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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 nineteenth 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.

12.1 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 *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, entropy, and exergy 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.

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 *thermodynamic 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* (for discussion see Moran and Shapiro, 2000).

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 (for discussion see Moran and Shapiro, 2000). *Chemical* equilibrium is also established in terms of chemical potentials. For complete equilibrium the several types of equilibrium must exist individually.

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. 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. On the Kelvin scale the unit is the kelvin (K).

The Celsius temperature 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, the *triple point* of water (Fig. 12.1b), as shown by the following relationship between the Celsius temperature and the Kelvin temperature:

$$T(^\circ\mathrm{C}) = T(\mathrm{K}) - 273.15 \tag{12.1}$$

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

$$T(^\circ\mathrm{R}) = 1.8T(\mathrm{K}) \tag{12.2}$$

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

$$T(^\circ\mathrm{F}) = T(^\circ\mathrm{R}) - 459.67 \tag{12.3}$$

Substituting Eqs. (12.1) and (12.2) into Eq. (12.3) gives

$$T(^\circ\mathrm{F}) = 1.8T(^\circ\mathrm{C}) + 32 \tag{12.4}$$

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).

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 both the system and surroundings cannot be restored to their initial states. 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.

Laws of Thermodynamics

The first steps in a thermodynamic analysis are definition of the system and identification of the relevant interactions with the surroundings. Attention then turns to the pertinent physical laws and relationships that allow the behavior of the system to be described in terms of an engineering model, which is a simplified representation of system behavior that is sufficiently faithful for the purpose of the analysis, even if features exhibited by the actual system are ignored.

Thermodynamic analyses of control volumes and closed systems typically use, directly or indirectly, one or more of three basic laws. The laws, which are independent of the particular substance or substances under consideration, are

- the conservation of mass principle,
- the conservation of energy principle,
- the second law of thermodynamics.

The second law may be expressed in terms of entropy or exergy.

The laws of thermodynamics must be supplemented by appropriate thermodynamic property data. For some applications a momentum equation expressing Newton's second law of motion also is required. Data for transport properties, heat transfer coefficients, and friction factors often are needed for a comprehensive engineering analysis. Principles of engineering economics and pertinent economic data also can play prominent roles.

12.2 Extensive Property Balances

The laws of thermodynamics can be expressed in terms of *extensive property balances* for mass, energy, entropy, and exergy. Engineering applications are generally analyzed on a control volume basis. Accordingly, the control volume formulations of the mass energy, entropy, and exergy balances are featured here. They are provided in the form of overall balances assuming one-dimensional flow. Equations of change for mass, energy, and entropy in the form of differential equations are also available in the literature (Bird et al., 1960).

Mass Balance

For applications in which inward and outward flows occur, each through one or more ports, the extensive property balance expressing the conservation of mass principle takes the form

$$\frac{dm}{dt} = \sum_i \dot{m}_i - \sum_e \dot{m}_e \tag{12.5}$$

where dm/dt represents the time rate of change of mass contained within the control volume, $\dot{m}_i$ denotes the mass flow rate at an inlet port, and $\dot{m}_e$ denotes the mass flow rate at an exit port.

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, v_n, times the area: $\mathrm{v}_n dA$. The mass flow rate through dA is $\rho(\mathrm{v}_n dA)$, where ρ denotes density. 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

$$\dot{m} = \rho \mathrm{v} A = \frac{\mathrm{v}A}{v} \tag{12.6}$$

where v denotes the specific volume (the reciprocal of density) and the subscript n has been dropped from velocity for simplicity.

Energy Balance

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 also can be transformed from one form to another and transferred between systems. Energy can be transferred by work, by heat transfer, and by flowing matter. The total amount of energy is conserved in all transformations and transfers. The extensive property balance expressing the conservation of energy principle takes the form

$$\frac{d(U+\mathrm{KE}+\mathrm{PE})}{dt} = \dot{Q}-\dot{W}+\sum_i \dot{m}_i\left(h_i+\frac{\mathrm{v}_i^2}{2}+gz_i\right)-\sum_e \dot{m}_e\left(h_e+\frac{\mathrm{v}_e^2}{2}+gz_e\right) \tag{12.7a}$$

where U, KE, and PE denote, respectively, the internal energy, kinetic energy, and gravitational potential energy of the overall control volume.

The right side of Eq. (12.7a) accounts for transfers of energy across the boundary of the control volume. Energy can enter and exit control volumes by work. Because work is done on or by a control volume when matter flows across the boundary, it is convenient to separate the work rate (or power) into two contributions. One contribution is the work rate associated with the force of the fluid pressure as mass is introduced at the inlet and removed at the exit. Commonly referred to as *flow work*, this contribution is accounted for by $\dot{m}_i(p_i v_i)$ and $\dot{m}_e(p_e v_e)$, respectively, where p denotes pressure and v denotes specific volume. The other contribution, denoted by $\dot{W}$ in Eq. (12.7a), includes all other work effects, such as those associated with rotating shafts, displacement of the boundary, and electrical effects. $\dot{W}$ is considered *positive* for energy transfer *from* the control volume.

Energy also can enter and exit control volumes with flowing streams of matter. On a one-dimensional flow basis, the rate at which energy enters with matter at inlet i is $\dot{m}_i(u_i+\mathrm{v}_i^2/2+gz_i)$, where the three terms in parentheses account, respectively, for the specific internal energy, specific kinetic energy, and specific gravitational potential energy of the substance flowing through port i. In writing Eq. (12.7a) the sum of the specific internal energy and specific flow work at each inlet and exit is expressed in terms of the specific enthalpy $h(=u+pv)$. Finally, $\dot{Q}$ accounts for the rate of energy transfer by heat and is considered *positive* for energy transfer *to* the control volume.

By dropping the terms of Eq. (12.7a) involving mass flow rates an energy rate balance for closed systems is obtained. In principle the closed system energy rate balance can be integrated for a process between two states to give the closed system energy balance:

$$\underset{\text{(closed systems)}}{(U_2-U_1)+(\mathrm{KE}_2-\mathrm{KE}_1)+(\mathrm{PE}_2-\mathrm{PE}_1) = Q-W} \tag{12.7b}$$

where 1 and 2 denote the end states. Q and W denote the *amounts* of energy transferred by heat and work during the process, respectively.

Entropy Balance

Contemporary applications of engineering thermodynamics express the second law, alternatively, as an entropy balance or an exergy balance. The entropy balance is considered here.

Like mass and energy, entropy can be stored within systems and transferred across system boundaries. However, unlike mass and energy, entropy is not conserved, but generated (or produced) by *irreversibilities* within systems. A control volume form of the extensive property balance for entropy is

$$\frac{dS}{dt} = \underbrace{\sum_j \frac{\dot{Q}_j}{T_j} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e}_{\text{rates of entropy transfer}} + \underbrace{\dot{S}_{\text{gen}}}_{\text{rate of entropy generation}} \tag{12.8}$$

where dS/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 accompanying mass flow. $\dot{Q}_j$ 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 accompanying rate of entropy transfer. $\dot{S}_{\text{gen}}$ denotes the time rate of entropy generation due to irreversibilities within the control volume. An entropy rate balance for closed systems is obtained by dropping the terms of Eq. (12.8) involving mass flow rates.

When applying the entropy balance in any of its forms, 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 normally is determined through comparison: the entropy generation within a given component would be compared with the entropy generation values of the other components included in an overall system formed by these components. This allows the principal contributors to the irreversibility of the overall system to be pinpointed.

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 changes continuously, but the total amount of mass remains constant. At steady state, the mass rate balance Eq. (12.5) reduces to

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e \tag{12.9a}$$

At steady state, the energy rate balance Eq. (12.7a) becomes

$$0 = \dot{Q} - \dot{W} + \sum_i \dot{m}_i \left(h_i + \frac{\mathrm{V}_i^2}{2} + gz_i \right) - \sum_e \dot{m}_e \left(h_e + \frac{\mathrm{V}_e^2}{2} + gz_e \right) \tag{12.9b}$$

At steady state, the entropy rate balance Eq. (12.8) reads

$$0 = \sum_j \frac{\dot{Q}_j}{T_j} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \dot{S}_{\text{gen}} \tag{12.9c}$$

Mass and energy are conserved quantities, but entropy is not generally conserved. Equation (12.9a) 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, Eq. (12.9b) 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, Eq. (12.9c) 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.

Many applications involve control volumes having a single inlet and a single exit. For such cases the mass rate balance, Eq. (12.9a), reduces to $\dot{m}_i = \dot{m}_e$. Denoting the common mass flow rate by $\dot{m}$, Eqs. (12.9b) and (12.9c) give, respectively,

$$0 = \dot{Q} - \dot{W} + \dot{m}\left[(h_i - h_e) + \left(\frac{\mathrm{v}_i^2 - \mathrm{v}_e^2}{2}\right) + g(z_i - z_e)\right] \tag{12.10a}$$

$$0 = \frac{\dot{Q}}{T_b} + \dot{m}(s_i - s_e) + \dot{S}_{\text{gen}} \tag{12.11a}$$

where for simplicity T_b denotes the temperature, or a suitable average temperature, on the boundary where heat transfer occurs.

When energy and entropy rate balances are applied to particular cases of interest, additional simplifications are usually made. The heat transfer term $\dot{Q}$ is dropped when it is insignificant relative to other energy 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 $\dot{W}$ 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 effects of kinetic and potential energy are frequently negligible relative to other terms of the energy rate balance.

The special forms of Eqs. (12.10a) and (12.11a) listed in Table 12.1 are obtained as follows: When there is no heat transfer, Eq. (12.11a) gives

$$s_e - s_i = \frac{\dot{S}_{\text{gen}}}{\dot{m}} \geq 0 \tag{12.11b}$$

(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, Eq. (12.10a) gives

$$\dot{W} = \dot{m}\left[(h_i - h_e) + \left(\frac{\mathrm{v}_i^2 - \mathrm{v}_e^2}{2}\right) + g(z_i - z_e)\right] \tag{12.10b}$$

(no heat transfer)

A special form that is applicable, at least approximately, to compressors, pumps, and turbines results from dropping the kinetic and potential energy terms of Eq. (12.10b), leaving

$$\dot{W} = \dot{m}(h_i - h_e) \tag{12.10c}$$

(compressors, pumps, and turbines)

In *throttling devices* a significant reduction in pressure is achieved by introducing a restriction into a line through which a gas or liquid flows. For such devices $\dot{W} = 0$ and Eq. (12.10c) reduces further to read

$$h_i \cong h_e \tag{12.10d}$$

(throttling process)

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

TABLE 12.1 Energy and Entropy Balances for One-Inlet, One-Outlet Control Volumes at Steady State and No Heat Transfer

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Energy balance

$$\dot{W} = \dot{m}\left[(h_i - h_e) + \left(\frac{\mathrm{v}_i^2 - \mathrm{v}_e^2}{2}\right) + g(z_i - z_e)\right] \qquad (12.10b)$$

Compressors, pumps, and turbines[a]

$$\dot{W} = \dot{m}(h_i - h_e) \qquad (12.10c)$$

Throttling

$$h_e \cong h_i \qquad (12.10d)$$

Nozzles, diffusers[b]

$$\mathrm{v}_e = \sqrt{\mathrm{v}_i^2 + 2(h_i - h_e)} \qquad (12.10e)$$

Entropy balance

$$s_e - s_i = \frac{\dot{S}_{\text{gen}}}{\dot{m}} \geq 0 \qquad (12.11b)$$

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[a] For an ideal gas with constant c_p, Eq. (1′) of Table 12.4 allows Eq. (12.10c) to be written as

$$\dot{W} = \dot{m}c_p(T_i - T_e) \qquad (12.10c')$$

The power developed in an *isentropic process* is obtained with Eq. (5′) of Table 12.4 as

$$\dot{W} = \dot{m}c_p T_i[1 - (p_e/p_i)^{(k-1)/k}] \quad (s = c) \qquad (12.10c'')$$

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

[b] For an ideal gas with constant c_p, Eq. (1′) of Table 12.4 allows Eq. (12.10e) to be written as

$$\mathrm{v}_e = \sqrt{\mathrm{v}_i^2 + 2c_p(T_i - T_e)} \qquad (12.10e')$$

The exit velocity for an *isentropic process* is obtained with Eq. (5′) of Table 12.4 as

$$\mathrm{v}_e = \sqrt{\mathrm{v}_i^2 + 2c_p T_i[1 - (p_e/p_i)^{(k-1)/k}]} \quad (s = c) \qquad (12.10e'')$$

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

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, $\dot{W} = 0$. The heat transfer and potential energy change are generally negligible. Then Eq. (12.10b) reduces to

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

Solving for the exit velocity

$$\mathrm{v}_e = \sqrt{\mathrm{v}_i^2 + 2(h_i - h_e)} \qquad (12.10e)$$

(nozzle, diffuser)

The steady-state forms of the mass, energy, and entropy rate balances can be applied to control volumes with multiple inlets and/or exits, for example, cases involving heat-recovery steam generators, feedwater heaters, and counterflow and crossflow heat exchangers. Transient (or unsteady) analyses can be conducted with Eqs. (12.5), (12.7a), and (12.8). Illustrations of all such applications are provided by Moran and Shapiro (2000).

Exergy Balance

Exergy provides an alternative to entropy for applying the second law. When exergy concepts are combined with principles of engineering economy, the result is known as *thermoeconomics*. Thermoeconomics allows the real cost sources to be identified: capital investment costs, operating and maintenance costs, and the costs associated with the destruction and loss of exergy. Optimization of 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 Moran (1989), Bejan et al. (1996), Moran and Tsatsaronis (2000), and Moran and Shapiro (2000). 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 system of interest and environment 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 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, like entropy, generally is not conserved.

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 typical ambient values, such as 1 atm and 25°C (77°F). However, these properties may be specified differently depending on the application.

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 Transfer and Exergy Destruction

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 also is 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 alternatively as Eqs. (12.12a) and (12.12b).

$$0 = \underbrace{\sum_j \dot{E}_{q,j} - \dot{W} + \sum_i \dot{E}_i - \sum_e \dot{E}_e}_{\substack{\text{rates of}\\ \text{exergy}\\ \text{transfer}}} - \underbrace{\dot{E}_D}_{\substack{\text{rate of}\\ \text{exergy}\\ \text{destruction}}} \tag{12.12a}$$

$$0 = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j - \dot{W} + \sum_i \dot{m}_i e_i - \sum_e \dot{m}_e e_e - \dot{E}_D \tag{12.12b}$$

$\dot{W}$ has the same significance as in Eq. (12.7a): 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

$$\dot{E}_{q,j} = \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j \tag{12.13}$$

As for other control volume rate balances, the subscripts *i* and *e* denote inlets and exits, respectively. The exergy transfer rates at control volume inlets and exits 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

$$\dot{E}_D = T_0 \dot{S}_{\text{gen}} \tag{12.14}$$

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}:

$$e = e^{\text{PH}} + e^{\text{KN}} + e^{\text{PT}} + e^{\text{CH}} \tag{12.15a}$$

The first three components are evaluated as follows:

$$e^{\text{PH}} = (h - h_0) - T_0(s - s_0) \tag{12.15b}$$

$$e^{\text{KN}} = \frac{1}{2}\text{v}^2 \tag{12.15c}$$

$$e^{\text{PT}} = gz \tag{12.15d}$$

In Eq. (12.15b), h_0 and s_0 denote, respectively, the specific enthalpy and specific entropy at the restricted dead state. In Eqs. (12.15c) and (12.15d), v and *z* denote velocity and elevation relative to coordinates in the environment, respectively.

To evaluate the chemical exergy (the exergy component associated with the departure of the chemical composition of a system from that of the environment), alternative models of the environment can be employed depending on the application; 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. Standard environments also include a set of reference substances with standard concentrations reflecting as closely as possible the chemical makeup of the natural environment. Standard chemical exergy data is provided by Szargut et al. (1988), Bejan et al. (1996), and Moran and Shapiro (2000).

Guidelines for Improving Thermodynamic Effectiveness

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.

Chemical reaction is a significant source of thermodynamic inefficiency. Accordingly, 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 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, 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.

Although irreversibilities related to friction, unrestrained expansion, and mixing are often less significant than 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.

TABLE 12.2 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	$\sqrt{-v^2(\partial p/\partial v)_s}$

- 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 flow rate the greater the need to use the exergy of the stream effectively.

Discussion of means for improving thermodynamic effectiveness also is provided by Bejan et al. (1996) and Moran and Tsatsaronis (2000).

12.3 Property Relations and Data

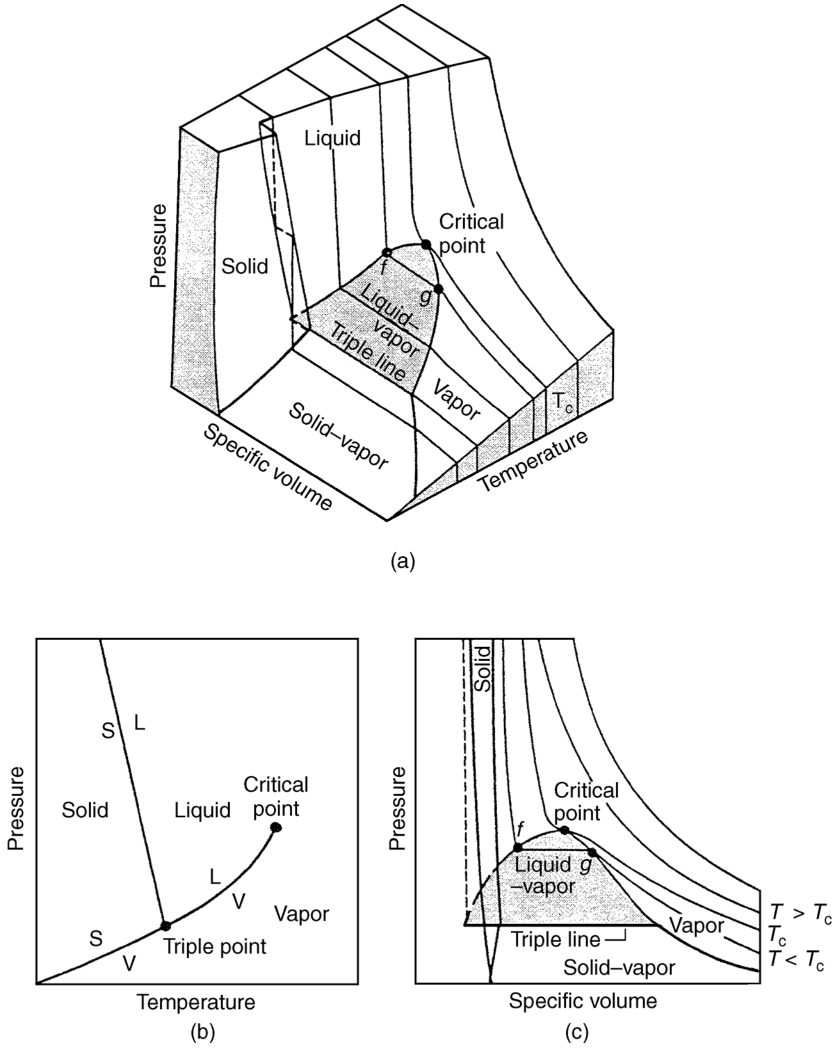
Engineering thermodynamics uses a wide assortment of thermodynamic properties and relations among these properties. Table 12.2 lists several commonly encountered properties. Pressure, temperature, and specific volume can be found experimentally. Specific internal energy, entropy, and enthalpy are among 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.

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 Engineers (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 also are retrievable from various commercial online data bases. Computer software increasingly is available for this purpose as well.

P-v-T Surface

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 graphical, tabular, and analytical forms. Figure 12.1(a) shows the p-v-T relationship for water. Figure 12.1(b) shows the projection of the *p-v-T surface* onto the pressure-temperature plane, called the *phase diagram*. The projection onto the p-v plane is shown in Fig. 12.1(c).

Figure 12.1(a) 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



(a)

(b)

(c)

FIGURE 12.1 Pressure-specific volume-temperature surface and projections for water (not to scale).

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.

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

$$v = (1-x)v_f + xv_g = v_f + xv_{fg} \tag{12.16a}$$

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

$$u = (1-x)u_f + xu_g = u_f + xu_{fg} \tag{12.16b}$$

$$h = (1-x)h_f + xh_g = h_f + xh_{fg} \tag{12.16c}$$

$$s = (1-x)s_f + xs_g = s_f + xs_{fg} \tag{12.16d}$$

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 (2000).

The sample *steam table data* presented in Table 12.3 are representative of data available for substances commonly encountered in engineering practice. The form of the tables 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 12.3a, 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 must be exercised. The approach followed when composition changes due to chemical reaction is considered in Moran and Shapiro (2000).

Liquid water data (see Table 12.3d) 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:

$$v(T, p) \approx v_f(T) \tag{12.17a}$$

$$u(T, p) \approx u_f(T) \tag{12.17b}$$

$$h(T, p) \approx h_f(T) + v_f[p - p_{\text{sat}}(T)] \tag{12.17c}$$

$$s(T, p) \approx s_f(T) \tag{12.17d}$$

The subscript f denotes the saturated liquid state at the temperature T, and p_{sat} is the corresponding saturation pressure. The underlined term of Eq. (12.17c) is usually negligible, giving $h(T, p) \approx h_f(T)$.

Graphical representations of property data also are commonly used. These include the p-T and p-v diagrams of Fig. 12.1, the T-s diagram of Fig. 12.2, the h-s (Mollier) diagram of Fig. 12.3, and the p-h diagram of Fig. 12.4. 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 Fig. 12.5. 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

$$Z = \frac{p\bar{v}}{\bar{R}T} \tag{12.18}$$

In this expression $\bar{v}$ is the specific volume on a molar basis (m^3/kmol, for example) and $\bar{R}$ is the *universal gas constant* (8314 N · m/kmol · K, for example). The reduced properties are

$$p_R = \frac{p}{p_c}, \qquad T_R = \frac{T}{T_c}, \qquad v'_R = \frac{\bar{v}}{(\bar{R}T_c/p_c)} \tag{12.19}$$

where p_c and T_c denote the critical pressure and temperature, respectively. Values of p_c and T_c are obtainable from the literature—see, for example, Moran and Shapiro (2000). The reduced isotherms of Fig. 12.5 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.

Analytical Equations of State

Considering the isotherms of Fig. 12.5, 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,

$$Z = 1 + \hat{B}(T)p + \hat{C}(T)p^2 + \hat{D}(T)p^3 + \cdots \tag{12.20a}$$

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

$$Z = 1 + \frac{B(T)}{\bar{v}} + \frac{C(T)}{\bar{v}^2} + \frac{D(T)}{\bar{v}^3} + \cdots \tag{12.20b}$$

Such equations of state are known as *virial expansions*, and the coefficients $\hat{B}$, $\hat{C}$, $\hat{D}$ … and B, C, D… 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 the first few coefficients have been calculated 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.

TABLE 12.3 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

(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. 2000. *Fundamentals of Engineering Thermodynamics*, 4th 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.

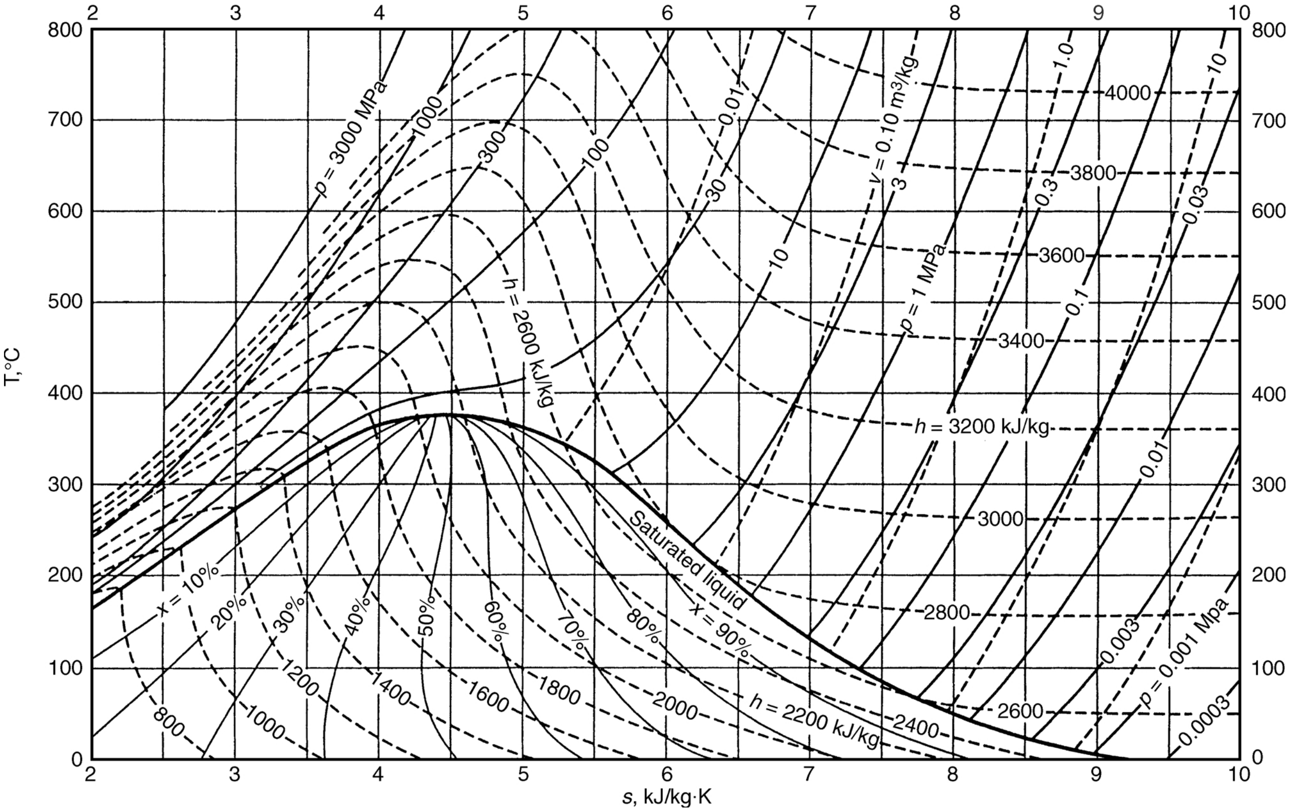


FIGURE 12.2 Temperature-entropy diagram for water. (*Source:* Jones, J.B. and Dugan, R.E. 1996. *Engineering Thermodynamics,* Prentice-Hall, Englewood Cliffs, NJ, based on data and formulations from Haar, L., Gallagher, J.S., and Kell, G.S. 1984. *NBS/NRC Steam Tables.* Hemisphere, Washington, D.C.)

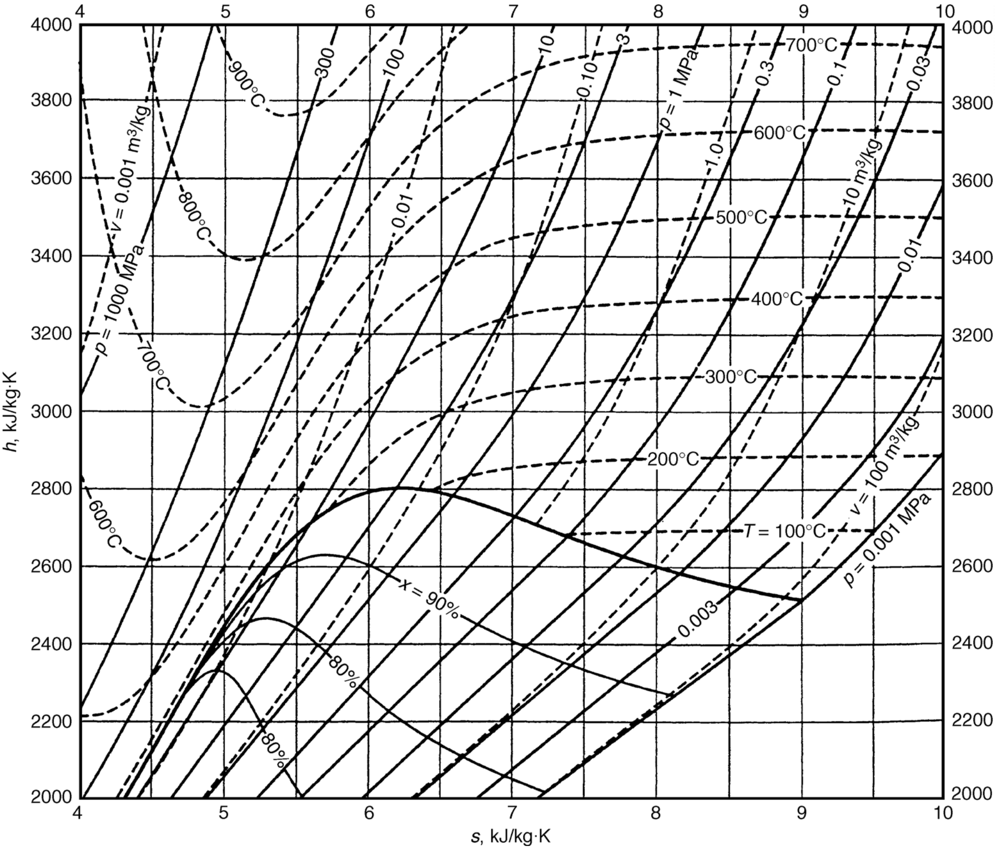


FIGURE 12.3 Enthalpy-entropy (Mollier) diagram for water. (*Source:* Jones, J.B. and Dugan, R.E. 1996. *Engineering Thermodynamics*. Prentice-Hall, Englewood Cliffs, NJ, based on data and formulations from Haar, L., Gallagher, J.S., and Kell, G.S. 1984. *NBS/NRC Steam Tables*. Hemisphere, Washington, D.C.)

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. For further discussion of equations of state see Reid and Sherwood (1966) and Reid et al. (1987).

Ideal Gas Model

Inspection of the generalized compressibility chart, Fig. 12.5, 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 $Z = 1$—i.e.,

$$p\bar{v} = \bar{R}T \qquad \text{or} \qquad pv = RT \tag{12.21a}$$

Other forms of this expression in common use are

$$pV = n\bar{R}T, \qquad pV = mRT \tag{12.21b}$$

In these equations, $n = m/\mathcal{M}$, $\bar{v} = \mathcal{M}v$, and the *specific gas constant* is $R = \bar{R}/\mathcal{M}$, where $\mathcal{M}$ denotes the molecular weight.

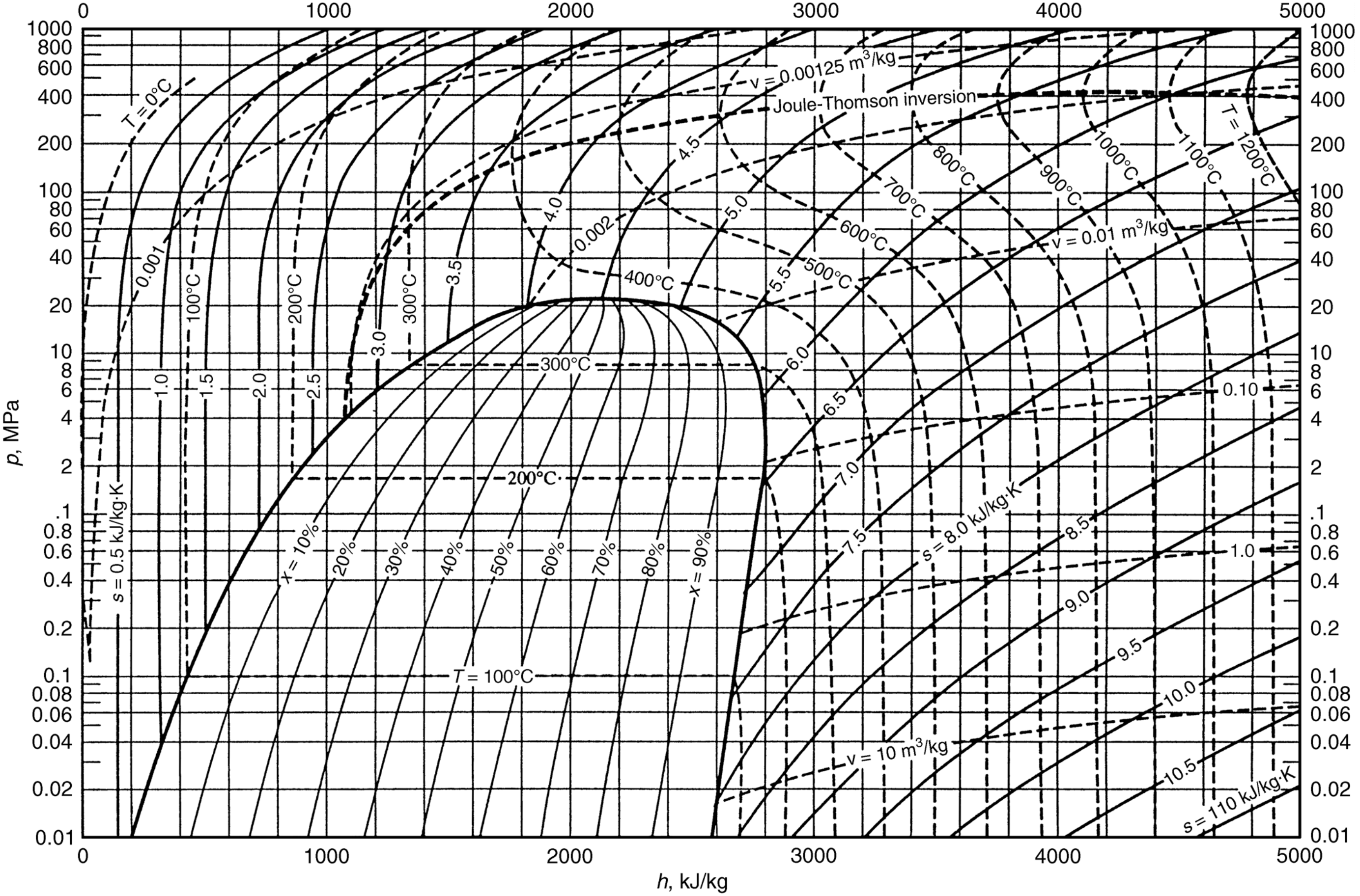


FIGURE 12.4 Pressure-enthalpy diagram for water. (*Source:* Jones, J.B. and Dugan, R.E. 1996. *Engineering Thermodynamics.* Prentice-Hall, Englewood Cliffs, NJ, based on data and formulations from Haar, L., Gallagher, J.S., and Kell, G.S. 1984. *NBS/NRC Steam Tables.* Hemisphere, Washington, D.C.)

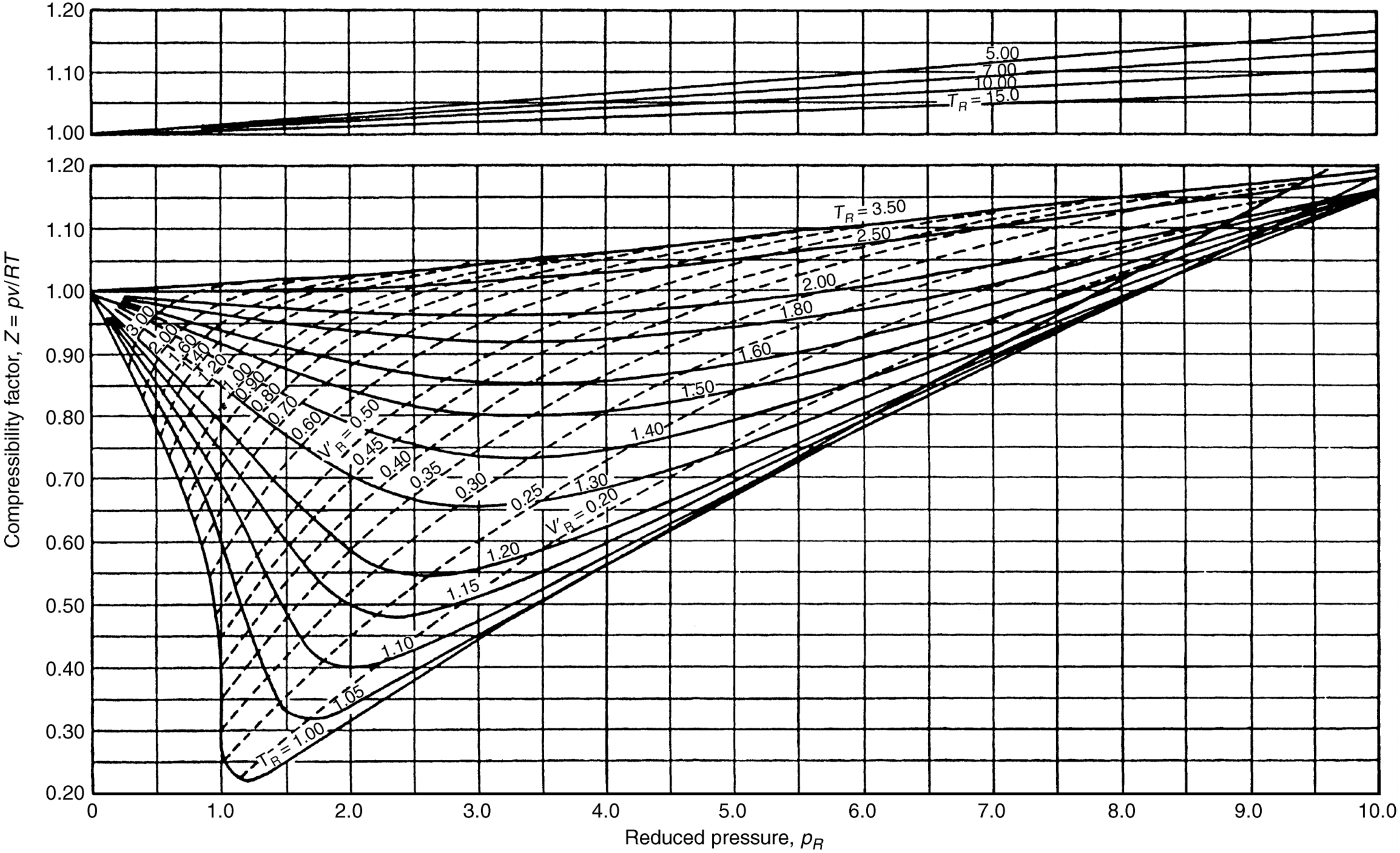


FIGURE 12.5 Generalized compressibility chart ($T_R = T/T_c$, $p_R = p/p_c$, $v'_R = \bar{v}p_c/\bar{R}T_c$) for $p_R \le 10$. (*Source:* Obert, E.F. 1960 *Concepts of Thermodynamics.* McGraw-Hill, New York.)

TABLE 12.4 Ideal Gas Expressions for Δh, Δu, and Δs

Variable Specific Heats		Constant Specific Heats[b]	
$h(T_2) - h(T_1) = \int_{T_1}^{T_2} c_p(T)\,dT$	(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)[a]	$s(T_2, p_2) - s(T_1, p_1) = c_p \ln\frac{T_2}{T_1} - R\ln\frac{p_2}{p_1}$	(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)	$\frac{T_2}{T_1} = \left(\frac{v_2}{v_1}\right)^{k-1}$	(6′)

[a] Alternatively, $s(T_2,p_2) - s(T_1,p_1) = s^\circ(T_2) - s^\circ(T_1) - R\ln\frac{p_2}{p_1}$.

[b] c_p and c_v are average values over the temperature interval from T_1 to T_2.

It can be shown that $(\partial u/\partial v)_T$ vanishes identically for a gas whose equation of state is exactly given by Eq. (12.21), 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.

The above considerations allow for an *ideal gas model* of each real gas: (1) the equation of state is given by Eq. (12.21) and (2) the internal energy, enthalpy, and specific heats (Table 12.2) 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 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. The following ideal gas-specific heat relations are frequently useful:

$$c_p(T) = c_v(T) + R \tag{12.22a}$$

$$c_p = \frac{kR}{k-1}, \qquad c_v = \frac{R}{k-1} \tag{12.22b}$$

where $k = c_p/c_v$.

For processes of an ideal gas between states 1 and 2, Table 12.4 gives expressions for evaluating the changes in specific enthalpy, Δh, specific entropy, Δs, and specific internal energy, Δu. Relations also are provided for processes of an ideal gas between states having the same specific entropy: $s_2 = s_1$. Property relations and data required by the expressions of Table 12.4: h, u, c_p, c_v, p_r, v_r, and s° are obtainable from the literature—see, for example, Moran and Shapiro (2000).

12.4 Vapor and Gas Power Cycles

Vapor and gas power systems develop electrical or mechanical power from 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 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 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 frequently is useful in gauging how changes in major operating parameters might affect actual performance. Elementary thermodynamic models also can provide simple settings to assess, at least approximately, the advantages and disadvantages of features proposed to improve thermodynamic performance.

Work and Heat Transfer in Internally Reversible Processes

Expressions giving work and heat transfer in internally reversible processes are useful in describing the themodynamic performance of vapor and gas cycles. Important special cases are presented in the discussion to follow. 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 internal expansion processes. However, for an internally reversible process p is not only the pressure at the moving boundary but also the pressure throughout the 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 per unit of system mass is

$$\left(\frac{W}{m}\right)_{\substack{\text{int}\\\text{rev}}} = \int_1^2 p\,dv \tag{12.23}$$

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 Fig. 12.6.

For one-inlet, one-exit control volumes in the absence of internal irreversibilities, the following expression gives the work developed per unit of mass flowing:

$$\left(\frac{\dot{W}}{\dot{m}}\right)_{\substack{\text{int}\\\text{rev}}} = -\int_i^e v\,dp + \frac{\mathrm{v}_i^2 - \mathrm{v}_e^2}{2} + g(z_i - z_e) \tag{12.24a}$$

where the integral is performed from inlet to exit (see Moran and Shapiro (2000) for discussion). If there is no significant change in kinetic or potential energy from inlet to exit, Eq. (12.24a) reads

$$\left(\frac{\dot{W}}{\dot{m}}\right)_{\substack{\text{int}\\\text{rev}}} = -\int_i^e v\,dp \quad (\Delta ke = \Delta pe = 0) \tag{12.24b}$$

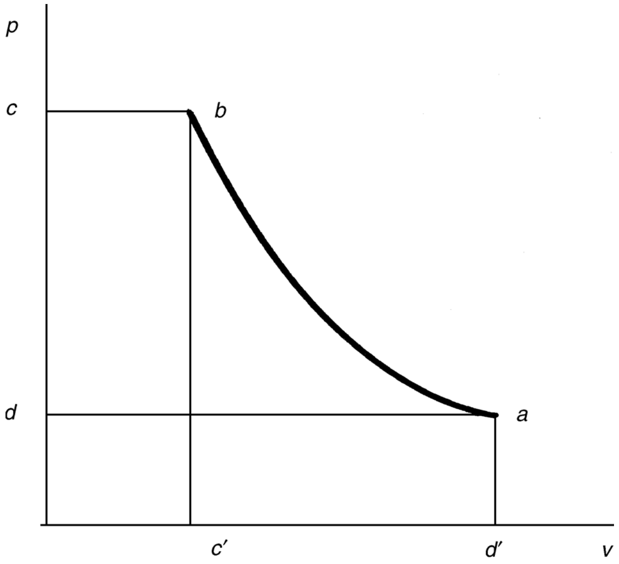


FIGURE 12.6 Internally reversible process on p-v coordinates.

The specific volume remains approximately constant in many applications with liquids. Then Eq. (12.24b) becomes

$$\left(\frac{\dot{W}}{\dot{m}}\right)_{\substack{\text{int}\\\text{rev}}} = -v(p_e - p_i) \quad (v = \text{constant}) \tag{12.24c}$$

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 pressure vs. specific volume, as shown in Fig. 12.6, the magnitude of the integral $\int v dp$ of Eqs. (12.24a) and (12.24b) is represented by the area a-b-c-d *behind* the curve.

For an internally reversible process of a closed system between state 1 and state 2, the heat transfer per unit of system mass is

$$\left(\frac{Q}{m}\right)_{\substack{\text{int}\\\text{rev}}} = \int_1^2 T\,ds \tag{12.25}$$

For a one-inlet, one-exit control volume in the absence of internal irreversibilities, the following expression gives the heat transfer per unit of mass flowing from inlet i to exit e:

$$\left(\frac{\dot{Q}}{\dot{m}}\right)_{\substack{\text{int}\\\text{rev}}} = \int_i^e T\,ds \tag{12.26}$$

When any such 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 mass.

Polytropic Processes

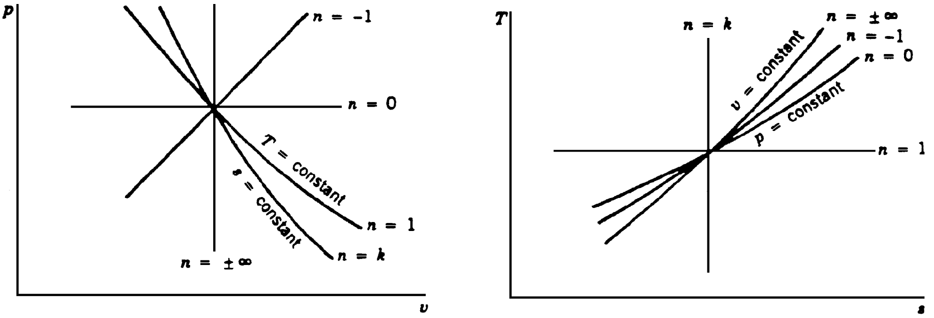
An internally reversible process described by the expression pv^n = constant is called a *polytropic process* and n is the *polytropic exponent*. In certain applications n can be obtained by fitting pressure-specific volume data. Although this expression can be applied when real gases are considered, it most generally appears in practice together with the use of the ideal gas model. Table 12.5 provides several expressions applicable to polytropic processes and the special forms they take when the ideal gas model is assumed. The expressions for $\int p dv$ and $\int v dp$ have application to work evaluations with Eqs. (12.23) and (12.24), respectively.

TABLE 12.5 Polytropic Processes: $pv^n = \text{Constant}$[a]

General		Ideal Gas[b]	
$\frac{p_2}{p_1} = \left(\frac{v_2}{v_1}\right)^n$	(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	
$n = 1$		$n = 1$	
$\int_1^2 p\,dv = p_1 v_1 \ln\frac{v_2}{v_1}$	(2)	$\int_1^2 p\,dv = RT\ln\frac{v_2}{v_1}$	(2′)
$-\int_1^2 v\,dp = -p_1 v_1 \ln\frac{p_2}{p_1}$	(3)	$-\int_1^2 v\,dp = -RT\ln\frac{p_2}{p_1}$	(3′)
$n \neq 1$		$n \neq 1$	
$\int_1^2 p\,dv = \frac{p_2 v_2 - p_1 v_1}{1-n}$ $= \frac{p_1 v_1}{n-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{(n-1)/n}\right]$	(4)	$\int_1^2 p\,dv = \frac{R(T_2 - T_1)}{1-n}$ $= \frac{RT_1}{n-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{(n-1)/n}\right]$	(4′)
$-\int_1^2 v\,dp = \frac{n}{1-n}(p_2 v_2 - p_1 v_1)$ $= \frac{np_1 v_1}{n-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{(n-1)/n}\right]$	(5)	$-\int_1^2 v\,dp = \frac{nR}{1-n}(T_2 - T_1)$ $= \frac{nRT_1}{n-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{(n-1)/n}\right]$	(5′)

[a] For polytropic processes of closed systems where volume change is the only work mode, Eqs. (2), (4), and (2′), (4′) are applicable with Eq. (12.23) 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, Eqs. (3), (5), and (3′), (5′) are applicable with Eqs. (12.24a) and (12.24b) to evaluate the power. Also note that generally, $-\int_1^2 v\,dp = n\int_1^2 p\,dv$.

[b]

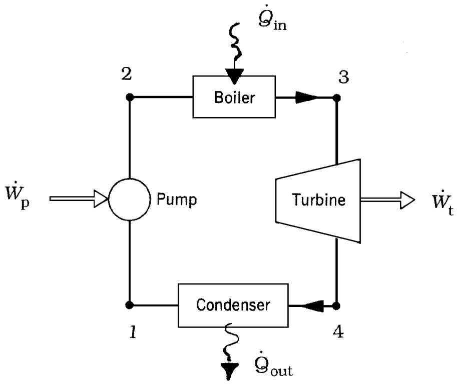


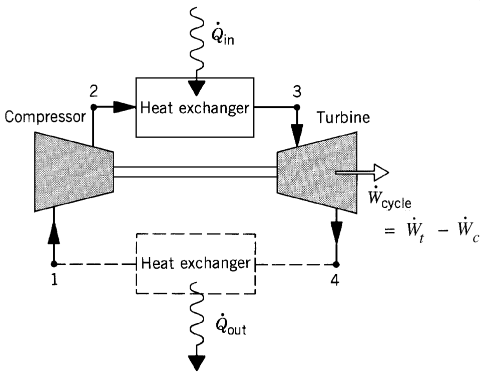
Rankine and Brayton Cycles

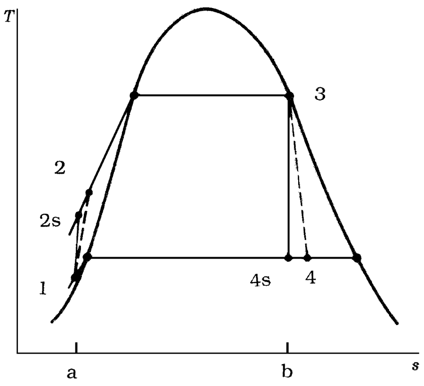
In their simplest embodiments vapor power and gas turbine power plants are represented conventionally in terms of four components in series, forming, respectively, the *Rankine cycle* and the *Brayton cycle* shown schematically in Table 12.6. The thermodynamically ideal counterparts of these cycles are composed of four internally reversible processes in series: two isentropic processes alternated with two constant pressure processes. Table 12.6 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 Eq. (12.26) 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

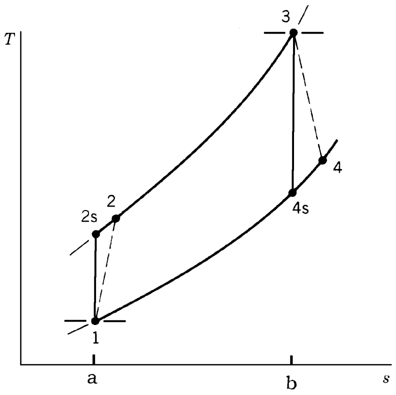
TABLE 12.6 Rankine and Brayton Cycles

Rankine Cycle	Brayton Cycle









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

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

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

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

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 12.6 are provided by Eqs. (1) to (4) of the table. They are obtained by reducing Eq. (12.10a) with the assumptions of negligible heat loss and negligible changes in kinetic and potential energy from the inlet to the exit of each component. All quantities are positive in the directions of the arrows on the figure.

The thermal efficiency of a power cycle is defined as the ratio of the *net* work developed to the total energy added by heat transfer. Using expressions (1)–(3) of Table 12.6, the thermal efficiency is

$$\begin{aligned}\eta &= \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2} \\ &= 1 - \frac{h_4 - h_1}{h_3 - h_2} \qquad (12.27)\end{aligned}$$

To obtain the thermal efficiency of the ideal cycle, h_{2s} replaces h_2 and h_{4s} replaces h_4 in Eq. (12.27).

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 erosion and wear by liquid droplets on the blades of the Rankine cycle steam turbine, at least 90% steam 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:

$$\text{bwr} = \frac{h_2 - h_1}{h_3 - h_4} \tag{12.28}$$

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 1–2%. 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*. Referring to Table 12.6 for the states, the isentropic turbine efficiency is

$$\eta_t = \frac{h_3 - h_4}{h_3 - h_{4s}} \tag{12.29a}$$

The isentropic compressor efficiency is

$$\eta_c = \frac{h_{2s} - h_1}{h_2 - h_1} \tag{12.29b}$$

In the isentropic pump efficiency, η_p, which takes the same form as Eq. (12.29b), the numerator is frequently approximated via Eq. (12.24c) 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 12.6 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 12.6, 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 12.4 apply generally to air-standard analyses. Equations (1′) to (6′)

of Table 12.4 apply to *cold* air-standard analyses, as does the following expression for the turbine power obtained from Table 12.1 (Eq. (10c″)):

$$\dot{W}_t = \dot{m}\frac{kRT_3}{k-1}[1-(p_4/p_3)^{(k-1)/k}] \tag{12.30}$$

An expression similar in form can be written for the power required by the compressor.

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 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 12.7 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 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

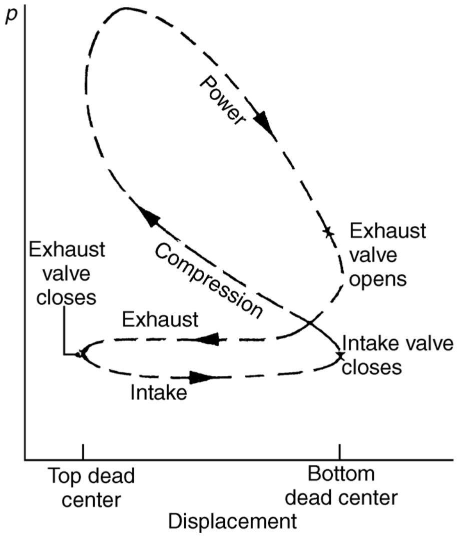


FIGURE 12.7 Pressure-displacement diagram for a reciprocating internal combustion engine.

piston during the power stroke, would produce the same net work as actually developed in one cycle. That is,

$$\text{mep} = \frac{\text{net work for one cycle}}{\text{displacement volume}} \tag{12.31}$$

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 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 12.7.

Reducing the closed system energy balance, Eq. (12.7b), gives the following expressions for work and heat applicable in each case shown in Table 12.7:

$$\frac{W_{12}}{m} = u_1 - u_2, \qquad \frac{W_{34}}{m} = u_3 - u_4, \qquad \frac{Q_{41}}{m} = u_1 - u_4 \tag{12.32}$$

Table 12.7 provides additional expressions for work, heat transfer, and thermal efficiency identified with each case individually. All expressions for work and heat adhere to the respective sign conventions of Eq. (12.7b). Equations (1) to (6) of Table 12.4 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 12.4 apply to cold air-standard analyses, as does Eq. (4′) of Table 12.5, with $n = k$ for the isentropic processes of these cycles.

Referring to Table 12.7, the ratio of specific volumes 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 12.8 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:

$$\eta = 1 - \frac{1}{r^{k-1}}\left[\frac{r_c^k - 1}{k(r_c - 1)}\right] \quad \text{(constant } k\text{)} \tag{12.33}$$

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

TABLE 12.7 Otto, Diesel, and Dual Cycles

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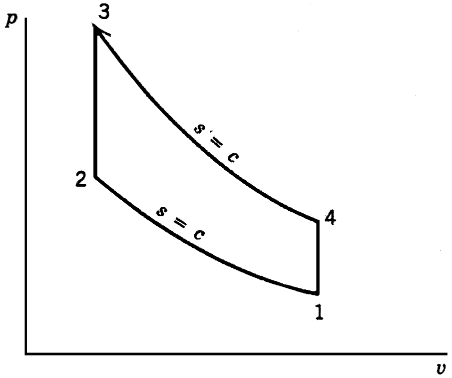
<td>
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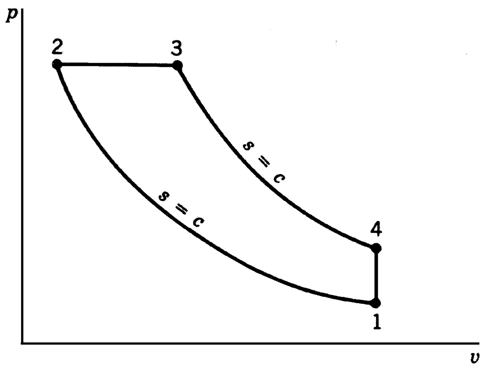
<td>
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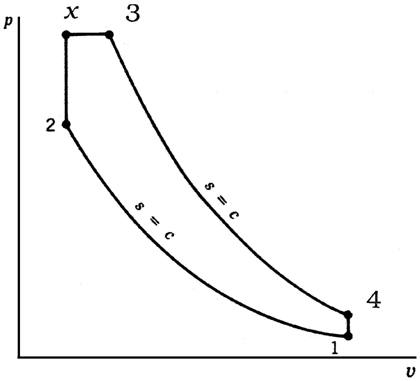
<td>
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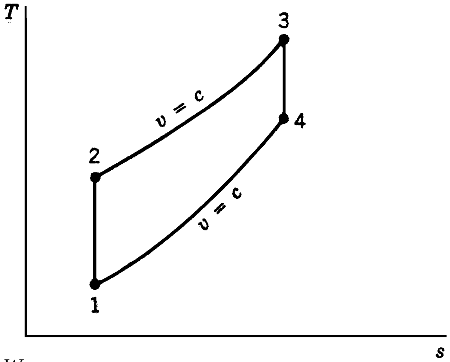
<td>
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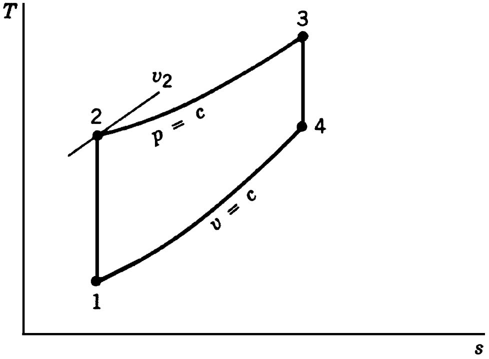
<td>
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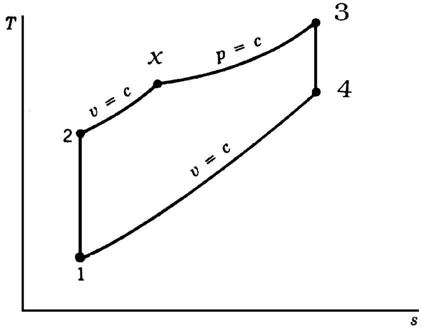
<td>
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$$\frac{W_{23}}{m} = 0$$

$$\frac{Q_{23}}{m} = u_3 - u_2$$

$$\eta = 1 - \frac{u_4 - u_1}{u_3 - u_2}$$

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$$\frac{W_{23}}{m} = p_2(v_3 - v_2)$$

$$\frac{Q_{23}}{m} = h_3 - h_2$$

$$\eta = 1 - \frac{u_4 - u_1}{h_3 - h_2}$$

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$$\frac{W_{2x}}{m} = 0\,, \quad \frac{Q_{2x}}{m} = u_x - u_2$$

$$\frac{W_{x3}}{m} = p_3(v_3 - v_2)\,, \quad \frac{Q_{x3}}{m} = h_3 - h_x$$

$$\eta = 1 - \frac{u_4 - u_1}{(u_x - u_2) + (h_3 - h_x)}$$

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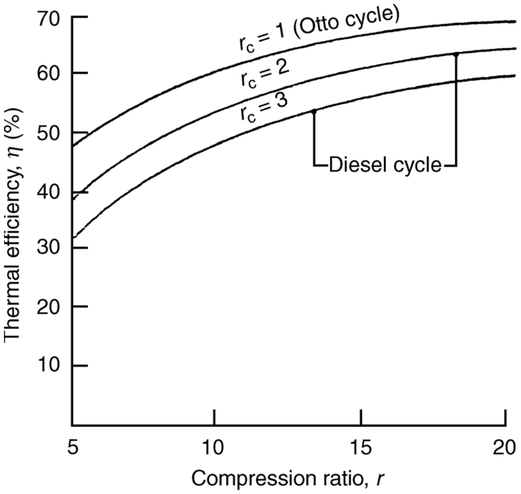

FIGURE 12.8 Thermal efficiency of the cold air-standard Otto and Diesel cycles, $k = 1.4$.

As all processes are internally reversible, areas on the p-v and T-s diagrams of Table 12.7 can be interpreted, respectively, as work and heat transfer. Invoking Eq. (12.23) 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 Eq. (12.25) 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 represents 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.

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