Chapter 2
Overview of Macroscopic Thermal Sciences

This chapter provides a concise description of the basic concepts and theories underlying classical thermodynamics and heat transfer. Different approaches exist in presenting the subject of thermodynamics. Most engineering textbooks first introduce temperature, then discuss energy, work, and heat, and define entropy afterward. Callen developed an axiomatic structure using a simple set of abstract postulates to combine the physical information that is included in the laws of thermodynamics [1]. Continuing the effort pioneered by Keenan and Hatsopoulos [2], Gyftopoulos and Beretta [3] developed a logical sequence to introduce the basic concepts with a rigorous definition of each thermodynamic term. Their book has been a great inspiration to the present author in comprehending and teaching thermodynamics. Here, an overview of classical thermodynamics is provided that is somewhat beyond typical undergraduate textbooks [4, 5]. Details on the historic development of classical thermodynamics can be found from Bejan [6] and Kestin [7], and references therein. The basic phenomena and governing equations in energy, mass, and momentum transfer will be presented subsequently in a self-consistent manner without invoking microscopic theories.

2.1 Fundamentals of Thermodynamics

A *system* is a collection of constituents (whose amounts may be fixed or varied within a specified range) in a defined space (e.g., a container whose volume may be fixed or varied within a specified range), subject to other external forces (such as gravitational and magnetic forces) and constraints. External forces are characterized by *parameters*. An example is the volume of a container, which is a parameter associated with the forces that confine the constituents within a specified space. Everything that is not included in the system is called the *environment* or *surroundings* of the system.

Quantities that characterize the behavior of a system at any instant of time are called *properties* of the system. Properties must be measurable, and their values are independent of the measuring devices. Properties supplement constituents and parameters to fully characterize a system. At any given time, the system is said to be in a *state*, which is fully characterized by the type and amount of constituents, a set of parameters associated with various types of external forces, and a set of properties. Two states are identical if the amount of each type of constituents and values of all the parameters and properties are the same. A system may experience a *spontaneous change of state*, when the change of state does not involve any interaction between the system and its environment. If the system changes its state through interactions with other systems in the environment, it is said to experience an *induced change of state*. If a system can experience only spontaneous changes of state, it is said to be an *isolated system*, that is, the change of state of the system does not affect the environment of the system. The study of the possible and allowed states of a system is called *kinematics*, and the study of the time evolution of the state is called *dynamics*.

The relation that describes the change of state of a system as a function of time is the *equation of motion*. In practice, the complete equations of motion are often not known. Therefore, in thermodynamics, the description of the change of state is usually given in terms of the end states (i.e., the initial and final states) and the *modes of interaction* (for example, work and heat, which are discussed later). The end states and the modes of interaction specify a *process*. A spontaneous change of state is also called a *spontaneous process*. A process is *reversible* if there is at least one way to restore both the system and its environment to their initial states. Otherwise, the process is *irreversible*; i.e., it is not possible to restore both the system and its environment to their initial states. A *steady state* is one that does not change as a function of time despite interactions between the system and other systems in the environment.

2.1.1 The First Law of Thermodynamics

Energy is a property of every system in any state. The first law of thermodynamics states that *energy can be transferred to or from a system but can be neither created nor destroyed*. The energy balance for a system can be expressed as

$$\Delta E = E_2 - E_1 = E_{net,in} \tag{2.1a}$$

where Δ denotes a finite change, subscripts 1 and 2 refer to the initial and final states, respectively, and $E_{net,in} = E_{in} - E_{out}$ is the net amount of energy transferred into the system. For an infinitesimal change, the differential form of the energy balance is

$$dE = \delta E_{net,in} \tag{2.1b}$$

Here, d is used to signify a differential change of the property of a system, and δ is used to specify a differentially small quantity that is not a property of any system. Clearly, the energy of an isolated system is conserved. Energy is an additive property, i.e., the energy of a composite system is the sum of the energies of all individual subsystems. Examples are kinetic energy and potential energy, as defined in classical mechanics, and internal energy, which will be discussed later. A similar expression for mass balance can also be written.

The term *mechanical effect* is used for the kind of processes described in mechanics, such as the change of the height of a weight in a gravitational field, the change of the relative positions of two charged particles, the change of the velocity of a point mass, the change of the length of a spring, or a combination of such changes. All mechanical effects are equivalent in the sense that it is always possible to arrange forces and processes that annul all the mechanical effects except one that we choose. It is common to choose the rise and fall of a weight in a gravity field to represent this kind of process.

A *cyclic process* (also called a *cycle*) is one with identical initial and final states. A *perpetual-motion machine of the first kind* (PMM1) is any device (or system) undergoing a cyclic process that produces no external effects but the rise or fall of a weight in a gravity field. A PMM1 violates the first law of thermodynamics, and hence, it is impossible to build a PMM1. Perpetual motion, however, may exist as long as it produces zero net external effect. Examples of perpetual motion are a lossless oscillating pendulum, an electric current through a superconducting coil, and so forth.

2.1.2 Thermodynamic Equilibrium and the Second Law

An *equilibrium* state is a state that cannot change spontaneously with time. There are different types of equilibrium: unstable, stable, and metastable. A *stable-equilibrium state* is a state that cannot be altered to a different state without leaving any net effect on the environment. In the following, a stable-equilibrium state is frequently referred to as a state at *thermodynamic equilibrium*.

The *stable-equilibrium-state principle*, or *state principle*, can be phrased as follows: *Among all states of a system with a given set of values of energy*, *parameters*, *and constituents*, *there exists one and only one stable-equilibrium state*. In other words, in a stable-equilibrium state, all properties are uniquely determined by the amount of energy, the value of each parameter, and the amount of each type of constituents. This principle is an integral part of the second law of thermodynamics [2, 3, 7]. It is important for the thermodynamic definition of temperature and the derivation of thermodynamic relations in stable-equilibrium states. Another aspect of the second law of thermodynamics is the definition of an important property, called *entropy*, as discussed next.

Entropy is an additive property of every system in any state. The second law of thermodynamics asserts that, *in an isolated system*, *entropy cannot be destroyed* but

can either be created (in an irreversible process) or remain the same (in a reversible process). The entropy produced as time evolves during an irreversible process is called the *entropy generation* (S_{gen}) due to *irreversibility*. Like energy, entropy can be transferred from one system to another. One can write the entropy balance as follows (keeping in mind that entropy generation must not be negative):

$$\Delta S = S_2 - S_1 = S_{net,in} + S_{gen} , \quad \text{with } S_{gen} \geq 0 \tag{2.2a}$$

or

$$dS = \delta S_{net,in} + \delta S_{gen} , \quad \text{with } \delta S_{gen} \geq 0 \tag{2.2b}$$

Here again, δ is used to indicate an infinitesimal quantity that is *not* a property of any system. For a system with fixed values of energy (E), parameters, and constituents, the entropy of the system is the largest in the stable-equilibrium state. This is *the highest entropy principle*. Applying this principle to an isolated system for which the energy is conserved, the entropy of the system will increase until a thermodynamic equilibrium is reached. Spontaneous changes of state are usually irreversible and accompanied by entropy generation.

The second law of thermodynamics can be summarized with the following three statements: (1) There exists a unique stable-equilibrium state for any system with given values of energy, parameters, and constituents. (2) Entropy is an additive property, and for an isolated system, the entropy change must be nonnegative. (3) Among all states with the same values of energy, parameters, and constituents, the entropy of the stable-equilibrium state is the maximum.

The energy of a system with volume (V) as its only parameter (neglecting other external forces) is called the *internal energy* (U). The state principle implies that there are $r + 2$ (where r is the number of different constituents) independent variables that fully characterize a stable-equilibrium state of such a system. Therefore, in a stable-equilibrium state, all properties are functions of $r + 2$ independent variables. Since entropy is a property of the system, we have

$$S = S(U, V, N_1, N_2, \ldots, N_r) \tag{2.3}$$

where N_i is the number of particles of the ith species (or type of constituents). This function is continuous and differentiable [1, 3], and furthermore, it is a monotonically increasing function of energy for fixed values of V and $N_{j's}$. Equation (2.3) can be uniquely solved for U so that

$$U = U(S, V, N_1, N_2, \ldots, N_r) \tag{2.4}$$

which is also continuous and admits partial derivatives of all orders. Each first-order partial derivative of Eqs. (2.3) or (2.4) represents a property of the stable-equilibrium state. For example, *temperature* and *pressure* are properties of a system at thermodynamic equilibrium. The (absolute) temperature is defined by

$$T = \left(\frac{\partial U}{\partial S}\right)_{V, N_{j's}} \tag{2.5a}$$

and the pressure is defined by

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S, N_{j's}} \tag{2.5b}$$

The partial derivative with respect to the ith type of constituents defines its chemical potential of that species,

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S, V, N_{j's}(j \neq i)} \tag{2.5c}$$

Equation (2.3) or (2.4) is called the *fundamental relation* for states at thermodynamic equilibrium. The differential form of Eq. (2.4) is the Gibbs relation:

$$dU = T dS - P dV + \sum_{i=1}^{r} \mu_i dN_i \tag{2.6}$$

where Eqs. (2.5a, 2.5b and 2.5c) have been used. The above equation may be rearranged into the form

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum_{i=1}^{r} \frac{\mu_i}{T} dN_i \tag{2.7}$$

Therefore,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V, N_{j's}}, \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U, N_{j's}}, \text{ and } \frac{\mu_i}{T} = -\left(\frac{\partial S}{\partial N_i}\right)_{U, V, N_{j's}(j \neq i)} \tag{2.8}$$

An interaction between two systems that results in a transfer of energy without net exchanges of entropy and constituents is called a *work interaction*. The amount of energy transferred in such an interaction is called *work* (W). An interaction that has only mechanical effects is a work interaction, but a work interaction may involve nonmechanical effects. A process that involves only work interaction is called an *adiabatic* process. Another kind of a typical interaction is *heat interaction*, in which both energy and entropy are transferred without net exchanges of constituents and parameters between two systems. The amount of energy transferred in a heat interaction is called *heat* (Q). Furthermore, the amount of entropy transferred (δS) is equal to the amount of energy transferred (δQ) divided by the boundary temperature (T_b) at which the heat interaction happens, i.e., $\delta S = \delta Q / T_b$. If a system cannot exchange constituents with other systems, it is said to be a *closed* system; otherwise, it is an *open* system.

Reversible processes are considered as the limiting cases of real processes, which are always accompanied by a certain amount of irreversibility. Such an ideal process is called a *quasi-equilibrium* (or *quasi-static*) process, in which each stage can be made as close to thermodynamic equilibrium as possible if the movement is frictionless and very slow. In an ideal process, a finite amount of heat can be transferred reversibly from one system to another at a constant temperature. In practice, heat transfer can only happen when there is a temperature difference, and the process is always irreversible.

A *perpetual-motion machine of the second kind* (PMM2) is a cyclic device that interacts with a system at thermodynamic equilibrium and produces no external effect other than the rise of a weight in a gravity field, without changing the value of any parameter or the amount of any constituent of the system. Historically, there exist different statements of the second law of thermodynamics: The Kelvin–Planck statement of the second law is that *it is impossible to build a* PMM2. The Clausius statement of the second law is that *it is not possible to construct a cyclic machine that will produce no effect other than the transfer of heat from a system at lower temperature to a system at higher temperature*. These statements can be proved using the three statements of the second law of thermodynamics given earlier in this chapter.

Example 2.1 *Criteria for thermodynamic equilibrium*. Consider a moveable piston (adiabatic and impermeable to matter) that separates a cylinder into two compartments (systems A and B), as shown in Fig. 2.1. We learned from mechanics that a mechanical equilibrium requires a balance of forces on both sides of the piston, that is to say, the pressure of system A must be the same as that of system B (i.e., $P_A = P_B$). If the piston wall is made of materials that are diathermal (allowing heat transfer) and permeable to all species, under what conditions will the composite system C consisting of systems A and B be at stable equilibrium?

Solution Assume system C is isolated from other systems, and each of the subsystems A and B is at a thermodynamic equilibrium state, whose properties are solely determined by its internal energy, volume, and amount of constituents: U_A, V_A, $N_{j's,A}$ and U_B, V_B, $N_{j's,B}$, respectively. There exist neighboring states for both subsystems with small differences in U, V, and $N_{j's}$, but the values of the composite system must be conserved, i.e., $dU_A = -dU_B, dV_A = -dV_B,$

Fig. 2.1 Illustration of two systems that may exchange work, heat, and species
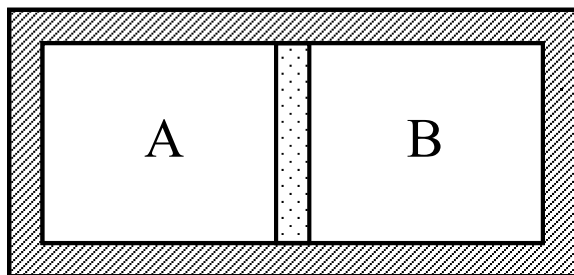
and $dN_{i,A} = -dN_{i,B}$ ($i = 1, 2, \dots r$). The differential entropy of system C can be expressed as

$$dS_C = dS_A + dS_B$$

$$= \frac{1}{T_A}dU_A - \frac{P_A}{T_A}dV_A + \sum_{i=1}^{r}\frac{\mu_{i,A}}{T_A}dN_{i,A} + \frac{1}{T_B}dU_B - \frac{P_B}{T_B}dV_B$$

$$+ \sum_{i=1}^{r}\frac{\mu_{i,B}}{T_B}dN_{i,B}$$

$$= \left(\frac{1}{T_A} - \frac{1}{T_B}\right)dU_A - \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)dV_A + \sum_{i=1}^{r}\left(\frac{\mu_{i,A}}{T_A} - \frac{\mu_{i,B}}{T_B}\right)dN_{i,A} \quad (2.9)$$

If system C is in a stable-equilibrium state, its entropy is maximum and $dS_C = 0$. Since the values of dU_A, dV_A, and $dN_{i,A}$ are arbitrary, we must have

$$\frac{1}{T_A} = \frac{1}{T_B}, \; \frac{P_A}{T_A} = \frac{P_B}{T_B} \text{ and } \frac{\mu_{i,A}}{T_A} = \frac{\mu_{i,B}}{T_B} \; (i = 1, 2, \dots r)$$

or

$$T_A = T_B, \; P_A = P_B \text{ and } \mu_{i,A} = \mu_{i,B} \; (i = 1, 2, \dots r) \quad (2.10)$$

These conditions correspond to thermal equilibrium, mechanical equilibrium, and chemical equilibrium, respectively. The combination forms the criteria for thermodynamic equilibrium.

Discussion. In the case when the piston is diathermal but rigid and impermeable to matter, the entropy change of system C must be nonnegative, that is,

$$dS_C = dS_A + dS_B = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)dU_A \geq 0 \quad (2.11)$$

The above expression implies that $dU_A \leq 0$ for $T_A > T_B$, and $dU_A \geq 0$ for $T_A < T_B$. Spontaneous heat transfer can occur only from regions of higher temperature to regions of lower temperature. This essentially proves the Clausius statement of the second law of thermodynamics.

The concept of thermal equilibrium provides the physical foundation for *thermometry*, which is the science of temperature measurement. The temperature of a system at a thermodynamic equilibrium state is measured through changes in resistance, length, volume, or other physical parameters of the sensing element used in the thermometer, which is brought to thermal equilibrium with the system. Based on the inclusive statement of the second law of thermodynamics given previously, it can be inferred that two systems are in thermal equilibrium with each other if they are separately in thermal equilibrium with a third system. This is sometimes referred to as the *zeroth law of thermodynamics* [6], especially in the thermometry literature.

Table 2.1 Two-phase points and the triple point of water

	Temperature	
	(K)	(°C)
Ice point[a]	273.15	0
Triple point[b]	273.16	0.01
Steam point[c]	373.124	99.974

[a]Solid and liquid phases are in equilibrium at a pressure of 1 atm (101.325 kPa)
[b]Solid, liquid, and vapor phases are in equilibrium
[c]Liquid and vapor phases are in equilibrium at 1 atm

The International Temperature Scale of 1990 (ITS-90) was adopted by the International Committee of Weights and Measures in 1989 [8]. The unit of thermodynamic temperature is kelvin (K), which is defined as 1/273.16 of the thermodynamic temperature of the triple point of water. The Celsius temperature is defined as the difference in the thermodynamic temperature and 273.15 K (the ice point). A difference in temperature may be expressed in either kelvins or degrees Celsius (°C). Although earlier attempts were made to define a temperature scale consistent with the original Celsius temperature scale (i.e., 0 °C for the ice point and 100 °C for the steam point), a 0.026 °C departure arose from more accurate measurements of the steam point, as shown in Table 2.1 [9]. The steam point is therefore no longer used as a defining fixed point in the ITS-90. More accurate Steam Tables were developed in the 1990s.

The ITS-90 defines 17 fixed points, which are determined by primary thermometry with standard uncertainties less than 0.002 K below 303 K and up to 0.05 K at the freezing point of copper (≈1358 K). Cryogenic thermometry is essentially based on ideal gas thermometers (up to about 20 K). Platinum resistance thermometers, calibrated at specified sets of fixed points, are used to define the temperature scale from the triple point of hydrogen (≈13.8 K) to the freezing point of silver (≈1235 K). Platinum resistance thermometers have been chosen because of their excellent reproducibility, even though they are not primary thermometers. Radiation thermometers based on Planck's law of thermal radiation are used to define the temperature scale above 1235 K.

It should be noted that the International System of Units (SI) is currently under revision, and the SI units are being redefined based on the fundamental constants without using any materials or prototypes, as documented in the 26th meeting of the General Conference on Weights and Measures (CGPM) [10].

### 2.1.3 The Third Law of Thermodynamics

For each given set of values of constituents and parameters, there exists a unique stable-equilibrium state with *zero absolute temperature* (though not physically attainable). Furthermore, the entropy of any pure substance (in the form of a crystalline

solid) vanishes at this state (zero absolute entropy). This is the third law of thermodynamics, also called *the Nernst theorem* after Walther Nernst who received the Nobel Prize in Chemistry in 1920. The energy is the lowest at this state, which is called the *ground-state energy* ($E_g > 0$). The ground-state energy of a system consisting of independent particles may be related to its mass (m) using the relativistic theory, i.e., $E_g = mc^2$, where c is the speed of light. Although absolute energy and entropy can be defined according to the third law of thermodynamics, in practice, reference states are often chosen so that the relative values of energy and entropy can be tabulated with respect to those of the reference states.

After reviewing the laws of thermodynamics, it is instructive to give a pictorial presentation to illustrate some of the fundamental concepts in thermodynamics as done by Gyftopoulos and Beretta [3]. For a system that contains a single type of constituents (i.e., pure substance) with fixed values of parameters and amount of constituents, the stable-equilibrium states can be represented as a *convex E–S curve*, whose slope $T = \partial E/\partial S$ defines the temperature of each state on the curve, as shown in Fig. 2.2. The stable-equilibrium-state curve intersects the vertical axis at the ground state, whose energy is the ground-state energy (E_g) and whose absolute entropy is zero. Furthermore, the temperature at the ground state is 0 K. This provides a graphical illustration of the third law of thermodynamics. Along the stable-equilibrium-state curve, temperature increases with increasing energy or entropy. The vertical axis above E_g represents *zero-entropy states*, which are not at stable equilibrium (except when $E = E_g$). These are states defined in mechanics, where entropy is not a concern. A spontaneous change of state can be illustrated with this graph as a horizontal line, e.g., from A_1 to A_{10}, where A_{10} corresponds to the stable-equilibrium state that has the same values of energy, parameters, and constituents as those of A_1. No states exist below the stable-equilibrium-state curve because this would violate the highest entropy principle. Each point in the shaded area may correspond to some

Fig. 2.2 The *E–S* graph for a pure substance with fixed values of parameters and amount of constituents
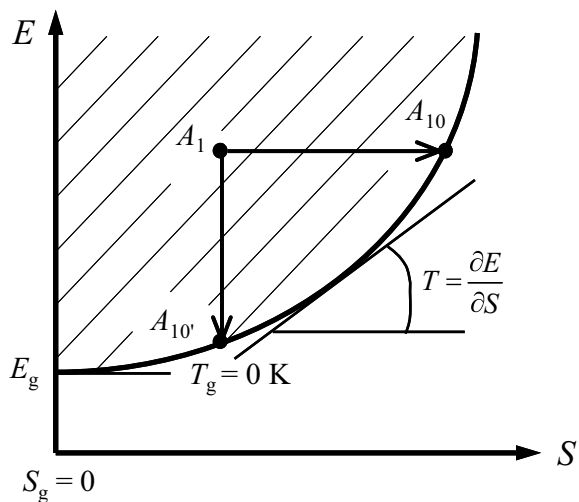
states that are not at thermodynamic equilibrium, for which macroscopic properties (such as temperature and pressure) may not be rigorously defined. A nonequilibrium state in general cannot be uniquely determined by the values of its energy (or entropy) and parameters and the amount of constituents. The *lowest energy principle* is expressed as follows: Among all states with the same values of entropy and parameters and the amount of constituents, there exists a stable-equilibrium state whose energy is the lowest. Starting with any state that is not at stable equilibrium, there exists a reversible adiabatic process, in which work can be done by the system until it reaches a stable-equilibrium state. This process is illustrated in the $E - S$ graph by a vertical line from A_1 to $A_{10'}$. The corresponding work, which is equal to the energy difference between A_1 and $A_{10'}$, is called the *adiabatic availability* [3]. It defines the largest amount of work that can be extracted from a system without any other net effect on the environment of the system.

2.2 Thermodynamic Functions and Properties

Several additional properties defined in this section are important in the study of states at thermodynamic equilibrium. The functional relations are derived based on the fundamental relation and are useful under specific circumstances. The phase equilibrium is summarized with an emphasis on pure substances. The concepts of specific heat and latent heat are then introduced. Combining the specific heat and the equation of state, we can evaluate the internal energy and entropy for ideal gases and incompressible solids and liquids.

2.2.1 Thermodynamic Relations

When dealing with substances within the container, the volume is a parameter that characterizes external forces, i.e., the interaction between the system and the wall of the container. If the constituents are confined within a surface, then the surface area will be a parameter instead of the volume. Parameters associated with other external forces (such as gravitational and magnetic forces) can also be included, if necessary. For simplicity, we assume that volume is the only parameter of the systems under investigation, unless otherwise specified.

Enthalpy is defined as $H = U + PV$, and thus we have $dH = dU + PdV + VdP$. From Eq. (2.6), we obtain

$$dH = TdS + VdP + \sum_{i=1}^{r} \mu_i dN_i \qquad (2.12a)$$

The significance of Eq. (2.12a) is that enthalpy can be expressed as a function of S, P, and $N_{j's}$,

$$H = H(S, P, N_1, N_2, \ldots, N_r) \tag{2.12b}$$

Furthermore,

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N_{j's}}, V = \left(\frac{\partial H}{\partial P}\right)_{S,N_{j's}}, \text{ and } \mu_i = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_{j's}(j\neq i)} \tag{2.12c}$$

Note that the subscripts in Eq. (2.12c) are different from those in Eqs. (2.5a, 2.5b and 2.5c). Enthalpy $H(S, P, N_{j's})$ is said to be a *characteristic function*, since it allows us to find out all the information about a stable-equilibrium state. A large number of characteristic functions may be defined. Depending on the particular situation and measurements available, it is advantageous to choose the most convenient one. Two other characteristic functions are now introduced. The first one is called *Helmholtz free energy* $A(T, V, N_{j's})$, defined as $A = U - TS$. It follows that

$$dA = -SdT - PdV + \sum_{i=1}^{r} \mu_i dN_i \tag{2.13a}$$

and

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N_{j's}}, P = -\left(\frac{\partial A}{\partial V}\right)_{T,N_{j's}}, \text{ and } \mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j's}(j\neq i)} \tag{2.13b}$$

The second is *Gibbs free energy* $G(T, P, N_{j's})$: $G = U + PV - TS = H - TS = A + PV$. It follows that

$$dG = -SdT + VdP + \sum_{i=1}^{r} \mu_i dN_i \tag{2.14a}$$

and

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N_{j's}}, V = \left(\frac{\partial G}{\partial P}\right)_{T,N_{j's}}, \text{ and } \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j's}(j\neq i)} \tag{2.14b}$$

Characteristic functions supplement the fundamental relation and are very useful in the evaluation of the properties of systems under thermodynamic equilibrium.

In a stable-equilibrium state, T, P, and μ_i ($i = 1, 2, \ldots r$) must be uniform everywhere in the system. If the system is divided into k equal-volume subsystems, the energy, entropy, and the amount of each type of constituents of the system are the sums of these quantities in all subsystems. If the energy and the amount of each type of constituents in every subsystem are the same, then all subsystems are exactly

identical to each other. If this is the case, the system is said to be in a *homogeneous* state; otherwise, it is *heterogeneous*. Examples of homogeneous states are air (which is a mixture of many different kinds of gases) and a well-mixed solution. Examples of heterogeneous states are ice water and water–steam mixture in a boiler.

A system that experiences only homogeneous states is called a *simple system*. In a simple system, T, P, and $\mu_{j's}$ of each subsystem are the same as those of the system itself and independent of k; hence, they are called *intensive properties*. Taking T as an example, we have

$$T\left(\frac{U}{k}, \frac{V}{k}, \frac{N_1}{k}, \frac{N_2}{k}, \dots \frac{N_r}{k}\right) = T(U, V, N_1, N_2, \dots, N_r) \tag{2.15}$$

The left-hand side of Eq. (2.15) is the temperature of the subsystem, while the right-hand side is the temperature of the whole system. Unlike temperature and pressure, properties such as U, S, V, and N of each subsystem are inversely proportional to k:

$$S\left(\frac{U}{k}, \frac{V}{k}, \frac{N_1}{k}, \frac{N_2}{k}, \dots, \frac{N_r}{k}\right) = \frac{1}{k} S(U, V, N_1, N_2, \dots, N_r) \tag{2.16}$$

Properties whose values are proportional to the total amount of constituents are called *extensive properties*. Therefore, U, V, S, and H are extensive properties. Notice that k cannot be arbitrarily large because of the continuum requirement.

The ratio or derivative of two extensive properties is an intensive property, e.g., the density (the ratio of mass to volume) is an intensive property and uniform in a simple system. Note that temperature, pressure, and chemical potentials are derivatives of two extensive properties. The properties T, P, and $\mu_{j's}$ distinguish themselves from other intensive properties in that they are uniform in both homogeneous and heterogeneous states, whereas others may or may not be uniform in a heterogeneous state. A *specific property* is the ratio of an extensive property to the total amount of constituents (expressed as mass, mole, or number). For example, the mass specific enthalpy is the enthalpy per kilogram of the substance. Specific properties are intensive properties.

For simple systems, the Gibbs relation given in Eq. (2.6) can be integrated to obtain

$$U = TS - PV + \sum_{i=1}^{r} \mu_i N_i \tag{2.17}$$

which is the *Euler relation*. By differentiating Eq. (2.17) and then subtracting Eq. (2.6) from it, we obtain the *Gibbs–Duhem relation*:

$$S dT - V dP + \sum_{i=1}^{r} N_i d\mu_i = 0 \tag{2.18}$$

The Euler relation for a system containing only one type of constituents ($r = 1$) is

$$G = U + PV - TS = \mu N$$

or

$$\mu(T, P) = \frac{G}{N} = g(T, P) \tag{2.19}$$

Hence, the chemical potential of a pure substance is nothing but the specific Gibbs free energy. For a system containing two or more types of constituents, Eq. (2.14b) relates the chemical potential to the partial derivative of the Gibbs free energy with respect to N_i for fixed T and P, which is called the *partial* Gibbs free energy of the ith type of constituents.

2.2.2 The Gibbs Phase Rule

In a heterogeneous state, we consider a subdivision of the system into subsystems, each being a simple system. The collection of all subsystems that have the same values of all intensive properties is called a *phase*. Solid, liquid, and gas (or vapor) are the three distinct phases. The boundary between subsystems of different phases is called an *interface*. Different phases may appear to be clearly separated or well mixed. In space, liquid water droplets could be dispersed throughout water vapor, whereas on the earth, the liquid would occupy the lower part of the container due to gravity.

Assume that there are q coexisting phases, called a q-phase heterogeneous state. We can write the Gibbs–Duhem relation for each phase, and thus reduce the independent variables for T, P, μ_i ($i = 1, 2, \ldots r$) by q. The number of independent variables among T, P, μ_i's is determined by the Gibbs phase rule:

$$\phi = r + 2 - q \tag{2.20}$$

For a pure substance, Eq. (2.20) implies that, for a single-phase state, there are only two independent variables among the three intensive properties T, P, and μ. If T and P are chosen as the independent variables, then all other intensive properties are functions of T and P, e.g., specific internal energy $u = u(T, P)$, specific enthalpy $h = h(T, P)$, and specific entropy $s = s(T, P)$. Extensive properties can be determined from the specific properties if the total mass or volume is specified. For a two-phase mixture, such as ice and water or water and steam, only one of T, P, and μ is independent. If T is chosen as the variable, then P and μ can be expressed as functions of T, i.e., $P = P(T)$ and $\mu = \mu(T)$. In order to completely describe the state, however, we will also need to know the amount of constituents in each phase

(which may be expressed by the total mass and a mass fraction x of one phase). For example, the specific entropy of a mixture can be expressed as $s = s(T, x)$ or $s = s(P, x)$. In a three-phase mixture, T, P, and μ are all fixed. For a pure substance, the solid, liquid, and vapor phases can only coexist at fixed temperature and pressure, which are called *triple-point* properties. Taking water as an example, we have $T_{\text{t.p.}} = 0.01 \,°C$ and $P_{\text{t.p.}} = 0.61 \,kPa$. One needs to know the amount of constituents in each phase to completely characterize the state. No more than three phases can coexist for any pure substance. It should be noticed that a substance can have different solid phases, e.g., diamond and graphite are allotropes of carbon but with distinct differences in their physical and chemical properties; silicon dioxide can exist in the forms of crystalline quartz or fused silica (glass).

Figure 2.3 shows regions of solid, liquid, and vapor in a P–T diagram. The S–L, S–V, and L–V lines indicate the coexistence of solid–liquid, solid–vapor, and liquid–vapor phases in thermodynamic equilibrium. The three lines merge to the triple point where all three phases can coexist in thermodynamic equilibrium. There are two S–L lines: the solid line represents a material that expands upon melting, and the dashed line represents a material that contracts upon melting (such as water). There exists a *critical point* or a critical state; the temperature and the pressure at the critical state are called *critical temperature* (T_c) and *critical pressure* (P_c). The distinction between liquid and vapor phases disappears beyond the critical point. This can be seen clearer in the T–v diagram shown in Fig. 2.4. The S–L line in Fig. 2.3 becomes an S–L region in Fig. 2.4; the L–V line becomes a dome, called *the saturation dome*. Starting from a solid state, in a constant pressure (isobaric) heating process with $P_{\text{t.p.}} < P < P_c$, the temperature increases until melting starts. As more energy is added to the system, the fraction of solid decreases, whereas the fraction of liquid increases, at a constant temperature. The amount of heat needed to completely melt a unit mass of solid to liquid is called the *specific latent heat of melting*. Once all the substance is in the liquid phase, the temperature rises again with increasing energy until a saturated liquid state is reached. Hereafter, vaporization occurs at constant

Fig. 2.3 Schematic of a P–T diagram for a pure substance
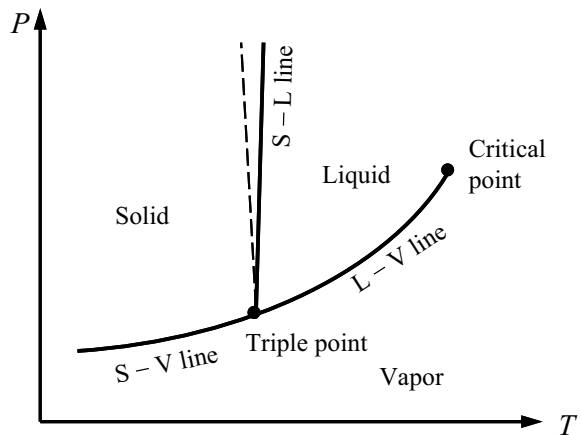
Fig. 2.4 Schematic of a T–v diagram for a material that expands upon melting
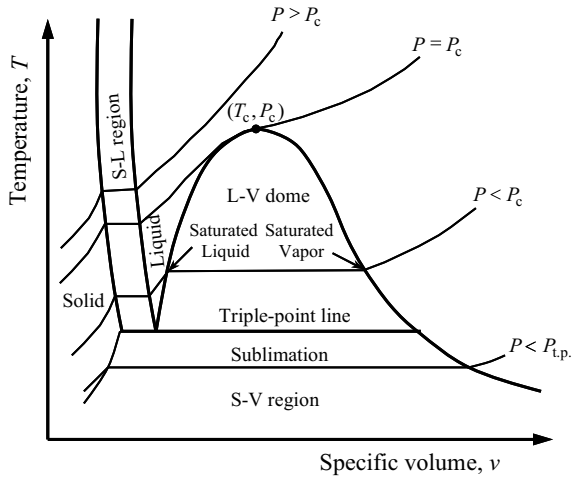
temperature (saturation temperature) until it reaches the right side of the saturation dome, which is a saturated vapor state. The amount of energy needed to vaporize a unit mass of a substance is called the *specific latent heat of vaporization*. When the pressure is higher than the critical pressure, however, no vaporization can happen. The liquid and gas forms of aggregation differ in degree rather than in kind. At a pressure lower than the triple-point pressure, the change from solid to vapor can occur without passing through a liquid phase. Such a process is called sublimation. An example is the sublimation of dry ice into cold CO_2 gas at room temperature and atmospheric pressure. It can be used to create some theatrical effects such as haze, fog, or smoke.

2.2.3 Specific Heats

Specific heats are properties of a system (at stable equilibrium). The *specific heat at constant volume* (c_v) and the *specific heat at constant pressure* (c_p) are defined as

$$c_v = \left(\frac{\partial u}{\partial T} \right)_V = T \left(\frac{\partial s}{\partial T} \right)_V \tag{2.21a}$$

and

$$c_p = \left(\frac{\partial h}{\partial T} \right)_P = T \left(\frac{\partial s}{\partial T} \right)_P \tag{2.21b}$$

where subscripts V and P signify fixed volume and fixed pressure, respectively. The *heat capacity* is the product of the corresponding specific heat and the mass of the

system. Note that only in a reversible process, the amount of heat transferred to a system is $\delta Q = T \mathrm{d}S$. The heat capacity at constant volume of a closed system can be measured in terms of the total amount of energy supplied to it divided by its temperature rise in a constant volume process. On the other hand, the heat capacity at constant pressure of a closed system (such as in a piston–cylinder arrangement) can be measured in terms of the amount of energy per unit mass supplied to the system, excluding the volume work done by the system ($\delta W = p \mathrm{d}V$), divided by the temperature rise in an isobaric process. For example, in a reversible isobaric process, $\mathrm{d}U = \delta Q - p \mathrm{d}V$ and $\mathrm{d}H = \delta Q$. Therefore, $c_p = \frac{1}{m}\frac{\mathrm{d}H}{\mathrm{d}T} = \frac{1}{m}\frac{\delta Q}{\delta T}$.

Specific heats are not defined for all equilibrium states. For example, enthalpy of a two-phase mixture can vary at a constant pressure, such as in a vaporization process, without any change in temperature. This means that the constant pressure specific heat approaches infinity in these states. In fact, the discontinuity in $c_p(T)$ suggests some kind of phase transformation.

A *heat reservoir* is an idealized system that experiences only reversible heat interactions. For any finite amount of energy transfer, its temperature remains unchanged. Therefore, the heat capacity of a reservoir is infinitely large. For a reservoir at temperature T_R, the change of the reservoir energy is proportional to its entropy change:

$$E_{R,2} - E_{R,1} = T_R(S_{R,2} - S_{R,1}) \tag{2.22a}$$

This suggests that a reservoir can be represented by a straight line in the E–S graph. Furthermore, the amount of heat transferred to the reservoir from state 1 to state 2 is given by

$$Q = E_{R,2} - E_{R,1} \tag{2.22b}$$

For a pure substance in a single phase, temperature and pressure are independent, and all other properties can be expressed as functions of T and P. The relation among temperature, pressure, and specific volume is called the *equation of state*, which can be expressed as

$$f(T, P, v) = 0 \text{ or } v = v(T, P) \tag{2.23}$$

This equation does not contain information about the internal energy or entropy. However, we can use the function $c_p = c_p(T, P)$, in addition to the equation of state, to fully determine all intensive properties. For example, $\mathrm{d}s = \left(\frac{\partial s}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial s}{\partial P}\right)_T \mathrm{d}P$. Using $\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_p(T,P)}{T}$, from the definition of specific heat, and the Maxwell relation $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$ (see Problem 2.11), we obtain

$$\mathrm{d}s = \frac{c_p(T, P)}{T}\mathrm{d}T - \left(\frac{\partial v}{\partial T}\right)_P \mathrm{d}P \tag{2.24}$$

Furthermore,

$$dh = c_p(T, P)dT + \left[v(T, P) - T\left(\frac{\partial v}{\partial T}\right)_P \right]dP \qquad (2.25)$$

Under certain circumstances, the equation of state is rather simple, and the specific heats can be assumed as functions of the temperature only, i.e., independent of the pressure. These ideal behaviors will be discussed in the next section.

Example 2.2 *Specific heat and latent heat.* A system consists of 10 kg of H_2O in a closed container that is maintained at a constant pressure of 100 kPa. Initially, the system is at -40 °C (ice), and it is heated to 130 °C (vapor). How much energy must be provided to the system? What is the entropy change of the system? The specific heats of H_2O in the solid, liquid, and vapor states are $c_{p,s} = 2$ kJ/kg K, $c_{p,f} = 4.2$ kJ/kg K, and $c_{p,g} = 2$ kJ/kg K, respectively. The specific latent heats of melting and evaporation are $h_{sf} = 334$ kJ/kg and $h_{fg} = 2257$ kJ/kg.

Solution From the first law of the closed system in an isobaric process, $\Delta U = Q - W$. Since $\Delta P = 0$, $W = P\Delta V$. Hence, $Q = \Delta H = H_2 - H_1$. Let $T_1 = 233.2$ and $T_2 = 403.2$ K be the initial and final temperatures, respectively, and $T_{sat,m} = 273.2$ and $T_{sat} = 373.2$ K be the saturation temperatures. Based on the definition of specific heats, we obtain

$$Q = H_2 - H_1 = m[c_{p,s}(T_{sat,m} - T_1) + h_{sf} + c_{p,f}(T_{sat} - T_{sat,m}) + h_{fg} + c_{p,g}(T_2 - T_{sat})]$$

which gives $Q = 31.51$ MJ. In the single-phase regions, the entropy difference can be evaluated by integrating Eq. (2.21b) or (2.24) since P is fixed. During the phase change, $\Delta S = \Delta H/T$ since the temperature is a constant.

$$S_2 - S_1 = m\left[c_{p,s}\ln\left(\frac{T_{sat,m}}{T_1}\right) + \frac{h_{sf}}{T_{sat,m}} + c_{p,f}\ln\left(\frac{T_{sat}}{T_{sat,m}}\right) + \frac{h_{fg}}{T_{sat}} + c_{p,g}\ln\left(\frac{T_2}{T_{sat}}\right) \right]$$

which gives $\Delta S = 90.6$ kJ/K.

Discussion. From the Steam Table or software accompanied with common thermodynamics text [4, 5], we can find the specific properties of water as follows: $h_1 = -411.7$ kJ/kg; $s_1 = -1.532$ kJ/kg K; $h_2 = 2737$ kJ/kg; $s_2 = 7.517$ kJ/kg K. Therefore, $Q = \Delta H = m(h_2 - h_1) = 31.49$ MJ; $\Delta S = m(s_2 - s_1) = 90.5$ kJ/K. The negligibly small difference is caused by the assumption of constant specific heat in each phase.

2.3   Ideal Gas and Ideal Incompressible Models

The amount of constituents is commonly expressed in terms of the amount of matter in mole. The *mole* is the amount of substance of a system that contains as many elementary entities as there are atoms in 0.012 kg of carbon 12. One mole of substance contains 6.022×10^{23} molecules, atoms, or other particles. This value is called the

Avogadro's constant, i.e., $N_A = 6.022 \times 10^{26}$ kmol^{-1}. Quantities like molecules and particles do not appear in the units. The mass of the system is $m = \bar{n}M$, where $\bar{n}$ is the amount of constituents (in kmol) and M is called the molecular weight. For example, $M = 18.012$ kg/kmol for water.

2.3.1 The Ideal Gas

At relatively high temperature and sufficiently low pressure, most substances behave as a single-phase fluid, in which the interactions between its molecules are generally negligible. The equation of state can be expressed as

$$P\bar{v} = \bar{R}T \text{ or } PV = \bar{n}\bar{R}T \tag{2.26a}$$

where $\bar{v} = V/\bar{n}$ is the molar specific volume in m^3/kmol, and $\bar{R}=$ 8314 J/kmol K is the *universal gas constant*. Equation (2.26a) is called the ideal gas equation since it can be considered as the definition of an ideal gas. Under *standard conditions* (temperature of 25 °C and pressure of 1 atm), 1 kmol of an ideal gas occupies a volume of 22.5 m^3. Dry air can be treated as an ideal gas with an average molecular weight of $M = 29$ kg/kmol. The ideal gas equation of state can be written in terms of the mass quantities for a given substance, i.e.,

$$Pv = RT \text{ or } PV = mRT \tag{2.26b}$$

In the above equation, $v = V/m$ is the specific volume, and $R = \bar{R}/M$ is called the gas constant of the particular substance. The Boltzmann constant is defined as $k_B = \bar{R}/N_A = 1.381 \times 10^{-23}$ J/K. It can be considered as the universal gas constant in terms of particles. Furthermore, if we denote the number density (number of particles per unit volume) as n, then the ideal gas equation can be written as $P = nk_BT$ since $n = N_A \bar{n}/V$.

For ideal gases, both c_p and c_v are independent of the pressure, as will be shown from statistical thermodynamics in Chap. 3, but are generally dependent on temperature. The specific internal energy and enthalpy are functions of temperature only, therefore,

$$du = c_v(T)dT \text{ and } dh = c_p(T)dT \tag{2.27}$$

The specific heats c_p and c_v are related by the Mayer relation as

$$\bar{c}_p - \bar{c}_v = \bar{R} \text{ or } c_p - c_v = R \tag{2.28}$$

If $c_v(T) = $ const., which is sometimes referred to as *perfect gas* behavior, then Eq. (2.27) can be integrated to yield

$$u_2 - u_1 = c_v(T_2 - T_1) \tag{2.29a}$$

and

$$h_2 - h_1 = c_p(T_2 - T_1) \tag{2.29b}$$

where subscripts 1 and 2 can be any two (thermodynamic equilibrium) states. The specific entropy depends on both the temperature and the pressure, i.e.,

$$ds = c_p \frac{dT}{T} - R \frac{dP}{P} \tag{2.30a}$$

Integrating the above equation from state 1 to state 2 yields

$$s_2 - s_1 = \int_1^2 \frac{c_p(T)}{T} dT - R \ln(P_2/P_1) \tag{2.30b}$$

In an isentropic process ($ds = 0$) of a perfect gas, it can be shown that $Pv^\gamma = $ const., where $\gamma = c_p/c_v$ is the *specific heat ratio*. Note that $Pv = $ const. in an isothermal process.

Example 2.3 A cylinder contains 0.01 kmol of N_2 gas (0.28 kg), which may be modeled as an ideal diatomic gas with $c_v = 2.5R$. A piston maintains the gas at constant pressure, $P_0 = 100$ kPa. The cylinder interacts with a cyclic machine, which in turn interacts with a reservoir at $T_R = 1000$ K. The cylinder, the reservoir, and the machinery cannot interact with any other systems. The cyclic machine may produce work W (which cannot be negative). A process brings the volume of the cylinder from $V_1 = 0.224$ to $V_2 = 0.448$ m^3.

(a) What is the least amount of energy that must be transferred out from the reservoir? In such a case, how much work does the cyclic machine produce? How much entropy is generated in the process?
(b) Find the maximum work that the cyclic machine can produce.

Analysis. A schematic drawing is made first as shown in Fig. 2.5. From the ideal gas equation, $T_1 = P_1 V_1 / \bar{n} \bar{R} = 269.4$ K and $T_2 = 538.8$ K. The initial and final states of the cylinder are fully prescribed. The work done by the cylinder is $W_B = \int P dV = P(V_2 - V_1) = 22.4$ kJ, which is also fixed. By applying the first law to the cylinder in an isobaric process, $Q_B = m(h_2 - h_1) = mc_p(T_2 - T_1) = 0.01 \times 3.5 \times P(V_2 - V_1) = 78.4$ kJ. The work done by the cyclic machine is $W = Q_R - Q_B$. Because Q_B is prescribed and $W \geq 0$, the least amount of energy that must be transferred from the reservoir is when $W = 0$ and $Q_R = Q_B$.
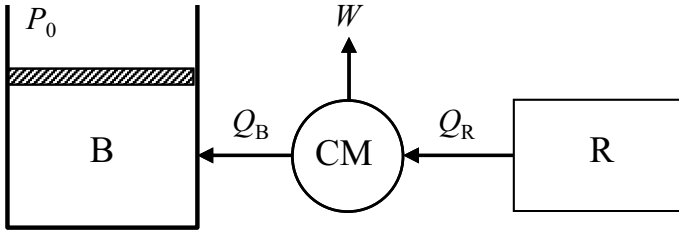
Fig. 2.5 Schematic drawing for Example 2.3

Solution

(a) $Q_R = Q_B = 78.4$ kJ and $W = 0$. We can evaluate the entropy change of the combined system by the following:

$$\begin{aligned} \Delta S &= m(s_2 - s_1) + \Delta S_{CM} + (-Q_R/T_R) \\ &= m[c_p \ln(T_2/T_1) - R\ln(P_2/P_1)] + 0 - 78.4/1000 \\ &= (201.7 - 78.4)\text{ kJ/K} = 123.3\text{ J/K} \end{aligned}$$

Since the system does not have any interactions with any other systems, the entropy change is caused solely by entropy generation.

(b) The maximum work that can be produced is through a reversible process (*not a Carnot cycle since the temperature of the cylinder is not constant*). By setting $\Delta S = m(s_2 - s_1) - Q_R/T_R = 0$, we find $Q_R = T_R m c_p \ln(T_2/T_1) = 201.7$ kJ. The maximum amount of work is therefore $W_{max} = Q_R - Q_B = 123.3$ kJ.

2.3.2 Incompressible Solids and Liquids

The assumption for *ideal incompressible* behavior is $v = $ const., which is the equation of state for incompressible solids and liquids. It can be shown that in this case $c_p = c_v$ and, to a good approximation, the specific heat depends on temperature only. It is common to use c_p for the specific heat of solids and liquids. Using Eqs. (2.24) and (2.25), we obtain the specific internal energy, enthalpy, and entropy for an ideal incompressible solid or liquid as follows:

$$du = c_p(T)dT \tag{2.31}$$

$$ds = c_p(T)\frac{dT}{T} \tag{2.32}$$

and

$$dh = c_p(T)dT + vdP \tag{2.33}$$

Notice that while the internal energy and the entropy are functions of temperature only, the enthalpy depends on both temperature and pressure as can be seen from Eq. (2.33). Sometimes only one of the terms on the right-hand side of Eq. (2.33) needs to be considered if the other term is much smaller. For example, if the pressure change is small, the second term can be dropped. Examples when the pressure effect can be neglected are (1) a solid under the normal pressure range and (2) a liquid that flows through a pipeline in a heat exchanger without significant pressure drop. An example when the temperature effect is negligible is pumping water in a reversible adiabatic process, where the enthalpy change between the outlet and inlet of the pump is proportional to the pressure change.

Example 2.4 In a Rankine cycle, water at 15 °C, 100 kPa is compressed through a pump to 10 MPa before entering the boiler. Model the water as an incompressible liquid with a constant specific heat $c_p = 4.2$ kJ/kg K. What is the least amount of work required to pump 1 kg of water? What is the exit temperature of the water? If the pump efficiency is 80%, what is the actual specific work and exit temperature of the pump?

Solution Take $v = 0.001$ m^3/kg as an approximation. The least amount of work is needed in a reversible process. It has been shown that the reversible work *done by the system* between bulk flow states is $\delta w = -vdP$. Hence, the work needed in a reversible process is $w_{\text{rev}} = h_{2s} - h_1 = 0.001(10,000 - 100) = 9.9$ kJ/kg

Because it is an adiabatic and reversible process, it must be isentropic or $s_{2s} - s_1 = c_p \ln(T_{2s}/T_1) = 0$. Hence, $T_{2s} = T_1 = 15$ °C. Actual work $w = w_{\text{rev}}/\eta_p = 12.38$ kJ/kg. Since $w = h_2 - h_1 = c_p(T_2 - T_1) + v(P_2 - P_1)$,

$$T_2 = T_1 + \frac{h_2 - h_1}{c_p} - \frac{v}{c_p}(P_2 - P_1) = T_1 + \frac{w - w_{\text{rev}}}{c_p} = 15.59\,°C$$

which is less than 1 K higher. The entropy generation is $s_{\text{gen}} = c_p \ln(T_2/T_1) = 8.6$ J/K kg.

Discussion. We can use the Steam Table and notice that all states are compressed liquid. The properties at state 1 can be evaluated at $T_1 = 15$ °C and $P_1 = 100$ kPa, at state 2s (reversible) can be evaluated at $P_{2s} = 10$ MPa and $s_{2s} = s_1$, and at state 2 can be evaluated at $P_2 = 10$ MPa and $h_2 = h_1 + w$. Hence, $w_{\text{rev}} = 9.88$ kJ/kg, $T_{2s} = 15.11$ °C, $w = 12.35$ kJ/kg, $T_2 = 15.67$ °C, and $s_{\text{gen}} = 8.2$ J/K kg. The differences are negligibly small compared with those obtained from the incompressible assumption. Note that the temperature change in the pump is usually very small. On a T–s diagram, it is difficult to distinguish states 1, 2s, and 2. In fact, state 2 crosses the saturated liquid line to overlap with a two-phase-mixture state at T_2 and s_2. This is because T and s together cannot uniquely determine a stable-equilibrium state.

2.4 Heat Transfer Basics

Classical thermodynamics focuses on the changes of mass, energy, and entropy of a system between equilibrium states, and establishes the required balance equations between end states during a given process. For example, we have learned that spontaneous transfer of energy can occur only from a higher temperature to a lower temperature. In thermodynamics, heat interaction is defined as the transfer of energy at the mutual (interface) temperature between two systems. Heat transfer is a subject that extends the thermodynamic principles to detailed energy transport processes that occur as a consequence of temperature differences. Heat transfer phenomena are abundant in our everyday life and play an important role in many industrial, environmental, and biological processes. Examples include energy conversion and storage, electrical power generation, combustion processes, heat exchangers, building-temperature regulation, thermal insulation, refrigeration, microelectronic cooling, materials processing, manufacturing, global thermal budget, agriculture, food industry, and biological systems. Based on the local-equilibrium assumption, heat transfer analysis deals with the rate of heat transfer and/or the temperature distributions (steady state or transient) for given geometries, materials, and initial and boundary conditions. Thermal design, on the other hand, determines the necessary geometric structure and materials for use to achieve optimum performance for a specific task, such as a heat exchanger.

Heat conduction refers to the transfer of heat in a stationary (from the macroscopic point of view) medium, which may be a solid, a liquid, or a gas. Energy can also be transferred between objects by the emission and absorption of electromagnetic waves without any intervening medium; this is called *thermal radiation*, such as the radiation from the sun. When the transfer of heat involves fluid motion, we call it *convection heat transfer*, or simply, *convection*. Examples of convection are cooling with a fan, hot water flowing in a pipe, and cold air blowing outside the wall of a building. The basic macroscopic formulations of conduction, convection, and radiation heat transfer are summarized in this section. The microscopic mechanisms, such as the effects of small dimension and short duration on the thermal transfer processes, will be the subject of the remaining chapters.

2.4.1 Conduction

In a stationary medium, heat transfer occurs if the medium is not at thermal equilibrium. The assumption of local equilibrium allows us to define the temperature at each location. Fourier's law states that the heat flux (or heat transfer rate per unit area) $\mathbf{q}''$ is proportional to the temperature gradient ∇T, i.e.,

$$\mathbf{q}'' = -\kappa \nabla T \tag{2.34}$$

where κ is called *thermal conductivity*, which is a material property that may depend on temperature. Notice that $\mathbf{q}''$ is a vector and its direction is always perpendicular to the isotherms and opposite to the temperature gradient. In an anisotropic medium, such as a thin film or a thin wire, the thermal conductivity depends on the direction along which it is measured.

By doing a control volume analysis using energy balance, a differential equation can be obtained for the transient temperature distribution $T(t, \mathbf{r})$ in a homogeneous isotropic medium; that is [11, 12]

$$\nabla \cdot (\kappa \nabla T) + \dot{q} = \rho c_p \frac{\partial T}{\partial t} \tag{2.35}$$

where $\nabla \cdot$ is the divergence operator, $\dot{q}$ is the volumetric thermal energy generation rate, and ρc_p can be considered as volumetric heat capacity. Equation (2.35) is called the heat diffusion equation or heat equation. Note that the concept of thermal energy generation is very different from the concept of entropy generation. Thermal energy generation refers to the conversion of other types of energy (such as electrical, chemical, or nuclear energies) to the internal energy of the system, while the total energy is always conserved. Entropy need not be conserved, and entropy generation refers to the creation of entropy by an irreversible process. If there is no thermal energy generation and the thermal conductivity can be assumed to be independent of temperature, Eq. (2.35) reduces to $\nabla^2 T = 0$ at steady state, where $\nabla^2 T = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}$ in the Cartesian coordinates. With the prescribed initial temperature distribution and boundary conditions, the heat equation can be solved analytically for simple cases and numerically for more complex geometries as well as initial and boundary conditions. Typical boundary conditions include (a) constant temperature, (b) constant heat flux, (c) convection, and (d) radiation.

Generally speaking, metals with high electric conductivities and some crystalline solids have very high thermal conductivities ranging from 100 to 1000 W/m K; alloys and metals with low electric conductivities have slightly lower thermal conductivities ranging from 10 to 100 W/m K; water, soil, glass, and rock have thermal conductivities from 0.5 to 5 W/m K; thermal insulation materials usually have a thermal conductivity on the order of 0.1 W/m K; and gases have the lowest thermal conductivity, e.g., the thermal conductivity of air at 300 K is 0.026 W/m K. Notice that thermal conductivity generally depends on temperature. A comprehensive collection of thermal-property data can be found from Touloukian and Ho [13]. At room temperature, Diamond IIa has the highest thermal conductivity, $\kappa = 2300$ W/m K among all natural materials. Researchers have shown that single-walled carbon nanotubes can have even higher thermal conductivity at room temperature. More detailed discussion about the mechanisms of thermal conduction and thermal properties of nanostructures will be provided in subsequent chapters.

Example 2.5 Consider the steady-state heat conduction through a solid rod, whose sides are insulated, between a constant temperature source at $T_1 = 600$ K and a constant temperature sink at $T_2 = 300$ K. Assume the thermal conductivity of the rod

Fig. 2.6 Illustration of the control volume for energy and entropy balances in a solid rod with heat conduction
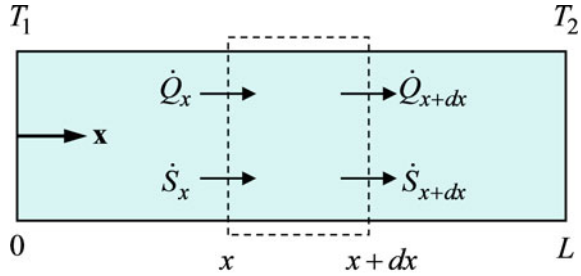
$$\dot{Q}_x = -\kappa A \frac{dT}{dx} \quad \text{and} \quad \dot{S}_x = \frac{\dot{Q}_x}{T(x)}$$

is independent of temperature, $\kappa = 150$ W/m K. The rod has a length $L = 0.2$ m and cross-sectional area $A = 0.001$ m^2. Show that the temperature distribution along the rod is linear. What is the heat transfer rate? What is the volumetric entropy generation rate? What is the total entropy generation rate?

Solution This is a 1D heat conduction problem with no thermal energy generation, as shown in Fig. 2.6. Fourier's law can be written as $\dot{Q}_x = -\kappa A (dT/dx)$. At steady state, the heat transfer rate $\dot{Q}_x$ is independent of x, since there is no thermal energy generation. Because both κ and A are constant, dT/dx must not be a function of x. Hence, the spatial temperature distribution is a straight line. From the boundary conditions $T(0) = T_1$ and $T(L) = T_2$, we have $T(x) = T_1 + (T_2 - T_1)(x/L)$. Furthermore, $\dot{Q}_x = \kappa A (T_1 - T_2)/L = 225$ W. To evaluate the entropy generation rate, we can apply Eq. (2.2b) to the control volume Adx to obtain $\dot{s}_{\text{gen}}(x)Adx$. The net entropy transferred to the control volume is $\dot{S}_x - \dot{S}_{x+dx} = -d\left(\frac{\dot{Q}_x}{T}\right)$. The sum of the entropy generation and entropy transferred is equal to the entropy change, which is zero at steady state. Therefore, $\dot{s}_{\text{gen}}(x) = q_x'' \frac{d(1/T)}{dx} = \frac{\kappa}{T^2}\left(\frac{dT}{dx}\right)^2$, where $q_x'' = \frac{\dot{Q}_x}{A}$ is the heat flux. To calculate the total entropy generation rate, we can integrate $\dot{s}_{\text{gen}}(x)$ over the whole rod. Alternatively, we perform an entropy balance for the rod as a whole, which gives the rate of entropy generation for a heat transfer rate $\dot{Q}_x$ from T_1 to T_2 as $\dot{S}_{\text{gen}} = \dot{Q}_x\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = 0.375$ W/K. This example shows that the entropy generation occurs in a finite volume, while the entropy flows through the interface. The amount of entropy flux increases with x as more and more entropy is generated through the irreversible process. More discussion on the entropy generation in heat transfer and fluid flow processes can be found in Bejan [14].

Contact resistance is important in microelectronics thermal management and cryogenic heat transfer. A large thermal resistance may exist due to imperfect contact, such as surface roughness. The result is a large temperature difference across the interface. The value of contact resistance depends on the surface conditions, adjacent materials, and contact pressure. As an example, assume a contact resistance

between two stainless steel plates to be $R_c'' = 0.001$ m^2 K/W and the thermal conductivity of the stainless steel $\kappa = 50$ W/m K. If the thickness of each plate is $L = 5$ mm and the area of the plate is $A = 0.01$ m^2, the total thermal resistance is then $R_t = L/(\kappa A) + R_c''/A + L/(\kappa A) = (0.01 + 0.1 + 0.01)$ K/W = 0.12 K/W, which is mostly due to the contact resistance. Interfacial fluids and interstitial (filler) materials can be applied to reduce the contact resistance in some cases. Even with a perfect contact, thermal resistance exists between dissimilar materials due to acoustic mismatch, which is especially important at low temperatures [15].

2.4.2 Convection

Convection heat transfer refers to the heat transfer from solid to fluid near the boundary when the fluid is in bulk motion relative to the solid. The combination of the bulk motion, known as *advection*, with the random motion of the fluid molecules (i.e., diffusion) is the key for convection heat transfer. Examples are flows over an object or inside a tube, a spray leaving a nozzle that is impinged on a microelectronic component for cooling purposes, and boiling in a pan. The velocity and temperature distributions for a fluid flowing over a heated flat plate are illustrated in Fig. 2.7. A *hydrodynamic boundary layer* or *velocity boundary layer* (VBL) is formed near the surface, and the fluid moves at the free-stream velocity outside the boundary layer. Similarly, a *thermal boundary layer* (TBL) is developed near the surface of the plate where a temperature gradient exists. When the flow speed is not very high and the density of the fluid not too low, the average velocity of the fluid is zero, and the fluid temperature equals the wall temperature in the vicinity of the wall, i.e., $v_x(y = 0) = 0$ and $T(y = 0) = T_w$. For Newtonian fluids, a linear relationship exists between the stress components and the velocity gradients. Many common fluids like air, water, and oil belong to this catalog. The shear stress in the fluid is
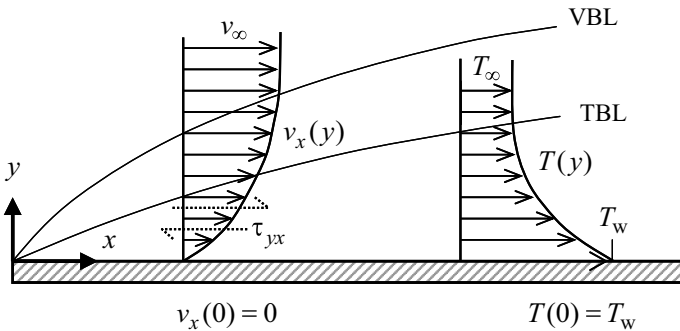

Fig. 2.7 Illustration of the velocity boundary layer and the thermal boundary layer

$$\tau_{yx} = -\mu \frac{\partial v_x}{\partial y} \tag{2.36}$$

where μ is the viscosity. Throughout this book, we will use $v_x, v_y,$ and v_z (or v_i with $i = 1, 2,$ and 3) for the velocity components in the x-, y-, and z-directions, respectively. When Eq. (2.36) is evaluated at the boundary $y = 0$, it gives the force per unit area exerted to the fluids by the wall and is used to calculate the *friction factor* in fluid mechanics [16].

The heat flux between the solid and the fluid can be predicted by applying Fourier's law to the fluid at the boundary; thus,

$$q_{\mathrm{w}}'' = -\kappa \left. \frac{\partial T}{\partial y} \right|_{y=0} \tag{2.37}$$

where κ is the thermal conductivity of the fluid. Equation (2.37) shows that the basic heat transfer mechanism for convection is the same as that for conduction, i.e., both are caused by heat diffusion and governed by the same equation. Without bulk motion, however, the temperature gradient at the boundary would be smaller. Therefore, advection generally increases the heat transfer rate. Newton's law of cooling is a phenomenological equation for convection. It states that the convective heat flux is proportional to the temperature difference, therefore,

$$q_{\mathrm{w}}'' = h(T_{\mathrm{w}} - T_\infty) \tag{2.38}$$

where h is called the *convection heat transfer coefficient*, or *convection coefficient*, T_{w} is the surface temperature, and T_∞ is the fluid temperature. From Eqs. (2.37) and (2.38), we have

$$h = \frac{-\kappa}{T_{\mathrm{w}} - T_\infty} \left. \frac{\partial T}{\partial y} \right|_{y=0} \tag{2.39}$$

Although h depends on the location, the average convection coefficient is often used in heat transfer calculations. The convection coefficient depends on the fluid thermal conductivity, velocity, and flow conditions (laminar versus turbulent flow, internal versus external flow, and forced versus free convection). Convection can also happen with phase change, such as boiling, which usually causes vigorous fluid motion and enhanced heat transfer. Convection correlations are recommended in most heat transfer textbooks to determine the convection coefficient. For laminar flow over a flat plate of length L with a free-stream velocity v_∞, the following equation correlates the average Nusselt number to the Reynolds number at $x = L$ and the Prandtl number [11]:

$$\overline{Nu_L} = \frac{\bar{h}_L L}{\kappa} = 0.664 Re_L^{1/2} Pr^{1/3}, \text{ for } Pr > 0.6 \text{ and } Re_L < 5 \times 10^5 \tag{2.40}$$

The Reynolds number, defined as $Re_L = \rho v_\infty L/\mu$, is key to the study of hydrodynamics. The Prandtl number $Pr = \nu/\alpha$ is the ratio of *kinematic viscosity* $\nu = \mu/\rho$, which is also known as the *momentum diffusivity*, to the thermal diffusivity $\alpha = \kappa/(\rho c_p)$ of the fluid. A detailed understanding of the fluid flow and convection heat transfer requires the solution of the conservation equations, as summarized in the following.

The differential form of the continuity equation or mass conservation is

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{v} = 0 \tag{2.41}$$

where $\frac{D}{Dt} = \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right)$ is called the substantial derivative or material derivative. Notice that for an incompressible fluid, the continuity equation reduces to $\nabla \cdot \mathbf{v} = 0$.

Using Stokes' hypothesis that relates the second coefficient of viscosity to the viscosity for Newtonian fluids, the Navier–Stokes equation that describes the momentum conservation can be expressed as follows [16]:

$$\frac{D\mathbf{v}}{Dt} = -\frac{\nabla P}{\rho} + \mathbf{a} + \nu \nabla^2 \mathbf{v} + \frac{\nu}{3} \nabla(\nabla \cdot \mathbf{v}) \tag{2.42}$$

where $\mathbf{a}$ is the body force per unit mass exerted on the fluid, i.e., the acceleration vector.

Energy equation for constant thermal conductivity without thermal energy generation for a moving fluid can be expressed as

$$\rho \frac{Du}{Dt} = \kappa \nabla^2 T - P \nabla \cdot \mathbf{v} + \mu \Phi \tag{2.43a}$$

where u is the specific internal energy ($du = c_v dT$) and the last term accounts for the viscous dissipation, which is

$$\Phi = 2\left[\left(\frac{\partial v_x}{\partial x}\right)^2 + \left(\frac{\partial v_y}{\partial y}\right)^2 + \left(\frac{\partial v_z}{\partial z}\right)^2\right] + \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right)^2 + \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right)^2 +$$

$$+ \left(\frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z}\right)^2 - \frac{2}{3}(\nabla \cdot \mathbf{v})^2 \tag{2.43b}$$

in the Cartesian coordinates. Equation (2.41) through (2.43a, 2.43b) is usually simplified for specific conditions and solved analytically or numerically using computation fluid dynamics software. In Chap. 4, we will show that the conservation equations can also be derived from the microscopic theories, which are also applicable for rarefied flows and microfluidics.

2.4.3 Radiation

Thermal radiation refers to the electromagnetic radiation in a broad wavelength range from approximately 100 nm to 1000 μm. It includes a portion of the ultraviolet region, the entire visible (380–760 nm) region, and the infrared region. Monochromatic radiation refers to radiation at a single wavelength (or a very narrow spectral band), such as lasers and some atomic emission lines. Radiation emitted from a thermal source, such as the sun, an oven, or a blackbody cavity, covers a broad spectral region and can be considered as the spectral integration of monochromatic radiation. In contrast to conduction or convection heat transfer, radiative energy propagates in the form of electromagnetic waves that do not require an intervening medium. Regardless of its wavelength, an electromagnetic wave travels in vacuum at the speed of light, $c_0 = 2.998 \times 10^8$ m/s. Radiation can also be viewed as a collection of particles, called photons, whose energy is proportional to the frequency of radiation. Starting with the definition of intensity and its linkage to the radiative energy flux, radiative transfer between surfaces and in participating media will be briefly described later in this section. More detailed treatment of the mechanism of thermal radiation, radiative properties, and radiative transfer at small length scales will be given in Chaps. 8, 9, and 10.

The *spectral intensity* or *radiance* is defined as the radiative power received within a solid angle, a unit projected area, and a unit wavelength interval; hence [11],

$$I_\lambda(\lambda, \theta, \phi) = \frac{\mathrm{d}\dot{Q}}{\mathrm{d}A \cos\theta \, \mathrm{d}\Omega \, \mathrm{d}\lambda} \tag{2.44}$$

where (θ, ϕ) is the direction of propagation, measured with respect to the surface normal, $\mathrm{d}A \cos\theta$ is therefore the projected area, and $\mathrm{d}\Omega$ is an element solid angle. It is convenient to describe the relationship between intensity and radiative power using the spherical coordinates, as shown in Fig. 2.8, where an element area dA whose surface normal is in the z-direction is placed at the origin. Note that $r = (x^2 + y^2 + z^2)^{1/2}$, $\theta = \cos^{-1}(z/r)$, $\phi = \tan^{-1}(y/x)$. The solid angle, defined as $\mathrm{d}\Omega = \mathrm{d}A_\mathrm{n}/r^2$, can be expressed as $\mathrm{d}\Omega = (r\mathrm{d}\theta)(r\sin\theta\mathrm{d}\phi)/r^2 = \sin\theta\mathrm{d}\theta\mathrm{d}\phi$.
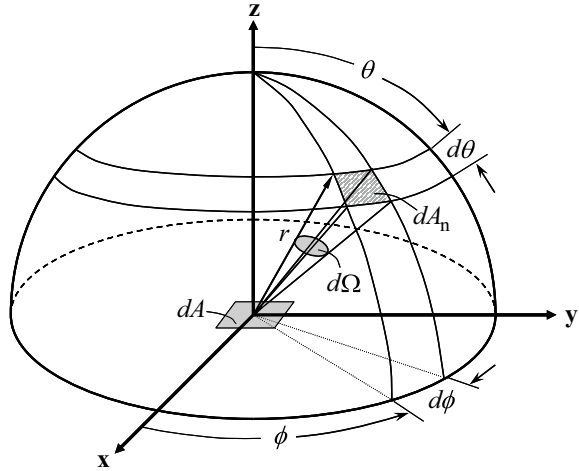
The spectral heat flux from an element surface dA to the upper hemisphere can be obtained by integrating Eq. (2.44), i.e.,

$$q_\lambda''(\lambda) = \int_0^{2\pi} \int_0^{\pi/2} I_\lambda(\lambda, \theta, \phi) \cos\theta \sin\theta \mathrm{d}\theta \mathrm{d}\phi \tag{2.45}$$

The total heat flux is equal to the heat flux integrated over all wavelengths:

$$q_\mathrm{rad}'' = \int_0^\infty q_\lambda''(\lambda)\mathrm{d}\lambda \tag{2.46}$$

Fig. 2.8 Illustration of the solid angle in spherical coordinates

We can also define the total intensity as the integral of the spectral intensity over all wavelengths, $I(\theta, \phi) = \int_0^\infty I(\lambda, \theta, \phi)d\lambda$. An equation similar to Eq. (2.45) holds between the total heat flux and the total intensity. If the radiation is emitted from a surface, the radiative heat flux q''_{rad} is termed as the (hemispherical) *emissive power*. When the intensity is same in all directions, the surface is said to be diffuse, and Eq. (2.45) can be integrated to obtain the relation, $q''_\lambda = \pi I_\lambda(\lambda, \theta, \phi)$. Similarly, we can obtain $q'' = \pi I$.

The maximum power that can be emitted by a thermal source at a given temperature is from a blackbody. A blackbody is an ideal surface which absorbs all incoming radiation and gives out the maximum emissive power. Radiation inside an isothermal enclosure behaves like a blackbody. In practice, a blackbody cavity is made with a small aperture on an isothermal cavity. The emissive power of a blackbody is given by the Stefan–Boltzmann law, also proportional to the absolute temperature to the fourth power, viz.,

$$e_b(T) = \pi I_b(T) = \sigma_{SB} T^4 \tag{2.47}$$

where $\sigma_{SB} = 5.67 \times 10^{-8}$ W/m^2 K^4 is the Stefan–Boltzmann constant. A blackbody is also a diffuse emitter, i.e., its intensity is independent of the direction. The spectral distribution of blackbody emission is described by Planck's law, which gives the spectral intensity as a function of temperature and wavelength as follows:

$$I_{b,\lambda}(\lambda, T) = \frac{e_{b,\lambda}(\lambda, T)}{\pi} = \frac{2hc^2}{\lambda^5(e^{hc/k_B\lambda T} - 1)} \tag{2.48}$$

where $h = 6.626 \times 10^{-34}$ J s is the Planck constant, c is the speed of light, and k_B is the Boltzmann constant. The derivation of Planck's law will be given in Chap. 8.

The ratio of the emissive power of a real material to that of the blackbody defines the (total hemispherical) *emissivity* (or *emittance*), $\varepsilon(T) = e(T)/e_b(T)$. The spectral directional emissivity is defined as the spectral intensity emitted by the surface to $I_{b,\lambda}$, i.e.,

$$\varepsilon_\lambda'(\lambda, \theta, \phi, T) = \frac{I_\lambda(\lambda, \theta, \phi, T)}{e_{b,\lambda}(\lambda, T)/\pi} \tag{2.49}$$

Using $e(T) = \int_0^\infty d\lambda \left[\int_0^{2\pi} \int_0^{\pi/2} I_\lambda(\lambda, \theta, \phi, T) \cos\theta \sin\theta d\theta d\phi \right]$, we have

$$\varepsilon(T) = \frac{\pi}{\sigma T^4} \int_0^\infty e_{b,\lambda}(\lambda, T) d\lambda \left[\int_0^{2\pi} \int_0^{\pi/2} \varepsilon_\lambda'(\lambda, \theta, \phi, T) \cos\theta \sin\theta d\theta d\phi \right] \tag{2.50}$$

This equation suggests that the relationship between the total hemispherical emissivity and the spectral directional emissivity is rather complicated in general. For a gray surface, the spectral emissivity is not a function of the wavelength. For a diffuse surface, the intensity emitted by the surface is independent of the direction. For a diffuse-gray surface, Eq. (2.49) reduces to a simple form $\varepsilon = \varepsilon_\lambda'$, because the emissivity is independent of wavelength and the direction.

Real materials also reflect radiation in contrast to a blackbody. The reflection may be specular for mirrorlike surfaces and more diffuse for rough surfaces. Some window material and thin films are semitransparent. Generally speaking, reflection and transmission are highly dependent on the wavelength, angle of incidence, and polarization status of the incoming electromagnetic wave. The *absorptance*, *reflectance*, and *transmittance* of a material can be defined as the fraction of the absorbed, reflected, and transmitted radiation. The (spectral) directional absorptance, directional–hemispherical reflectance, and directional–hemispherical transmittance are related by

$$A_\lambda' + R_\lambda' + T_\lambda' = 1 \tag{2.51}$$

For an opaque material, the transmittance $T_\lambda' = 0$. It is common to use absorptivity α_λ' and reflectivity ρ_λ' for opaque materials with smooth surfaces. Note that $\alpha_\lambda' + \rho_\lambda' = 1$. However, the distinction between words ending with "-tivity" and "-tance" is not always clear and both endings are used interchangeably in the literature. The complete nomenclature of radiative quantities and properties can be found from Siegel and Howell [17]. Further discussion about the mechanisms and applications of radiation heat transfer will be provided in Chap. 8.

Kirchhoff's law states that the spectral directional emissivity is always the same as the spectral directional absorptivity, i.e., $\varepsilon_\lambda' = \alpha_\lambda'$. For diffuse-gray surfaces, it can also be shown that $\varepsilon = \alpha$, which may not be generally true for surfaces that are not diffuse-gray, unless they are in thermal equilibrium with the surroundings.

Example 2.6 Find the net radiative heat flux between two, large parallel surfaces. Surface 1 at $T_1 = 600\ °C$ has an emissivity $\varepsilon_1 = 0.8$, and surface 2 at $T_2 = 27\ °C$ has an emissivity $\varepsilon_2 = 0.5$.

Solution Assume that the medium in between is transparent, and both surfaces are opaque and diffuse-gray. Note that radiation from one surface to another will be partially absorbed and partially reflected back. Furthermore, the reflected radiation will continue to experience the absorption/reflection processes between the two surfaces. Surface 1 emits $\varepsilon_1 \sigma_{SB} T_1^4$ radiation toward surface 2. The fraction of this emitted radiation that is absorbed by surface 2 can be calculated by tracing the rays between the two surfaces, which is $\varepsilon_2 + (1 - \varepsilon_2)(1 - \varepsilon_1)\varepsilon_2 + (1 - \varepsilon_2)^2(1 - \varepsilon_1)^2\varepsilon_2 + \cdots$ since the reflectivity is one *minus* the emissivity. The radiative heat flux from surface 1 to surface 2 is

$$q''_{1 \to 2} = \frac{\varepsilon_1 \varepsilon_2 \sigma_{SB} T_1^4}{1 - (1 - \varepsilon_1)(1 - \varepsilon_2)} = \frac{\sigma_{SB} T_1^4}{1/\varepsilon_1 + 1/\varepsilon_2 - 1},$$

and that from surface 2 to surface 1 is

$$q''_{2 \to 1} = \frac{\sigma_{SB} T_2^4}{1/\varepsilon_1 + 1/\varepsilon_2 - 1}.$$

Subsequently, the net radiative flux from surface 1 to surface 2 is

$$q''_{12} = q''_{1 \to 2} - q''_{2 \to 1} = \frac{\sigma_{SB}(T_1^4 - T_2^4)}{1/\varepsilon_1 + 1/\varepsilon_2 - 1} \tag{2.52}$$

Plugging in $T_1 = 873.2\ K$, $T_2 = 300.2\ K$, and other numerical values, we obtain $q''_{12} = 14.4\ kW/m^2$.

Gas emission, absorption, and scattering are important for atmospheric radiation and combustion. When radiation travels through a cloud of gas, some of the energy may be absorbed. The absorption of photons raises the energy levels of individual molecules. At sufficiently high temperatures, gas molecules may spontaneously lower their energy levels and emit photons. These changes in energy levels are called *radiative transitions*, which include bound–bound transitions (between nondissociated molecular states), bound–free transitions (between nondissociated and dissociated states), and free–free transitions (between dissociated states). Bound–free and free–free transitions usually occur at very high temperatures (greater than about 5000 K) and emit in the ultraviolet and visible regions. The most important transitions for radiative heat transfer are bound–bound transitions between vibrational energy levels coupled with rotational transitions. The photon energy (or frequency) must be exactly the same as the difference between two energy levels in order for the photon to be absorbed or emitted; therefore, the quantization of the energy levels results

in discrete spectral lines for absorption and emission. The rotational lines superimposed on a vibrational line give a band of closely spaced spectral lines, called the vibration–rotation spectrum. Additional discussion will be given in Chap. 3 about quantized transitions in atoms and molecules.

Particles can also scatter electromagnetic waves or photons, causing a change in the direction of propagation. In the early twentieth century, Gustav Mie developed a solution of Maxwell's equations for the scattering of electromagnetic waves by spherical particles, known as the Mie scattering theory. This solution can be used to predict the scattering phase function. In the case when the particle sizes are small compared with the wavelength, the formulation reduces to the simple expression obtained earlier by Lord Rayleigh. The phenomenon is called Rayleigh scattering, in which the scattering efficiency is inversely proportional to the wavelength to the fourth power. The wavelength-dependent characteristic of light scattering by small particles helps explain why the sky is blue and why the sun appears red at sunset. For spheres whose diameters are much greater than the wavelength, geometric optics can be applied by treating the surface as specular or diffuse.

The spectral intensity in a *participating medium*, $I_\lambda = I_\lambda(\xi, \Omega, t)$, depends on the location (the coordinate ξ), its direction (the solid angle Ω), and time t. In a time interval dt, the beam travels from ξ to $\xi + d\xi$ ($d\xi = c dt$), and the intensity is attenuated by absorption and out-scattering, but enhanced by emission and in-scattering. The macroscopic description of the radiation intensity is known as the *equation of radiative transfer* (ERT) [17].

$$\frac{1}{c}\frac{\partial I_\lambda}{\partial t} + \frac{\partial I_\lambda}{\partial \xi} = a_\lambda I_{b,\lambda}(T) - (a_\lambda + \sigma_\lambda)I_\lambda + \frac{\sigma_\lambda}{4\pi}\int_{4\pi} I_\lambda(\xi, \Omega', t)\Phi_\lambda(\Omega', \Omega)\, d\Omega'$$

(2.53)

where a_λ and σ_λ are the absorption and scattering coefficients, respectively, and $\Phi_\lambda(\Omega', \Omega)$ is the *scattering phase function* $\Phi_\lambda = 1$, which satisfies the equation: $\frac{1}{4\pi}\int_{4\pi}\Phi_\lambda(\Omega', \Omega)d\Omega' \equiv 1$. For isotropic scattring, $\Phi_\lambda = 1$. The right-hand side of Eq. (2.53) is composed of three terms: the first accounts for the contribution of emission (which depends on the local gas temperature T); the second is the attenuation by absorption and out-scattering; and the third is the contribution of in-scattering from all directions (solid angle 4π) to the direction Ω.

Unless ultrafast laser pulses are involved, the transient term is negligible. The ERT for the steady state can be simplified as

$$\frac{\partial I_\lambda(\zeta_\lambda, \Omega)}{\partial \zeta_\lambda} + I_\lambda(\zeta_\lambda, \Omega) = (1 - \eta_\lambda)I_{b,\lambda} + \frac{\eta_\lambda}{4\pi}\int_{4\pi} I_\lambda(\zeta_\lambda, \Omega')\Phi_\lambda(\Omega', \Omega)d\Omega' \quad (2.54)$$

where $\zeta_\lambda = \int_0^\xi (a_\lambda + \sigma_\lambda)d\xi$ is the *optical path length*, and $\eta_\lambda = \sigma_\lambda/(a_\lambda + \sigma_\lambda)$ is called the *scattering albedo*. This is an integrodifferential equation, and its right-hand side is called the source function. The integration of the spectral intensity over all

wavelengths and all directions gives the radiative heat flux. Unless the temperature field is prescribed, Eq. (2.54) is coupled with the heat conduction equation in a macroscopically stationary medium and the energy conservation equation in a fluid with convection.

Analytical solutions of the ERT rarely exist for applications with multidimensional and nonhomogeneous media. Approximate models have been developed to deal with special types of problems, including Hottel's *zonal method*, the *differential and moment methods* (often using the spherical harmonics approximation), and the *discrete ordinates method*. The statistical model using the Monte Carlo method is often used for complicated geometries and radiative properties [17]. Analytical solutions can be obtained only for limited simple cases.

Example 2.7 A gray, isothermal gas at a temperature $T_g = 3000$ K occupies the space between two, large parallel blackbody surfaces. Surface 1 is heated to a temperature $T_1 = 1000$ K, while surface 2 is maintained at a relatively low temperature by water cooling. It is desired to know the amount of heat that must be removed from surface 2. If the scattering is negligible, calculate the heat flux at surface 2 for $a_\lambda L = 0.01, 0.1, 1$, and 10, where L is the distance between the two surfaces.

Solution For a gray medium without scattering, Eq. (2.53) becomes $\frac{dI(\theta)}{a_\lambda d\xi} + I(\theta) = I_b(T_g)$, where θ is the angle between ξ and x. With $I_b(T_g) = \sigma_{SB}T_g^4/\pi$ and $I(0) = I_b(T_1) = \sigma_{SB}T_1^4/\pi$, the ERT can be integrated from $x = 0$ to $x = L$. The result is $I(\theta)|_{x=L} = \frac{\sigma_{SB}}{\pi}\left[T_1^4 e^{-a_\lambda L/\cos\theta} + T_g^4(1 - e^{-a_\lambda L/\cos\theta})\right]$. The radiative flux at $x = L$ can be obtained by integrating the intensity over the hemisphere, i.e.,

$$q''(a_\lambda L) = \int_0^{2\pi}\int_0^{\pi/2} \frac{\sigma_{SB}}{\pi}\left[T_g^4 - (T_g^4 - T_1^4)e^{-a_\lambda L/\cos\theta}\right]\cos\theta\sin\theta d\theta d\phi$$

$$= \sigma_{SB}T_g^4 - 2\sigma_{SB}(T_g^4 - T_1^4)E_3(a_\lambda L)$$

where $E_3(\zeta) = \int_0^1 e^{-\zeta/\mu}d\mu$ is called the *exponential integral function of the third kind* and can be numerically evaluated. The final results are tabulated as follows:

$a_\lambda L$	0.01	0.1	1	10
$E_3(a_\lambda L)$	0.49	0.416	0.11	3.48×10^{-6}
q'' (W/m^2)	1.474×10^5	8.187×10^5	3.595×10^6	4.593×10^6

Discussion. In the optically thick limit ($a_\lambda L \gg 1$), $q'' \approx \sigma_{SB}T_g^4$, and all radiation leaving surface 1 will be absorbed by the gas before reaching surface 2. On the other hand, the heat flux is much greater than $\sigma_{SB}T_1^4 = 56.7$ kW/m^2 at $a_\lambda L = 0.01$. The gas absorption can be neglected in the optically thin limit; however, its emission contributes significantly to the radiative flux at surface 2. This is because the gas

temperature is much higher than that of surface 1 and $L/\cos\theta$ can be much longer than L for large θ values.

2.5 Summary

This chapter provided an overview of classical thermodynamics, derived following logical steps and on a general basis, as well as the functional relations and thermodynamic properties of simple systems and ideal pure substances. The basic heat transfer modes were elaborated in a coherent way built upon the foundations of thermodynamics. Entropy generation is inevitably associated with any heat transfer process. The connection between heat transfer and entropy generation, which has been omitted by most heat transfer textbooks, was also discussed. The introduction of thermal radiation not only covered most of the undergraduate-level materials but also linked to some basic graduate-level materials. This chapter should serve as a bridge or a reference to the rest of the book, dealing with energy transfer processes in micro/nanosystems and/or from a microscopic viewpoint of macroscopic phenomena.

Problems

2.1. Give examples of steady state. Give examples of thermodynamic equilibrium state. Give an example of spontaneous process. Is the growth of a plant a spontaneous process? Give an example of adiabatic process.

2.2. What is work? Describe an experiment that can measure the amount of work. What is heat? Describe an apparatus that can be used to measure heat. Are work and heat properties of a system?

2.3. Expand Eqs. (2.1a, 2.1b) and (2.2a) in terms of the rate of energy and entropy change of an open system, which is subjected to work output, heat interactions, and multiple inlets and outlets of steady flow.

2.4. Discuss the remarks of Rudolf Clausius in 1867:

    (a) The energy of the universe is constant.

    (b) The entropy of the universe strives to attain a maximum value.

2.5. For a cyclic device experiencing heat interactions with reservoirs at $T_1, T_2, \ldots$, the Clausius inequality can be expressed as $\sum_i \frac{\delta Q_i}{T_i} \leq 0$ or $\oint \frac{\delta Q}{T} \leq 0$, regardless of whether the device produces or consumes work. Note that δQ is positive when heat is received by the device. Prove the Clausius inequality by applying the second law to a closed system.

2.6. In the stable-equilibrium states, the energy and the entropy of a solid are related by $E = 3 \times 10^5 \exp\left(\frac{S-S_0}{1000}\right)$, where E is in J, S is in J/K, and S_0 is the

entropy of the solid at a reference temperature of 300 K. Plot this relation in an E–S graph. Find expressions for E and S in terms of its temperature T and $S0$.

2.7. For an isolated system, give the mathematical expressions of the first and second laws of thermodynamics. Give graphic illustrations using E–S graph.

2.8. Place two identical metal blocks A and B, initially at different temperatures, in contact with each other but without interactions with any other systems. Assume thermal equilibrium is reached quickly and let system C represents the combined system of both A and B.

(a) Is the process reversible or not? Which system has experienced a spontaneous change of state? Which systems have experienced an induced change of state?

(b) Assume that the specific heat of the metal is independent of temperature, $c_p = 240$ J/kg K, the initial temperatures are $T_{A1} = 800$ K and $T_{B1} = 200$ K, and the mass of each block is 5 kg. What is the final temperature? What is the total entropy generation in this process?

(c) Show the initial and final states of systems A, B, and C in a u–s diagram, and indicate which state is not an equilibrium state. Determine the adiabatic availability of system C in the initial state.

2.9. Two blocks made of the same material with the same mass are allowed to interact with each other but isolated from the surroundings. Initially, block A is at 800 K and block B at 200 K. Assuming that the specific heat is independent of temperature, show that the final equilibrium temperature is 500 K. Determine the maximum and minimum entropies that may be transferred from block A to block B.

2.10. A cyclic machine receives 325 kJ heat from a 1000 K reservoir and rejects 125 kJ heat to a 400 K reservoir in a cycle that produces 200 kJ work. Is this cycle reversible, irreversible, or impossible?

2.11. If $z = z(x, y)$, then $dz = f dx + g dy$, where $f(x, y) = \partial z/\partial x$, $g(x, y) = \partial z/\partial y$. Therefore, $\frac{\partial f}{\partial y} = \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial g}{\partial x}$. The second-order derivatives of the fundamental equation and each of the characteristic function yield a Maxwell relation. Maxwell's relations are very useful for evaluating the properties of a system in the stable-equilibrium states. For a closed system without chemical reactions, we have $dN_i \equiv 0$. Show that $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$, $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, and $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$.

2.12. The *isobaric volume expansion coefficient* is defined as $\beta_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$, the isothermal compressibility is $\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$, and the *speed of sound* is $v_a = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_S}$. For an ideal gas, show that $\beta_P = 1/T$, $\kappa_T = 1/P$, and $v_a = \sqrt{\gamma RT}$.

2.13. For a system with single type of constituents, the fundamental relation obtained by experiments gives $S = \alpha(NVU)^{1/3}$, where α is a positive constant, and $N, V, S,$ and U are the number of molecules, the volume, the entropy,

and the internal energy of the system, respectively. Obtain expressions of the temperature and the pressure in terms of N, V, U, and α. Show that $S = 0$ at zero temperature for constant N and V.

2.14. For blackbody radiation in an evacuated enclosure of uniform wall temperature T, the energy density can be expressed as $u_v = \frac{U}{V} = \frac{4}{c}\sigma_{SB}T^4$, where U is the internal energy, V the volume, c the speed of light, and σ_{SB} the Stefan–Boltzmann constant. Determine the entropy $S(T, V)$ and the pressure $P(T, V)$, which is called the *radiation pressure*. Show that the radiation pressure is a function of temperature only and negligibly small at moderate temperatures. Hint: $S = \int_0^T \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT$ and $P = T\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial U}{\partial V}\right)_T$.

2.15. A cyclic machine can only interact with two reservoirs at temperatures $T_A = 298$ K and $T_B = 77.3$ K, respectively.

  (a) If heat is extracted from reservoir A at a rate of $\dot{Q} = 1000$ W, what is the maximum rate of work that can be generated ($\dot{W}_{max}$)?
  (b) If no work is produced, what is the rate of entropy generation ($\dot{S}_{gen}$) of the cyclic machine?
  (c) Plot $\dot{S}_{gen}$ versus $\dot{W}$ (the power produced).

2.16. An engineer claimed that it requires much more work to remove 0.1 J of heat from a cryogenic chamber at an absolute temperature of 0.1 K than to remove 270 J of heat from a refrigerator at 270 K. Assuming that the environment is at 300 K, justify this claim by calculating the minimum work required for each refrigeration task.

2.17. A solid block [$m = 10$ kg and $c_p = 0.5$ kJ/kg K], initially at room temperature ($T_{A,1} = 300$ K) is cooled with a large tank of liquid–gas mixture of nitrogen at $T_B = 77.3$ K and atmospheric pressure.

  (a) After the block reaches the liquid nitrogen temperature, what is the total entropy generation Sgen?
  (b) Given the specific enthalpy of evaporation of nitrogen, $h_{fg} = 198.8$ kJ/kg, what must be its specific entropy of evaporation s_{fg} in kJ/kg K, in order for the nitrogen tank to be modeled as a reservoir? Does $h_{fg} = T_{sat} \times s_{fg}$ always hold?

2.18. Two same-size solid blocks of the same material are isolated from other systems [specific heat $c_p = 2$ kJ/kg K; mass $m = 5$ kg]. Initially, block A is at a temperature $T_{A1} = 300$ K and block B at $T_{B1} = 1000$ K.

  (a) If the two blocks are put together, what will be the equilibrium temperature (T_2) and how much entropy will be generated (S_{gen})?
  (b) If the two blocks are connected with a cyclic machine, what is the maximum work that can be obtained (W_{max})? What would be the final temperature of the blocks (T_3) if the maximum work was obtained?

2.19. A rock [density $\rho = 2800$ kg/m^3 and specific heat $c_p = 900$ J/kg K] of 0.8 m^3 is heated to 500 K using solar energy. A heat engine (cyclic machine) receives

heat from the rock and rejects heat to the ambient at 290 K. The rock therefore cools down.

(a) Find the maximum energy (heat) that the rock can give out.
(b) Find the maximum work that can be done by the heat engine, W_{max}.
(c) (c) In an actual process, the final temperature of the rock is 330 K and the work output from the engine is only half of W_{max}. Determine the entropy generation of the actual process.

2.20. Consider three identical solid blocks with a mass of 5 kg each, initially at 300, 600, and 900 K, respectively. The specific heat of the material is $c_p = 2000$ J/kg K. A cyclic machine is available that can interact only with the three blocks.

(a) What is the maximum work that can be produced? What are the final temperatures of each block? Is the final state in equilibrium?
(b) If no work is produced, i.e., simply putting the three blocks together, what will be the maximum entropy generation? What will be the final temperature?
(c) If the three blocks are allowed to interact via cyclic machine but not with any other systems in the environment, what is the highest temperature that can be reached by one of the blocks?
(d) If the three blocks are allowed to interact via cyclic machine but not with any other systems in the environment, what is the lowest temperature that can be reached by one of the blocks?

2.21. Electrical power is used to raise the temperature of a 500 kg rock from 25 to 500 °C. The specific heat of the rock material is $c_p = 0.85$ kJ/kg K.

(a) If the rock is heated directly through resistive (Joule) heating, how much electrical energy is needed? Is this process reversible? If not, how much entropy is generated in this process?
(b) By using cyclic devices that can interact with both the rock and the environment at 25 °C, what is the minimum electrical energy required?

2.22. An insulated cylinder of 2 m^3 is divided into two parts of equal volume by an initially locked piston. Side A contains air at 300 K and 200 kPa; side B contains air at 1500 K and 1 MPa. The piston is now unlocked so that it is free to move and it conducts heat. An equilibrium state is reached between the two sides after a while.

(a) Find the masses in both A and B.
(b) Find the final temperatures, pressures, and volumes for both A and B.
(c) Find the entropy generation in this process.

2.23. A piston–cylinder contains 0.56 kg of N_2 gas, initially at 600 K. A cyclic machine receives heat from the cylinder and releases heat to the environment at 300 K. Assume that the specific heat of N_2 is $c_p = 1.06$ kJ/kg K, and the pressure inside the cylinder is maintained at 100 kPa by the environment.

What is the maximum work that can be produced by the machine? What is the thermal efficiency (defined as the ratio of the work output to the heat received)? The thermodynamic efficiency can be defined as the ratio of the actual work produced to the maximum work. Plot the thermodynamic efficiency as a function of the entropy generation. What is the maximum entropy generation?

2.24. An airstream [$c_p = 1$ kJ/kg K and $M = 29.1$ kg/kmol] flows through a power plant. The stream enters a turbine at $T_1 = 750$ K and $P_1 = 6$ MPa, and exits at $P_2 = 1.2$ MPa into a recovery unit, which can exchange heat with the environment at 25 °C and 100 kPa. The stream then exits the recovery unit to the environment. The turbine is thermally insulated and has an efficiency $\eta_t = 0.85$.

  (a) Find the power per unit mass flow rate produced by the turbine.
  (b) Calculate the entropy generation rate in the turbine.
  (c) Determine the largest power that can be produced by the recovery unit.

2.25. Water flows in a perfectly insulated, steady-state, horizontal duct of variable cross-sectional area. Measurements were taken at two ports, and the data were recorded in a notebook as follows. For port 1, speed $\xi_1 = 3$ m/s, pressure $P_1 = 50$ kPa, and temperature $T_1 = 40$ °C; for port 2, $\xi_2 = 5$ m/s and $P_2 = 45$ kPa. Some information was accidentally left out by the student taking the notes. Can you determine $T2$ and the direction of the flow based on the available information? Hint: Model the water as an ideal incompressible liquid with $c_p = 4.2$ kJ/kg) and specific volume $v = 10^{-3}$ m³/kg.

2.26. An insulated rigid vessel contains 0.4 kmol of oxygen at 200 kPa separated by a membrane from 0.6 kmol of carbon dioxide at 400 kPa; both sides are initially at 300 K. The membrane is suddenly broken and, after a while, the mixture comes to a uniform state (equilibrium).

  (a) Find the final temperature and pressure of the mixture.
  (b) Determine the entropy generation due to irreversibility.

2.27. Pure N_2 and air (21% O_2 and 79% N_2 by volume), both at 298 K and 120 kPa, enter a chamber at a flow rate of 0.1 and 0.3 kmol/s, respectively. The new mixture leaves the chamber at the same temperature and pressure as the incoming streams.

  (a) What are the mole fractions and the mass fractions of N_2 and O_2 at the exit?
  (b) Find the enthalpy change in the mixing process. Find the entropy generation rate of the mixing process.
  (c) Consider a process in which the flow directions are reversed. The chamber now contains necessary devices for the separation, and it may transfer heat to the environment at 298 K. What is the minimum amount of work per unit time needed to operate the separation devices?

2.28. A Carnot engine receives energy from a reservoir at T_H and rejects heat to the environment at T_0 via a heat exchanger. The engine works reversibly between T_H and T_L, where T_L is the temperature of the higher temperature side of the heat exchanger. The *product* of the area and the heat transfer coefficient of the heat exchanger is α. Therefore, the heat that must be rejected to the environment through the heat exchanger is $\dot{Q}_L = \alpha(T_L - T_0)$. Given $T_H = 800$ K, $T_0 = 300$ K, and $\alpha = 2300$ W/K. Determine the value of T_L so that the heat engine will produce maximum work, and calculate the power production and the entropy generation in such a case.

2.29. To measure the thermal conductivity, a thin film electric heater is sandwiched between two plates whose sides are well insulated. Each plate has an area of 0.1 m^2 and a thickness of 0.05 m. The outside of the plates are exposed to air at $T_\infty = 25$ °C with a convection coefficient of $h = 40$ W/m^2 K. The electric power of the heat is 400 W and a thermocouple inserted between the two plates measures a temperature of $T_1 = 175$ °C at steady state. Determine the thermal conductivity of the plate material. Find the total entropy generation rate. Comment on the fraction of entropy generation due to conduction and convection.

2.30. An electric current, $I = 2$ A, passes through a resistive wire of diameter $D = 3$ mm with a resistivity $r_e = 1.5 \times 10^{-4}$ Ω m. The cable is placed in ambient air at 27 °C with a convection coefficient $h = 20$ W/m^2 K. Assume a steady state has been reached and neglect radiation. Determine the radial temperature distribution inside the wire. Determine the volumetric entropy generation rate $\dot{s}_{gen}$ as a function of radius. Determine the total entropy generation rate per unit length of the cable. Hint: For steady-state conduction, $\dot{s}_{gen} = \frac{1}{T}\nabla \cdot \mathbf{q}'' - \frac{1}{T^2}\mathbf{q}'' \cdot \nabla T$. [Hint: Consider $\kappa = 10$ W/m K and $\kappa = 1$ W/m K.]

2.31. Find the thermal conductivity of intrinsic (undoped) silicon, heavily doped silicon, quartz, glass, diamond, graphite, and carbon from 100 to 1000 K from Touloukian and Ho [13]. Discuss the variations between different materials, crystalline structures, and doping concentrations.

2.32. Find the thermal conductivity of copper from 1 to 1000 K from Touloukian and Ho [13]. Discuss the general trend in terms of temperature dependence, and comment on the effect of impurities.

2.33. For laminar flow over a flat plate, the velocity and thermal boundary layer thicknesses can be calculated by $\delta(x) = 5x/\sqrt{Re_x}$ and $\delta_t(x) = 5x\,Re_x^{-1/2}Pr^{-1/3}$, respectively. Use room temperature data to calculate and plot the boundary layer thicknesses for air, water, engine oil, and mercury for different values of U_∞. Discuss the main features. Hint: Property data can be found from Incropera and DeWitt [11].

2.34. Air at 14 °C and atmospheric pressure is in parallel flow over a flat plate of 2×2 m^2. The air velocity is 3 m/s, and the surface is maintained at 140 °C. Determine the average convection coefficient and the rate of heat transfer from the plate to air. (For air at 350 K, which is the average temperature between the surface and fluid, $\kappa = 0.03$ W/m K, $\nu = 20.9 \times 10^{-6}$ m^2/s, and $Pr = 0.7$.)

2.35. Plot the blackbody intensity (Planck's law) as a function of wavelength for several temperatures. Discuss the main features of this function. Show that in the long-wavelength limit, the blackbody function can be approximated by $e_{b,\lambda}(\lambda, T) \approx 2\pi c k_B T/\lambda^4$, which is the Rayleigh–Jeans formula.

2.36. Calculate the net radiative heat flux from the human body at a surface temperature of $T_s = 308$ K, with an emissivity $\varepsilon = 0.9$, to the room walls at 298 K. Assume air is at 298 K and has a natural convection coefficient of 5 W/m^2 K. Neglect evaporation, calculate the natural convection heat flux from the person to air. Comment on the significance of thermal radiation.

2.37. Combustion occurs in a spherical enclosure of diameter $D = 50$ cm with a constant wall temperature of 600 K. The temperature of the combustion gases may be approximated as uniform at 2300 K. The absorption coefficient of the gas mixture is $a_\lambda = 0.01$ cm^{-1}, which is independent of wavelength. Assuming that the wall is black and neglecting the scattering effect, determine the net heat transfer rate between the gas and the inner wall of the sphere.

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