the corresponding real-world systems. Yet such information is frequently useful in gauging how changes in major operating parameters might affect actual performance. Elementary thermodynamic models can also provide simple settings to assess, at least approximately, the advantages and disadvantages of features proposed to improve thermodynamic performance.

Rankine and Brayton Cycles

In their simplest embodiments vapor power and gas turbine power plants are represented conventionally in terms of four components in series, forming, respectively, the Rankine cycle and the Brayton cycle shown schematically in Table 2.14. The thermodynamically ideal counterparts of these cycles are composed of four internally reversible processes in series: two isentropic processes alternated with two constant pressure processes. Table 2.14 provides property diagrams of the actual and corresponding ideal cycles. Each actual cycle is denoted 1-2-3-4-1; the ideal cycle is 1-2s-3-4s-1. For simplicity, pressure drops through the boiler, condenser, and heat exchangers are not shown. Invoking Equation 2.29 for the ideal cycles, the heat added per unit of mass flowing is represented by the area *under* the isobar from state 2s to state 3: area a-2s-3-b-a. The heat rejected is the area *under* the isobar from state 4s to state 1: area a-1-4s-b-a. Enclosed area 1-2s-3-4s-1 represents the net heat added per unit of mass flowing. For any power cycle, the net heat added equals the net work done.

Expressions for the principal energy transfers shown on the schematics of Table 2.14 are provided by Equations 1 to 4 of the table. They are obtained by reducing Equation 2.27a with the assumptions of negligible heat loss and negligible changes in kinetic and potential energy from the inlet to the outlet of each component. All quantities are positive in the directions of the arrows on the figure. Using these expressions, the thermal efficiency is

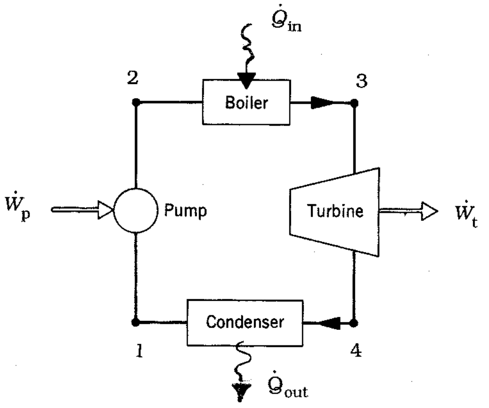
$$\eta = \frac{\left(h_3 - h_4\right) - \left(h_2 - h_1\right)}{h_3 - h_2} \tag{2.94}$$

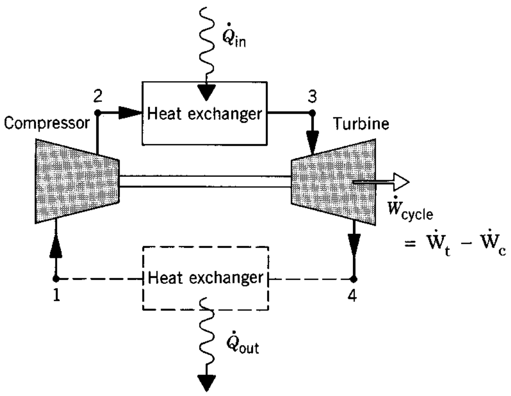
To obtain the thermal efficiency of the ideal cycle, h_{2s} replaces h_2 and h_{4s} replaces h_4 in Equation 2.94.

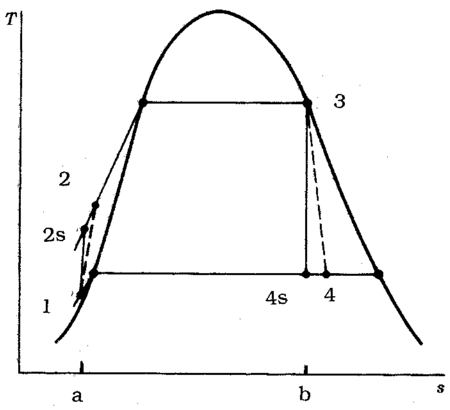
Decisions concerning cycle operating conditions normally recognize that the thermal efficiency tends to increase as the average temperature of heat addition increases and/or the temperature of heat rejection decreases. In the Rankine cycle, a high average temperature of heat addition can be achieved by superheating the vapor prior to entering the turbine, and/or by operating at an elevated steam-generator pressure. In the Brayton cycle an increase in the compressor pressure ratio p_2/p_1 tends to increase the average temperature of heat addition. Owing to materials limitations at elevated temperatures and pressures, the state of the working fluid at the turbine inlet must observe practical limits, however. The turbine inlet temperature of the Brayton cycle, for example, is controlled by providing air far in excess of what is required for combustion. In a Rankine cycle using water as the working fluid, a low temperature of heat rejection is typically achieved by operating the condenser at a pressure below 1 atm. To reduce

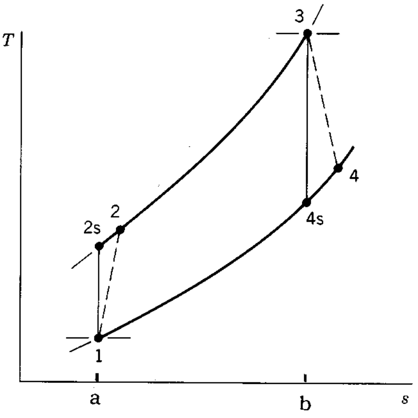
TABLE 2.14 Rankine and Brayton Cycles

Rankine Cycle	Brayton Cycle









$$\left.\begin{matrix}\dot{W}_p \\ \dot{W}_c\end{matrix}\right\} = \dot{m}\left(h_2 - h_1\right) \qquad (> 0) \tag{1}$$

$$\dot{Q}_{in} = \dot{m}\left(h_3 - h_2\right) \qquad (> 0) \tag{2}$$

$$\dot{W}_t = \dot{m}\left(h_3 - h_4\right) \qquad (> 0) \tag{3}$$

$$\dot{Q}_{out} = \dot{m}\left(h_1 - h_4\right) \qquad (> 0) \tag{4}$$

erosion and wear by liquid droplets on the blades of the Rankine cycle steam turbine, at least 90% quality should be maintained at the turbine exit: $x_4 > 0.9$.

The *back work ratio,* bwr, is the ratio of the work required by the pump or compressor to the work developed by the turbine:

$$bwr = \frac{h_2 - h_1}{h_3 - h_4} \tag{2.95}$$

As a relatively high specific volume vapor expands through the turbine of the Rankine cycle and a much lower specific volume liquid is pumped, the back work ratio is characteristically quite low in vapor power plants — in many cases on the order of 1 to 2%. In the Brayton cycle, however, both the turbine and compressor handle a relatively high specific volume gas, and the back ratio is much larger, typically 40% or more.

The effect of friction and other irreversibilities for flow-through turbines, compressors, and pumps is commonly accounted for by an appropriate *isentropic efficiency.* The isentropic turbine efficiency is

$$\eta_t = \frac{h_3 - h_4}{h_3 - h_{4s}} \tag{2.95a}$$

The isentropic compressor efficiency is

$$\eta_c = \frac{h_{2s} - h_1}{h_2 - h_1} \tag{2.95b}$$

In the isentropic pump efficiency, η_p, which takes the same form as Equation 2.95b, the numerator is frequently approximated via Equation 2.30c *as* $h_{2s} - h_1 \approx v_1 \Delta p$, where Δp is the pressure rise across the pump.

Simple gas turbine power plants differ from the Brayton cycle model in significant respects. In actual operation, excess air is continuously drawn into the compressor, where it is compressed to a higher pressure; then fuel is introduced and combustion occurs; finally the mixture of combustion products and air expands through the turbine and is subsequently discharged to the surroundings. Accordingly, the low-temperature heat exchanger shown by a dashed line in the Brayton cycle schematic of Table 2.14 is not an actual component, but included only to account formally for the cooling in the surroundings of the hot gas discharged from the turbine.

Another frequently employed idealization used with gas turbine power plants is that of an *air-standard analysis.* An air-standard analysis involves two major assumptions: (1) as shown by the Brayton cycle schematic of Table 2.14, the temperature rise that would be brought about by combustion is effected instead by a heat transfer from an external source; (2) the working fluid throughout the cycle is air, which behaves as an ideal gas. In a *cold* air-standard analysis the specific heat ratio k for air is taken as constant. Equations 1 to 6 of Table 2.7 together with data from Table A.8 apply generally to air-standard analyses. Equations 1′ to 6′ of Table 2.7 apply to cold air-standard analyses, as does the following expression for the turbine power obtained from Table 2.1 (Equation 27c″):

$$\dot{W}_t = \dot{m}\frac{kRT_3}{k-1}\left[1 - \left(p_4/p_3\right)^{(k-1)/k}\right] \tag{2.96}$$

(Equation 2.96 also corresponds to Equation 5′ of Table 2.8 when $n = k$.) An expression similar in form can be written for the power required by the compressor.

For the simple Rankine and Brayton cycles of Table 2.14 the results of sample calculations are provided in Table 2.15. The Brayton cycle calculations are on an air-standard analysis basis.

Otto, Diesel, and Dual Cycles

Although most gas turbines are also internal combustion engines, the name is usually reserved to *reciprocating* internal combustion engines of the type commonly used in automobiles, trucks, and buses. Two principal types of reciprocating internal combustion engines are the *spark-ignition* engine and the *compression-ignition* engine. In a spark-ignition engine a mixture of fuel and air is ignited by a spark

TABLE 2.15 Sample Calculations for the Rankine and Brayton Cycles of Table 2.14

Rankine Cycle

Given data: $p_1 = p_4 = 8$ kPa (saturated liquid at 1)
$T_3 = 480°C$ (superheated vapor at 3)
$p_2 = p_3 = 8$ MPa
$\dot{W}_{net} = 100$ MW
Ideal cycle: $\eta_t = \eta_p = 100\%$
Actual cycle: $\eta_t = 85\%$, $\eta_p = 70\%$

Parameter	Ideal Cycle	Actual Cycle
x_4	0.794	0.873
h_2 (kJ/ kg)	181.9[a]	185.4
$\dot{m}$ (kg/h)	2.86×10^5	3.38×10^5
η (%)	39.7	33.6
$\dot{Q}_{out}$ (MW)	151.9	197.6
$\dot{E}_{q,out}$ (MW)[b]	8.2	10.7

[a] $h_{2s} \approx h_1 + v_1 \Delta p$

[b] Equation 2.86 with $T_0 = 298$ K, $T_j = T_{sat}$ (8 kPa) = 315 K

Brayton Cycle

Given data: $p_1 = p_4 = 1$ bar
$p_2 = p_3 = 10$ bar
$T_3 = 1400$ K
$\eta_t = \eta_c = 100\%$

Parameter	Air-Standard Analysis	Cold Air-Standard Analysis $k = 1.4$
T_2 (K)	574.1	579.2
T_4 (K)	787.7	725.1
$\dot{W}_{net}/\dot{m}$ (kJ/kg)	427.2	397.5
η (%)	45.7	48.2
bwr	0.396	0.414

plug. In a compression ignition engine air is compressed to a high-enough pressure and temperature that combustion occurs spontaneously when fuel is injected.

In a *four-stroke* internal combustion engine, a piston executes four distinct strokes within a cylinder for every two revolutions of the crankshaft. Figure 2.17 gives *a* pressure-displacement diagram as it might be displayed electronically. With the intake valve open, the piston makes an *intake stroke* to draw a fresh charge into the cylinder. Next, with both valves closed, the piston undergoes a *compression stroke* raising the temperature and pressure of the charge. A combustion process is then initiated, resulting in a high-pressure, high-temperature gas mixture. A *power* stroke follows the compression stroke, during which the gas mixture expands and work is done on the piston. The piston then executes an *exhaust stroke* in which the burned gases are purged from the cylinder through the open exhaust valve. Smaller engines operate on *two-stroke* cycles. In two-stroke engines, the intake, compression, expansion, and

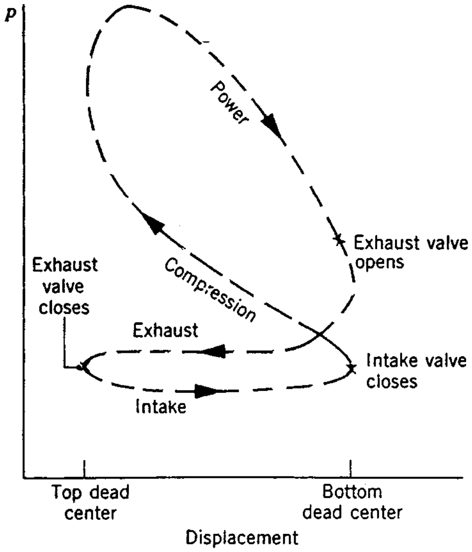


FIGURE 2.17 Pressure-displacement diagram for a reciprocating internal combustion engine.

exhaust operations are accomplished in one revolution of the crankshaft. Although internal combustion engines undergo *mechanical* cycles, the cylinder contents do not execute a *thermodynamic* cycle, since matter is introduced with one composition and is later discharged at a different composition.

A parameter used to describe the performance of reciprocating piston engines is the *mean effective pressure*, or mep. The mean effective pressure is the theoretical constant pressure that, if it acted on the piston during the power stroke, would produce the same *net* work as actually developed in one cycle. That is,

$$\text{mep} = \frac{\text{net work for one cycle}}{\text{displacement volume}} \tag{2.97}$$

where the displacement volume is the volume swept out by the piston as it moves from the top dead center to the bottom dead center. For two engines of equal displacement volume, the one with a higher mean effective pressure would produce the greater net work and, if the engines run at the same speed, greater power.

Detailed studies of the performance of reciprocating internal combustion engines may take into account many features, including the combustion process occurring within the cylinder and the effects of irreversibilities associated with friction and with pressure and temperature gradients. Heat transfer between the gases in the cylinder and the cylinder walls and the work required to charge the cylinder and exhaust the products of combustion also might be considered. Owing to these complexities, accurate modeling of reciprocating internal combustion engines normally involves computer simulation.

To conduct *elementary* thermodynamic analyses of internal combustion engines, considerable simplification is required. A procedure that allows engines to be studied *qualitatively* is to employ an *air-standard analysis* having the following elements: (1) a fixed amount of air modeled as an ideal gas is the system; (2) the combustion process is replaced by a heat transfer from an external source and generally represented in terms of elementary thermodynamic processes; (3) there are no exhaust and intake processes as in an actual engine: the cycle is completed by a constant-volume heat rejection process; (4) all processes are internally reversible.

The processes employed in air-standard analyses of internal combustion engines are selected to represent the events taking place within the engine simply and mimic the appearance of observed pressure-displacement diagrams. In addition to the constant volume heat rejection noted previously, the compression stroke and at least a portion of the power stroke are conventionally taken as isentropic. The heat addition is normally considered to occur at constant volume, at constant pressure, or at constant volume followed by a constant pressure process, yielding, respectively, the Otto, Diesel, and Dual cycles shown in Table 2.16.

Reducing the closed system energy balance, Equation 2.8, gives the following expressions for heat and work applicable in each case shown in Table 2.16:

$$\frac{W_{12}}{m} = u_1 - u_2 \qquad (< 0)$$

$$\frac{W_{34}}{m} = u_3 - u_4 \qquad (> 0)$$

$$\frac{Q_{41}}{m} = u_1 - u_4 \qquad (< 0)$$

Table 2.16 provides additional expressions for work, heat transfer, and thermal efficiency identified with each case individually. The thermal efficiency, evaluated from Equation 2.9, takes the form

$$\eta = 1 - \frac{\left|Q_{41}/m\right|}{Q_A/m}$$

Equations 1 to 6 of Table 2.7 together with data from Table A.8, apply generally to air-standard analyses. In a *cold* air-standard analysis the specific heat ratio k for air is taken as constant. Equations 1′ to 6′ of Table 2.7 apply to cold air-standard analyses, as does Equation 4′ of Table 2.8, with $n = k$ for the isentropic processes of these cycles.

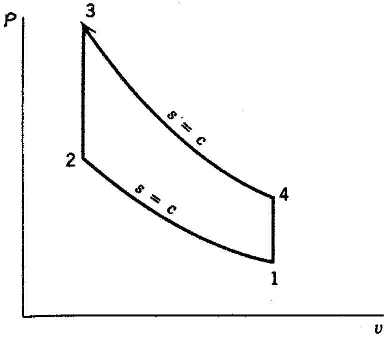
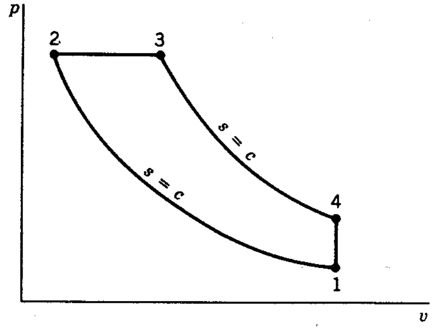
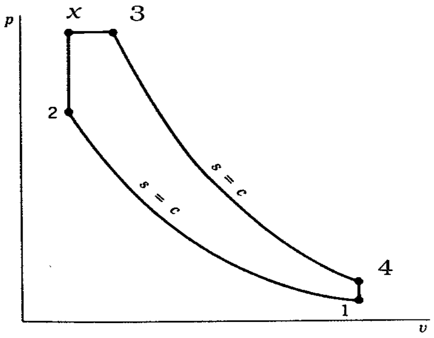
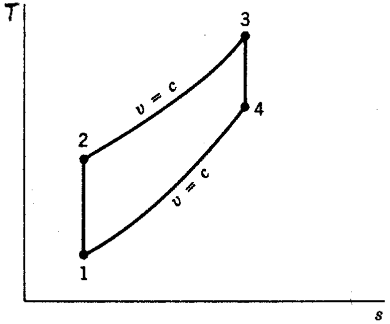
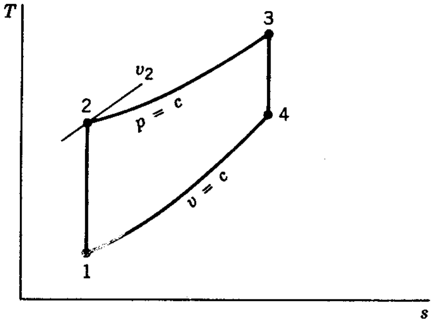
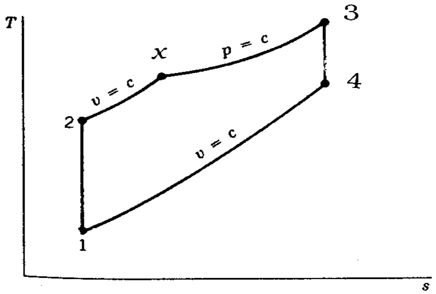
Referring to Table 2.16, the ratio v_1/v_2 is the *compression ratio, r*. For the Diesel cycle, the ratio v_3/v_2 is the *cutoff ratio*, r_c. Figure 2.18 shows the variation of the thermal efficiency with compression ratio for an Otto cycle and Diesel cycles having cutoff ratios of 2 and 3. The curves are determined on a cold air-standard basis with $k = 1.4$ using the following expression:

$$\eta = 1 - \frac{1}{r^{k-1}}\left[\frac{r_c^k - 1}{k\left(r_c - 1\right)}\right] \qquad (\text{constant } k) \tag{2.98}$$

where the Otto cycle corresponds to $r_c = 1$.

As all processes are internally reversible, areas on the *p-v* and *T-s* diagrams of Table 2.16 can be interpreted, respectively, as work and heat transfer. Invoking Equation 2.10 and referring to the *p-v* diagrams, the areas under process 3-4 of the Otto cycle, process 2-3-4 of the Diesel cycle, and process x-3-4 of the Dual cycle represent the work done by the gas during the power stroke, per unit of mass. For each cycle, the area under the isentropic process 1-2 represents the work done on the gas during the compression stroke, per unit of mass. The enclosed area of each cycle represents the net work done per unit mass. With Equation 2.15 and referring to the *T-s* diagrams, the areas under process 2-3 of the Otto and Diesel cycles and under process 2-x-3 of the Dual cycle represent the heat added per unit of mass. For each cycle, the area under the process 4-1 represent the heat rejected per unit of mass. The enclosed area of each cycle represents the net heat added, which equals the net work done, each per unit of mass.

TABLE 2.16 Otto, Diesel, and Dual Cycles

(a) Otto Cycle	(b) Diesel Cycle	(c) Dual Cycle
		
		
$\frac{W_{23}}{m} = 0$	$\frac{W_{23}}{m} = p_2\left(v_3 - v_2\right)$	$\frac{W_{2x}}{m} = 0, \quad \frac{Q_{2x}}{m} = u_x - u_2$
$\frac{Q_{23}}{m} = u_3 - u_2$	$\frac{Q_{23}}{m} = h_3 - h_2$	$\frac{W_{x3}}{m} = p_3\left(v_3 - v_2\right), \quad \frac{Q_{x3}}{m} = h_3 - h_x$
$\eta = 1 - \frac{u_4 - u_1}{u_3 - u_2}$	$\eta = 1 - \frac{u_4 - u_1}{h_3 - h_2}$	$\eta = 1 - \frac{u_4 - u_1}{\left(u_x - u_2\right) + \left(h_3 - h_x\right)}$

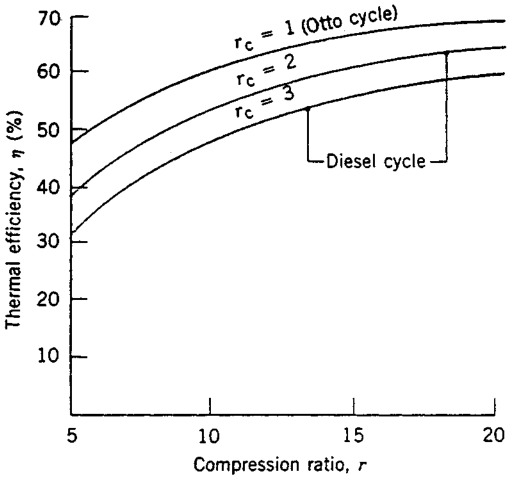


FIGURE 2.18 Thermal efficiency of the cold air-standard Otto and Diesel cycles, $k = 1.4$.

Carnot, Ericsson, and Stirling Cycles

Three thermodynamic cycles that exhibit the Carnot efficiency (Equation 2.12) are the Carnot, Ericsson, and Stirling cycles shown in Figure 2.19. Each case represents a reversible power cycle in which heat is added from an external source at a constant temperature T_H (process 2-3) and rejected to the surroundings at a constant temperature T_C (process 4-1). Carnot cycles can be configured both as vapor power cycles and as cycles executed by a gas in a piston-cylinder assembly (see, e.g., Moran and Shapiro, 1995). Carnot cycles also can be executed in systems where a capacitor is charged and discharged, a paramagnetic substance is magnetized and demagnetized, and in other ways. Regardless of the type of device and the working substance used, the Carnot cycle always has the same four internally reversible processes in series: two isentropic processes alternated with two isothermal processes.

The Ericsson and Stirling cycles also consist of four internally reversible processes in series: heating from state 1 to state 2 (at constant pressure in the Ericsson cycle and at constant volume in the Stirling cycle), isothermal heating from state 2 to state 3 at temperature T_H, cooling from state 3 to state 4 (at constant pressure in the Ericsson cycle and at constant volume in the Stirling cycle), and isothermal cooling from state 4 to state 1 at temperature T_C. An ideal regenerator allows the heat input required for process 1-2 to be obtained from the heat rejected in process 3-4. Accordingly, as in the Carnot cycle all the heat added externally occurs at T_H and all of the heat rejected to the surroundings occurs at T_C.

The Ericsson and Stirling cycles are principally of theoretical interest as examples of cycles that exhibit the same thermal efficiency as the Carnot cycle: Equation 2.12. However, a practical engine of the piston-cylinder type that operates on a closed regenerative cycle having features in common with the Stirling cycle has been under study in recent years. This engine, known as the *Stirling engine*, offers the opportunity for high efficiency together with reduced emissions from combustion products because the combustion takes place externally and not within the cylinder as in internal combustion engines. In the Stirling engine, energy is transferred to the working fluid from products of combustion, which are kept separate. It is an *external* combustion engine.

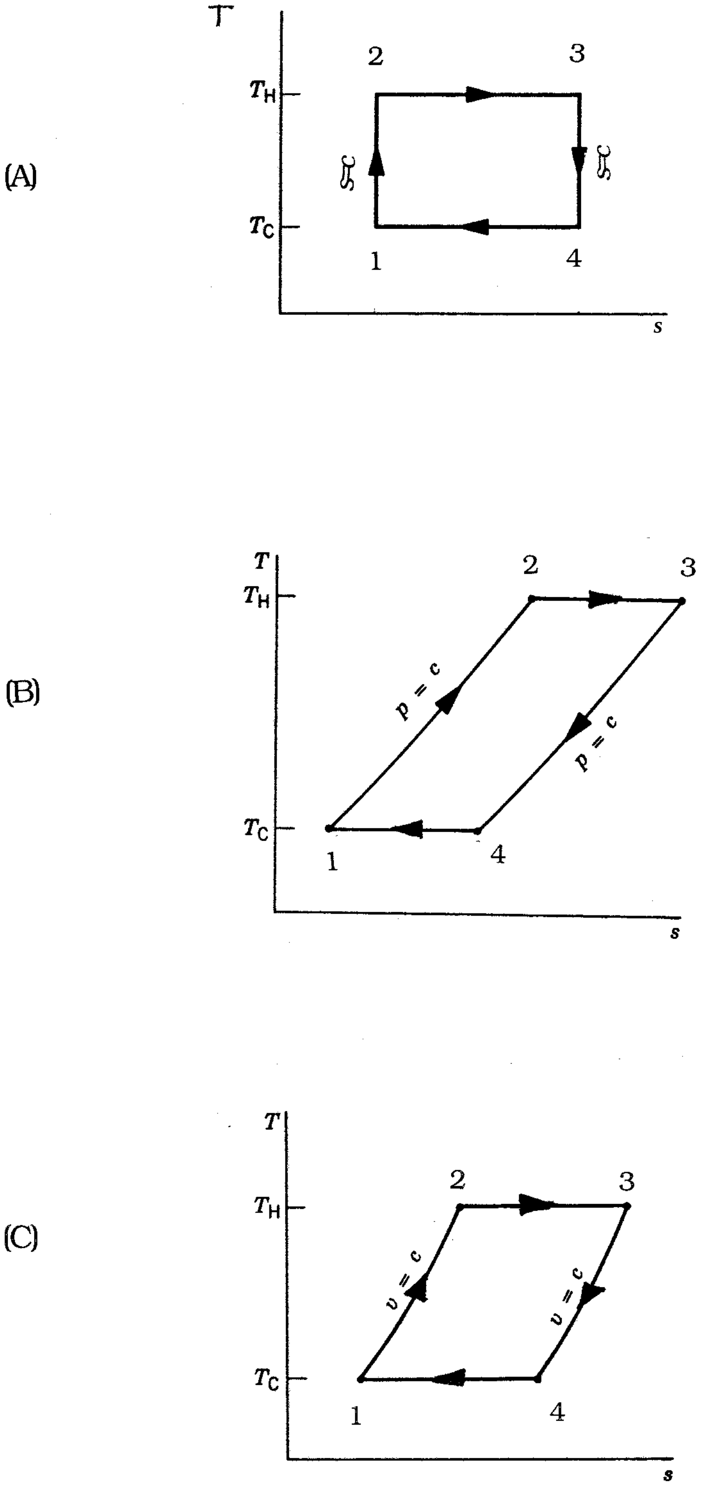


FIGURE 2.19 (A) Carnot, (B) Ericsson, and (C) Stirling cycles.

2.7 Guidelines for Improving Thermodynamic Effectiveness

Thermal design frequently aims at the most effective system from the cost viewpoint. Still, in the cost optimization process, particularly of complex energy systems, it is often expedient to begin by identifying a design that is nearly optimal thermodynamically; such a design can then be used as a point of departure for cost optimization. Presented in this section are guidelines for improving the use of fuels (natural gas, oil, and coal) by reducing sources of thermodynamic inefficiency in thermal systems. Further discussion is provided by Bejan et al. (1996).

To improve thermodynamic effectiveness it is necessary to deal directly with inefficiencies related to exergy destruction and exergy loss. The primary contributors to exergy destruction are chemical reaction, heat transfer, mixing, and friction, including unrestrained expansions of gases and liquids. To deal with them effectively, the principal sources of inefficiency not only should be understood qualitatively, but also determined quantitatively, at least approximately. Design changes to improve effectiveness must be done judiciously, however, for the cost associated with different sources of inefficiency can be different. For example, the unit cost of the electrical or mechanical power required to provide for the exergy destroyed owing to a pressure drop is generally higher than the unit cost of the fuel required for the exergy destruction caused by combustion or heat transfer.

Since chemical reaction is a significant source of thermodynamic inefficiency, it is generally good practice to minimize the use of combustion. In many applications the use of combustion equipment such as boilers is unavoidable, however. In these cases a significant reduction in the combustion irreversibility by conventional means simply cannot be expected, for the major part of the exergy destruction introduced by combustion is an inevitable consequence of incorporating such equipment. Still, the exergy destruction in practical combustion systems can be reduced by minimizing the use of excess air and by preheating the reactants. In most cases only a small part of the exergy destruction in a combustion chamber can be avoided by these means. Consequently, after considering such options for reducing the exergy destruction related to combustion, efforts to improve thermodynamic performance should focus on components of the overall system that are more amenable to betterment by cost-effective conventional measures. In other words, *some exergy destructions and energy losses can be avoided, others cannot. Efforts should be centered on those that can be avoided.*

Nonidealities associated with heat transfer also typically contribute heavily to inefficiency. Accordingly, unnecessary or cost-ineffective heat transfer must be avoided. Additional guidelines follow:

- The higher the temperature T at which a heat transfer occurs in cases where $T > T_0$, where T_0 denotes the temperature of the environment (Section 2.5), the more valuable the heat transfer and, consequently, the greater the need to avoid heat transfer to the ambient, to cooling water, or to a refrigerated stream. Heat transfer across T_0 should be avoided.
- The lower the temperature T at which a heat transfer occurs in cases where $T < T_0$, the more valuable the heat transfer and, consequently, the greater the need to avoid direct heat transfer with the ambient or a heated stream.
- Since exergy destruction associated with heat transfer between streams varies inversely with the temperature level, the lower the temperature level, the greater the need to minimize the stream-to-stream temperature difference.
- Avoid the use of intermediate heat transfer fluids when exchanging energy by heat transfer between two streams

Although irreversibilities related to friction, unrestrained expansion, and mixing are often secondary in importance to those of combustion and heat transfer, they should not be overlooked, and the following guidelines apply:

- Relatively more attention should be paid to the design of the lower temperature stages of turbines and compressors (the last stages of turbines and the first stages of compressors) than to the remaining stages of these devices.

- For turbines, compressors, and motors, consider the most thermodynamically efficient options.
- Minimize the use of throttling; check whether power recovery expanders are a cost-effective alternative for pressure reduction.
- Avoid processes using excessively large thermodynamic driving forces (differences in temperature, pressure, and chemical composition). In particular, minimize the mixing of streams differing significantly in temperature, pressure, or chemical composition.
- The greater the mass rate of flow, the greater the need to use the exergy of the stream effectively.
- The lower the temperature level, the greater the need to minimize friction.

Flowsheeting or *process simulation* software can assist efforts aimed at improving thermodynamic effectiveness by allowing engineers to readily model the behavior of an overall system, or system components, under specified conditions and do the required thermal analysis, sizing, costing, and optimization. Many of the more widely used flowsheeting programs: ASPEN PLUS, PROCESS, and CHEMCAD are of the *sequential-modular* type. SPEEDUP is a popular program of the *equation-solver* type. Since process simulation is a rapidly evolving field, vendors should be contacted for up-to-date information concerning the features of flowsheeting software, including optimization capabilities (if any). As background for further investigation of suitable software, see Biegler (1989) for a survey of the capabilities of 15 software products.

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