1

The First Law of Thermodynamics

1.1 ELEMENTS OF THERMODYNAMICS TERMINOLOGY

The first step in the thermodynamic analysis of anything must be the definition of the entity that is being subjected to analysis. We refer to this entity (collection of matter, region in space) as a *system.* Although the need for executing this first move and for doing it once and unambiguously is obvious, the temptation is great to assume the system definition itself obvious and omit it. This is a source of confusion, if not outright error. Paradoxical differences between two results claimed by two experts who attack "the same problem" are often explained by the realization that the two problem solvers were mentally addressing different systems. As we will see very soon, the precise definition of the system is critical when determining the location and magnitude of thermodynamic irreversibility.

The tendency to forget to define the system is due mainly to tradition. In considerably older disciplines such as solid-body mechanics, the system is indeed obvious, as the mere sketching of a body focuses the attention of both problem solver and critic. In fluid mechanics and heat transfer, the system is again understood once the boundary conditions necessary for solving the Navier–Stokes equations are specified. However, even in fluid mechanics and heat transfer, the unambiguous definition of the system is a must if the method is order of magnitude or *scale analysis* [1]—that is, if the analyst replaces the Navier–Stokes equations with approximate algebraic statements that cannot be subjected to boundary conditions.

To define the system means also to identify sharply the system's *environment,* or *surroundings.* The environment is the portion of matter or region in space that resides outside the system selected for analysis. What differentiates between the system and its environment is the surface called *boundary.* One very important defining feature that sometimes falls prey to the same forces of tradition is that the boundary is a surface, not another system (note that the thickness of a surface is zero; therefore, the boundary can neither contain matter nor fill a volume in space). Said another way, the value of a property that is measured at a point on the surface called boundary must be shared by both the system and the environment because, after all, the system and the environment are in contact at that point.

To see the importance of this observation, consider the heat interaction Q between two fluid masses whose absolute temperatures are different, $T_H > T_L$. The thermal conductivities of the two fluids (or their states of agitation) are such that each fluid can be regarded as isothermal. The temperature drop $T_H - T_L$ occurs through the wall. If the wall thickness is small relative to the size of the fluid masses (e.g., the skin of a hot-air balloon in flight), it is tempting to regard the wall as the boundary between, say, the system (T_H) and the environment (T_L). This incorrect choice is shown in Fig. 1.1. Its drawback is that unlike the heat transfer Q, the entropy transfer Q/T is not conserved as it passes through the boundary. If made, this choice serves as a permanent source of confusion: The unexperienced analyst has trouble deciding whether to use T_H or T_L in the denominator of Q/T, and the engineering component that is responsible for the generation of entropy (S_{gen}) is effectively hidden from view. The capricious augmentation of entropy transfer through "boundaries" of the kind shown in Fig. 1.1 perpetuates the mystery that surrounds the concepts of entropy, entropy transfer, and entropy generation.

Proper ways to select a system boundary between the masses T_H and T_L are exhibited in Fig. 1.2*a*–*c*. Because the temperature varies continuously across each boundary, the heat transfer and the entropy transfer are conserved. In Fig. 1.2*a* the wall (the temperature drop) is situated outside the T_H system, and for this reason the entropy generation due to the system–environment heat interaction can be termed "external." The opposite choice is made in Fig. 1.2*b*, where the entropy-generation effect is "internal" relative to the T_H system. Figure 1.2*c* shows that the system can be divided further into sub-

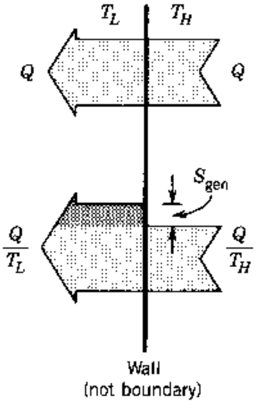

Figure 1.1 Discontinuity of entropy transfer through an incorrect boundary.

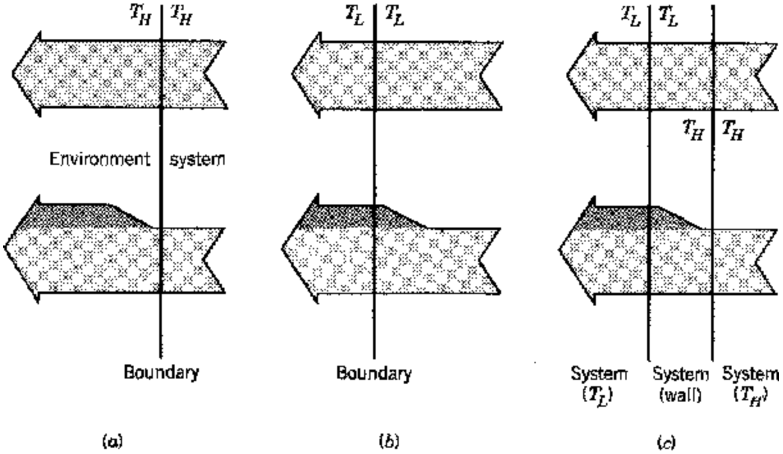

Figure 1.2 Continuity of entropy transfer, heat transfer, and temperature through correct boundaries.

systems if the precise identification of the source of entropy generation (the wall) is one of the objectives of the thermodynamic analysis.

The observation that properties must vary continuously across the surface chosen as boundary is general. The discontinuity of absolute temperature was used in Fig. 1.1 only for the purpose of illustration.

The boundary and the interactions that are present at the boundary play roles in the structure (organization) of the analysis devoted to solving a problem. One feature that must be recognized at an early stage is whether the boundary is crossed by the flow of mass. A system defined by a boundary impermeable to mass flow is a *closed system.* Most of the systems discussed in connection with the establishment of relationships between thermodynamic properties at equilibrium are closed systems (Chapters 4, 6, and 7). Conversely, systems whose defining boundaries can be crossed by the flow of mass are *open systems,* or *flow systems.* The engineering thermodynamics of open systems often relies on a special terminology; for example, the thermodynamic system itself is referred to as the *control volume,* the system boundary is the *control surface,* and the particular patches of the boundary that are crossed by mass flow are the *inlet* and *outlet ports.*

The condition, or the being, of a thermodynamic system at a particular point in time is described by an ensemble of quantities called *thermodynamic properties.* We refer to the condition described by properties as *state.* Not all the quantities (numerical values) that the analyst calculates in connection with a certain system are thermodynamic properties. Thermodynamic properties are only those quantities whose numerical values do not depend on the history of the system, as the system evolves between two different states. Quantities such as pressure and temperature are properties because their values depend strictly on the instantaneous condition during which they are measured. Examples of quantities that are not thermodynamic properties are work, heat and mass transfer, entropy transfer, entropy generation (Fig. 1.2), lost available work, and lost exergy.

The thermodynamic properties that we encounter in engineering are quite numerous: It seems that each generation has added to the list one or more new properties that proved to be useful relative to the engineering challenges of the period. Some properties can be measured directly (e.g., pressure, temperature, volume), whereas others can be derived based on such measurements (e.g., internal energy, entropy, enthalpy, exergy). Thermodynamic properties whose values depend on the size of the system are called *extensive properties* (e.g., volume, entropy, internal energy). *Intensive properties* are those whose values do not depend on the size of the system: for example, pressure and temperature. The collection of all the intensive properties of a system constitutes the *intensive state.*

A certain *phase* of a system is the collection of all the parts of the system that have the same intensive state and the same per-unit-mass values of the extensive properties. For example, liquid droplets dispersed in a liquid–vapor mixture in equilibrium have the same pressure, temperature, specific volume, specific enthalpy, and so on; taken together, the droplets represent the liquid phase.

Finally, we use the concept of *process* as a one-word reference to the change of state from an initial state to a final state. To know the process means to know not only the end states but also the *interactions* experienced by the system while in communication with its environment (e.g., work transfer, heat transfer, entropy transfer, mass transfer). The *path* of the process is the history, or the succession of states, followed by the system from the initial to the final state. Stressing again the fundamental difference between thermodynamic properties and quantities that are not properties, note that the changes in nonproperties depend not only on the end states but also on the path.

The thermodynamic *cycle* is a special process in which the final state coincides with the initial state. Starting with Sadi Carnot's 1824 memoir [2], the concept of cycle evolved into a key concept in the field of power engineering and a vehicle for logical deduction in thermodynamics theory.

1.2 THE FIRST LAW FOR CLOSED SYSTEMS

Two principles of classical thermodynamics must be stressed in an advanced treatment such as this. One principle is the equivalence of work transfer and heat transfer as possible forms of energy interactions. This principle is encapsulated in the First Law of Thermodynamics, which, in Max Planck's words, "is nothing more than the principle of the conservation of energy applied to phenomena involving the production or absorption of heat" [3].

The second principle is the inherent irreversibility of all processes that occur in nature. Everything flows in one direction, from high to low. It is the irreversibility, or the generation of entropy, that prevents humans from extracting the most possible work from various processes and from doing the most with the work that is already at our disposal. This second principle is summarized by the Second Law of Thermodynamics.

Traditionally, the first law is discussed first and the second law second. This ordering is based apparently on views—both questionable—that the first law is older than the second law and that the concept of internal energy defined by the first law is somehow easier to grasp than the concept of entropy introduced by the second law. The first view is fueled by the misinterpretation of statements of the kind quoted from Max Planck in the preceding paragraph: What is relatively older than the second law is the principle of conservation of energy known in mechanics, not the First Law of Thermodynamics. The first and second laws *emerged together* from the writings of William John MacQuorn Rankine, Rudolph Clausius, and William Thomson (Lord Kelvin) in the early 1850s (consult Ref. 4): They *had to* emerge together in order to resolve the conflict between Sadi Carnot's theory, which assumed the conservation of "caloric," and the growing evidence that work through friction can serve as an endless source of caloric. The second view—the feeling that internal energy is easier to understand than entropy—is again fueled by the engineer's relative familiarity with the aging concept of mechanical energy, not with internal energy.

The questioning of tradition aside, in this treatment I also start with the first law because, above all, this is a review of the student's first encounter with engineering thermodynamics, not a review of the history of the subject. Note that a number of captivating historical accounts already exist in book form [4–7] or in certain prefaces and introductions that convey some of the historical flavor [8–10]. Further observations on the historical development of the First Law of Thermodynamics are presented at the end of the chapter.

Consider the closed system shown schematically in Fig. 1.3: If this system experiences a change of state from the initial state (1) to the final state (2), the First Law of Thermodynamics requires that

$$\underbrace{\underset{\substack{\text{Heat}\\\text{transfer}}}{Q_{1-2}} - \underset{\substack{\text{Work}\\\text{transfer}}}{W_{1-2}}}_{\substack{\text{Energy interactions}\\\text{(Nonproperties)}}} = \underbrace{E_2 - E_1}_{\substack{\text{Energy}\\\text{change}\\\text{(Property)}}} \tag{1.1}$$

The difference between the net heat input Q_{1-2} and the net work output W_{1-2} represents the change in the thermodynamic property called energy. The first law proclaims the existence of energy as a thermodynamic property.

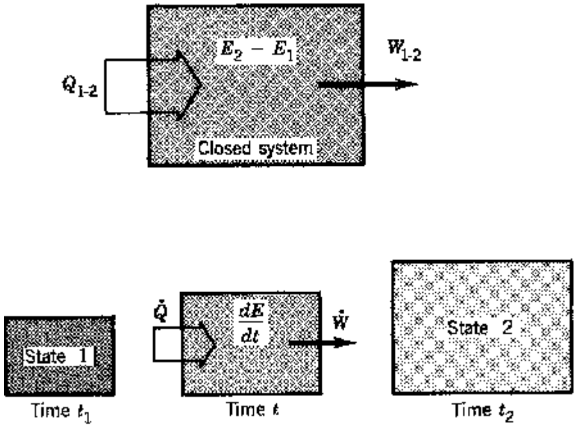

Figure 1.3 Graphic statements of the First Law of Thermodynamics for closed systems.

Evident in eq. (1.1) and Fig. 1.3 is the use of the *heat-engine sign convention* [11], whereby the heat transfer into the system and the work transfer out of the system are considered positive. This is a "heat-engine" sign convention because the purpose of a heat engine as a closed thermodynamic system is to deliver work to its environment. This sign convention is used consistently throughout the present treatment.

The energy change $E_2 - E_1$ depends only on the end states, whereas the energy interactions Q_{1-2} and W_{1-2} depend on the end states and the path of the process that links the end states. This important distinction is stressed with reference to the concept of property under each term appearing in eq. (1.1). Another way to stress this difference is to use a different notation for the infinitesimal increments in work and heat transfer relative to the exact differential notation that applies to the infinitesimal change in E. For this reason, the first law for a process between two states situated infinitely close to one another is written as

$$\delta Q - \delta W = dE \tag{1.2}$$

In the same notation, the energy interactions that appear on the left side of eq. (1.1) are

$$Q_{1-2} = \int_1^2 \delta Q \qquad \text{and} \qquad W_{1-2} = \int_1^2 \delta W \tag{1.3}$$

The peculiar notation "δ" may not be the ideal way to emphasize the difference between energy interactions and energy change. The alternative used by Truesdell [12] consists of introducing the concept of time in the description of the process (see the bottom of Fig. 1.3). In this new description, state (1) is the condition of the system at time t_1, state (2) is the condition at time t_2, and the net energy interactions Q_{1-2} and W_{1-2} are the time integrals

$$Q_{1-2} = \int_{t_1}^{t_2} \dot{Q}\, dt, \qquad W_{1-2} = \int_{t_1}^{t_2} \dot{W}\, dt \tag{1.4}$$

Quantities $\dot{Q}$ and $\dot{W}$ are the instantaneous heat transfer rate and the mechanical-power output, respectively (note that the $\dot{Q}$ and $\dot{W}$ notations are used routinely in the analysis of open systems in steady flow). By using the notation of eqs. (1.4), the First Law of Thermodynamics for a closed system can be written on a per-unit-time basis as

$$\dot{Q} - \dot{W} = \frac{dE}{dt} \tag{1.5}$$

Another way of stressing the path dependence of Q_{1-2} and W_{1-2} (or $\dot{Q}$ and $\dot{W}$) is presented graphically in Fig. 1.4 (see also Ref. 13). The system can proceed from state (1) to state (2) along an infinity of paths: for example, along paths A and B. Assuming that paths A and B are such that Q_{1-2}, W_{1-2}, and $E_2 - E_1$ are all positive, the first-law statement (1.1) requires stacking the three building blocks shown in Fig. 1.4. Although the difference $Q_{1-2} - W_{1-2}$ matches $E_2 - E_1$ along both paths, the sizes of Q_{1-2} and W_{1-2} vary from one path to the next. If the process executed by the closed system is a cycle, the first-law statement (1.1) reduces to

$$\oint \delta Q - \oint \delta W = 0 \tag{1.6}$$

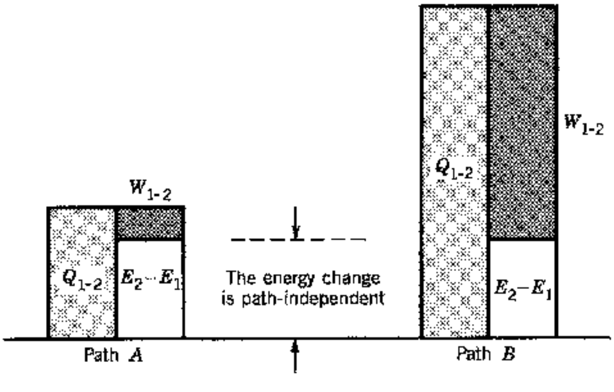

Figure 1.4 Path dependence of the energy interactions Q_{1-2} and W_{1-2}.

In other words, the white blocks in Fig. 1.4 shrink to zero thickness. This statement stresses again the difference between energy change and energy interactions: The latter depend on the path followed by the cycle.

1.3 WORK TRANSFER

The work interactions encountered most often in classical engineering thermodynamics are those associated with the displacement of the system's boundary in the presence of forces that act on the boundary. If **F** is the force experienced by the system at a certain point on its boundary (i.e., the force exerted by the environment on the system) and if $d\mathbf{r}$ is the infinitesimal displacement of the point of application, the infinitesimal work transfer is

$$\delta W = -\mathbf{F} \cdot d\mathbf{r} \tag{1.7}$$

Discussed already in connection with Fig. 1.3 is the convention that the work transfer is considered positive when the system does work on its environment; in other words, when the boundary displacement occurs against the force felt by the system, $\cos(\mathbf{F}, d\mathbf{r}) < 0$.

Two features must be present simultaneously if a system is to experience a work interaction with its environment: (1) A force must be present on the boundary, and (2) the point of application of this force (hence, the boundary) must move. The mere presence of forces on the boundary, without the displacement or the deformation of the boundary, does not amount to work transfer. Similarly, the occurrence of boundary displacement without a force opposing or driving this motion does not mean work transfer. For example, in the "free expansion" of a gas into an evacuated space, the gas as a closed system does not experience work transfer because the pressure is zero on the moving boundary.

One special application of expression (1.7) is encountered in the analytical description of the relations between the thermodynamic properties of a substance in equilibrium (Chapter 4). The same special form is also used routinely (however, only as an approximate engineering model) to estimate the work transfer when a batch of "working fluid" expands or contracts in a cylinder and piston apparatus. With reference to Fig. 1.5*a*, when the system is in equilibrium, the pressure P is uniform throughout the system; therefore, $-\mathbf{F} \cdot d\mathbf{r}$ can be replaced by $P\, dV$ in eq. (1.7):

$$\delta W_{\text{rev}} = P\, dV \tag{1.8}$$

The discussion of the subscript "rev," which stands for "reversible," is postponed until Chapter 2, where we review the concepts associated primarily with the Second Law of Thermodynamics. If eq. (1.8) is to be used to evaluate the work transfer transmitted through the movement of a piston, the pressure

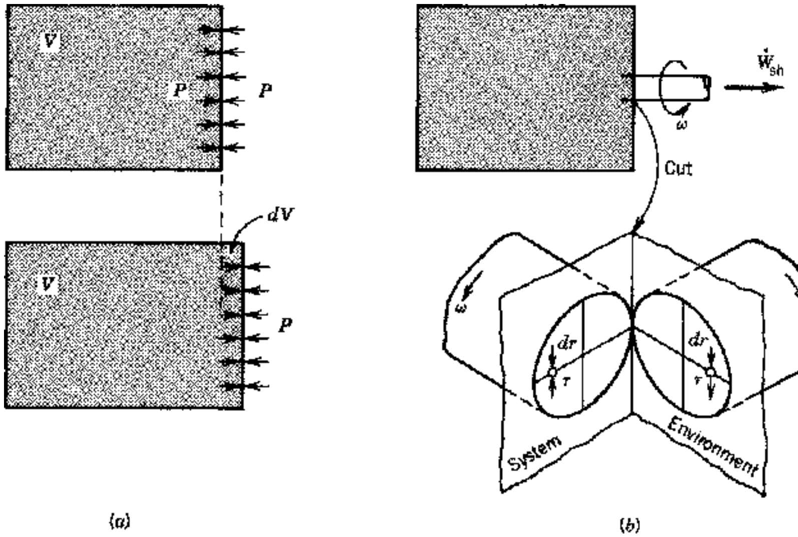

Figure 1.5 Examples of $P\ dV$ work transfer and shaft work transfer.

P at the boundary must be *known* at any instant during the volume change. This means that the analyst first has to solve the complete equations that govern convection inside the expanding fluid (i.e., the mass, momentum, and energy equations) in order to calculate the value of P versus time right on the moving boundary. However, in engineering thermodynamics the description is simpler: The engineer is taught to rely on eq. (1.8) to estimate the work transfer as the area under the $P(V)$ curve on Watt's famous "indicator diagram."[†] The assumption is that the expansion is slow enough so that the state of the fluid batch can be represented at all times by a single point in the two-dimensional plane P–V. In engineering thermodynamics, then, the requirement that P of eq. (1.8) must be known on the moving boundary is considerably more restrictive: The pressure P must also be instantaneously *uniform* throughout the expanding system.

The sufficiently slow process to which eq. (1.8) applies is called *quasistatic,* and the states along the path of such a process are *quasistatic states.* This terminology has served as a source of confusion—not that the word *quasistatic* is that difficult to grasp [literally, it means "seemingly (as if) static," which is an appropriate description for a process that is sufficiently slow], but because different schools of thermodynamics have attached different meanings to the word.

If we go back to the beginning of this century, we find that one influential author (Carathéodory) used *quasistatic* to describe an adiabatic process that

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[†] The mechanism for drawing this diagram was conceived by John Southern (see Fig. 2.1).

happens infinitely slowly so that it "can be regarded as a series of equilibrium states." Carathéodory was quite explicit in his argument that in systems in which rate-dependent processes (internal friction was his example) converge to zero as the pace of the process becomes infinitely slow, the quasistatic adiabatic process is reversible. Now, if we think of the simple systems that are of concern to us in the thermodynamics of power and refrigeration (i.e., batches of common gases and liquids—in other words, the same simple systems that were contemplated by the founders of classical thermodynamics), then, adiabatic or not, *any quasistatic process is a reversible process.* Carathéodory's special interest in adiabatic processes was essential only to his axiomatic reconstruction of classical thermodynamics, which consists of first ruling out heat transfer and, later, defining the heat transfer interaction as a derived concept (see Table 1.3).

Another interpretation of the words *quasistatic process* stops at the literal translation and stresses that an infinitely slow process is not necessarily a reversible process. There are two factors that fueled the emergence of this newer interpretation. First, it was the effort to generalize the science of thermodynamics to cover systems (bodies) whose internal constitution differs from that of the simple systems of the classical calorimetry–thermostatics line. Carathéodory noted that the quasistatic processes executed by substances in which the internal friction effect does not converge to zero are not reversible and that such substances would, in fact, require a new kind of thermodynamics.

The second reason is that by employing a mechanics-sounding name (quasi*static*) in a discussion that deliberately avoids the concept of heat transfer, Carathéodory left the impression that the infinite slowness implied by the word *quasistatic* refers only to the time scale of mechanical effects, say, to the time needed for the pressure to become uniform inside a working cylinder and piston expander. Obviously, if heat transfer takes place through the cylinder wall lined by the system boundary, temperature gradients and irreversibility will be present inside the system. Since the effect of thermal diffusion has a time scale that generally speaking is not the same as the scale of viscous slowdown or the scale of the imposed volume change, the process is not a sequence of equilibrium states even though it may be slow enough to be called quasistatic. Therefore, according to the newer interpretation, the concept of a reversible process is more restrictive than the concept of a quasistatic process: All the reversible processes are quasistatic, but not all the quasistatic processes are reversible.

As a summary to the two competing interpretations, the best I can do is to warn the engineer that the potential for confusion exists and that, because of this potential, the best course is to avoid using the word *quasistatic.* If the process is sufficiently slow so that it can be viewed as a sequence of equilibrium states, the process is reversible. If for any reason the intermediate states visited during the process cannot be regarded as equilibrium states (i.e., if each state cannot be represented as one point in a two-dimensional plane such as the P–v diagram of Fig. 2.2), the process is not reversible.

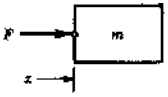
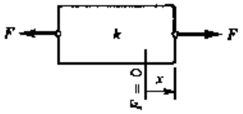
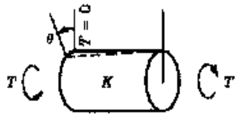
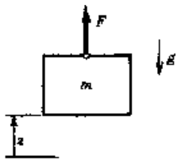
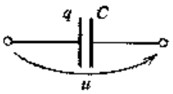
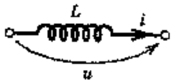
Another mode of work transfer that is very common in engineering applications is the shaft work W_{sh} transmitted through a shaft that penetrates through the system boundary. The origin of this work transfer mode may seem mysterious to the problem solver in view of (1) the exclusive use of the $P\,dV$ work transfer mode in thermodynamics, and (2) definition (1.7) and the fact that the boundary surface does not move. To clarify this issue, Fig. 1.5*b* shows the cut made by the boundary through the shaft. In the shaft cross section that is attached to the system, the point of application of each shear stress vector $\boldsymbol{\tau}$ moves as the shaft turns. By integrating the work done by each shear stress over the cross section [i.e., by applying definition (1.7)], it is easy to show that the infinitesimal work transfer δW_{sh} is equal to the angular displacement times the torque with which the environment opposes the turning of the shaft (or that the shaft power output $\dot{W}_{\text{sh}}$ is equal to the angular speed ω times the same torque).

Based on this discussion of Fig. 1.5*b* and on the coincidence that in English the words *shaft* and *shear* admit the same abbreviation, the symbol W_{sh} can also be used as notation for "shear work transfer." An example of work transfer associated with shear forces occurs in the derivation of the First Law of Thermodynamics for an infinitesimally small control volume in a flow field (e.g., 1, Chap. 1). An example of shear forces that although present along the system's boundary do not account for any shear work transfer is the distribution of shear stresses caused by fluid friction against a rigid wall that confines a fluid in motion. In this case, the work transfer is zero because the point of application of each shear force is stationary.

A more general definition of work transfer that also applies to electrical and magnetic work interactions was formulated by Hatsopoulos and Keenan [9, p. 22]: "Work is an interaction between two systems such that what happens in each system at the interaction boundary could be repeated while the sole effect external to each system was the change in level of a weight." Analogous definitions can be formulated in terms of the energy stored in a translational spring or in another conservative mechanical system. Hatsopoulos and Keenan refer to a footnote in Gibbs' second paper [14] as the origin of the idea behind their general definition of work transfer interactions. Furthermore, it has been standard engineering practice to evaluate the capacity of an engine in terms of the height to which it could raise a given weight [15]. Indeed, the weight lifted to a height was the British engineer's common unit of "duty" in the description of the early steam engines (Fig. 2.1).

The concept of *reversible* work transfer can be envisioned not only in the context of systems that expand or contract quasistatically [eq. (1.8)] but also for systems that can experience other modes of work transfer. A collection of such work interactions is presented in Table 1.1 next to examples of very simple mechanical and electrical systems whose energy storage capability is

TABLE 1.1 Examples of Simple (Uncoupled) Forms of Energy Storage and Corresponding Work Interactions

Macroscopic Forms of Energy Storage, $(E_2 - E_1)_i$ [Eq. (1.13)]	Relation Assumed in Writing Each $(E_2 - E_1)_i$ Expression	Infinitesimal Work Transfer, δW [Eq. (1.8)]	Notation
Kinetic, translational			
$\frac{1}{2} mV_2^2 - \frac{1}{2} mV_1^2$	$F = m \dfrac{dV}{dt}$	$-F\ dx$	
Kinetic, rotational			
$\frac{1}{2} J\omega_2^2 - \frac{1}{2} J\omega_1^2$	$T = J \dfrac{d\omega}{dt}$	$-T\ d\theta$	
Spring, translational			
$\frac{1}{2} kx_2^2 - \frac{1}{2} kx_1^2$	$F = kx$	$-F\ dx$	
Spring, rotational			
$\frac{1}{2} K\theta_2^2 - \frac{1}{2} K\theta_1^2$	$T = K\theta$	$-T\ d\theta$	
Gravitational spring (or constant-force translational spring)			
$mgz_2 - mgz_1$	$F = mg$	$-F\ dz$	
Electrical capacitance			
$\dfrac{1}{2}\dfrac{q^2}{C} = \dfrac{1}{2} Cu^2$	$u = \dfrac{q}{C}$	$-u\ dq$	
Electrical inductance			
$\dfrac{1}{2} Li^2 = \dfrac{1}{2}\dfrac{\Phi^2}{L}$	$\Phi = Li$	$-i\ d\Phi$	

the subject of the discussion that ends this section (and is the reason for constructing the table). It is sufficient to note that for systems that are capable of experiencing more than one work interaction, eq. (1.8) can be replaced by

$$\delta W_{\text{rev}} = - \sum_i Y_i \, dX_i \tag{1.8'}$$

The terms Y_i and X_i are *the generalized forces* and *the generalized displacements* (or *deformation* coordinates), respectively. The units of these quantities are not necessarily those of force and displacement. In this somewhat abstract terminology, it is the negative of the pressure P that plays the role of generalized force in the reversible work done by closed systems that expand quasistatically.

1.4 HEAT TRANSFER

The First Law of Thermodynamics does not distinguish between heat transfer and work transfer as two possible forms of energy interaction between a system and its environment. Indeed, the role of the first law is to place heat interaction and work interaction *on an equal footing.* In the earliest analytical statements of the first law made by Clausius and adopted by contemporary engineers, the work transfer and the energy change terms appear on the same side of the equal sign [16,17]. Clausius's arrangement of the terms was also adopted by Poincaré in his thermodynamics course taught in 1888–1889 at the Faculty of Sciences of the University of Paris [18]. These early works and their appearance are worth keeping in mind: Like Planck's [3] and Zeuner's [17] courses among the physicists and engineers educated in the German language, Poincaré's course [18] emerged as a dominant factor in the practice and writing of thermodynamics in the first half of the twentieth century.

The fundamental distinction between heat transfer and work transfer is made by the Second Law of Thermodynamics: Heat transfer is the energy interaction accompanied by entropy transfer, whereas work transfer is the energy interaction that takes place in the absence of entropy transfer. If this way of distinguishing δQ from δW sounds abstract, it is simply because the second law and related concepts such as entropy transfer are usually not practiced in the problems proposed during a first course in engineering thermodynamics. Nevertheless, it is a rigorous definition that has the additional benefit that it draws attention to the existence of entropy transfer of type $\delta Q/T$, where T is the thermodynamic (absolute) temperature of the boundary crossed by δQ (Fig. 1.2).

The intuitively more appealing description of heat transfer preferred by most engineering treatments of thermodynamics originated with Poincaré's course [18]: Heat transfer is the energy interaction driven by the temperature difference between the system and its environment. The same view has been held from the beginning in the field of heat transfer. The phenomenological treatment of heat transfer initiated by Poincaré makes sense because it appeals to the familiarity of modern man with the concepts of heating and temperature. Yet the phenomenological description has been criticized by those who favor a precise definition of each word that appears in the thermodynamics language. The challenge faced so successfully by Poincaré was not to "define" terminology to an audience already familiar with the essence of classical thermodynamics, but rather, to communicate and explain a new theory that had gelled only two decades earlier and was still unknown to waves of would-be inventors. To do this, Poincaré used (or misused) very effectively the terminology of his time.

No matter how rigorous the treatment and how strong the desire to pin the definition of each new concept on the definitions of older concepts, sooner or later the engineer must speak of thermal equilibrium and temperature. To review what is meant by *thermal equilibrium,* consider two closed systems whose boundaries are such that both systems cannot experience work transfer (e.g., two arbitrary amounts of air sealed in rigid containers, where *arbitrary* means that the mass, volume, and pressure of each system are not specified). If two systems of this kind are positioned close to one another, it is generally observed that changes are induced in both systems. In the air-filled containers of the example above, these changes can be documented by recording the air pressure versus time. It is commonly observed that there exists a time interval beyond which the changes triggered by the proximity of the two systems cease. The condition of the closed system is said to be one of *equilibrium* when after a sufficiently long period, changes cease to occur inside the system. In particular, when the closed system is incapable of experiencing work interactions, the condition is one of *thermal equilibrium.*

Let A and B be the closed systems that interact and reach thermal equilibrium in the preceding example. The same experiment can be repeated using system A and a third system C, which is also closed and unfit for work transfer. It is also a matter of common experience that if systems B and C are individually in thermal equilibrium with system A, then when placed in direct communication, systems B and C do not undergo any changes as time passes. This second observation can be summarized as follows: If systems B and C are separately in thermal equilibrium with a third system, they are in thermal equilibrium with each other. It was stressed more than a century ago by Maxwell that this summarizing statement carries the weight of physical law. After Maxwell's death, in fact more than half a century after the formulation and labeling of the First and Second Laws of Thermodynamics, this view has come to be recognized as the *Zeroth Law of Thermodynamics.* The zeroth law was first formulated and labeled in 1931 by Fowler [19].

Each law of thermodynamics can be thought of as a way to define a new system property: for example, the internal energy via the first law and the entropy via the second law. In this sense, the zeroth law defines the thermodynamic property called *temperature.* Returning to the vast experimental evidence on which the zeroth law and the much older science of thermometry are based, we recognize as temperature the property whose numerical value determines whether the system is in thermal equilibrium with another system. Two systems are in thermal equilibrium when their temperatures are identical.

The temperature of a system is measured by placing it in thermal communication with a special system (a test system) called a *thermometer.* The thermometer has to be sufficiently smaller than the actual system so that the heat interaction en route to thermal equilibrium is negligible from the point of view of the system. The thermometer, on the other hand, is designed so that the same heat interaction leads to measurable effects such as changes in volume or electrical resistance.

The development of the science concerning the measuring of temperature (the science of thermometry) has a long history that is tightly connected to that of calorimetry, caloric theory, and classical thermodynamics (see Table 1.2). The calibration of thermometers and the adoption of certain temperature scales is very much part of this history. Traditionally, calibration consisted of agreeing on two easy-to-reproduce states of the thermometer: Following a suggestion made in 1701 by Newton [20] that the interval between the freezing point of water and the human body temperature be a scale of 12 degrees, the most often used states were (1) the thermal equilibrium with a mixture of ice and water at atmospheric pressure, and (2) the thermal equilibrium with a batch of water boiling at atmospheric pressure. These traditional scales, named in order after Fahrenheit,[†] Réaumur,[‡] and Celsius,[§] are said to be based on two fiducial points (literally, on two points based on firm faith). In view of the arbitrariness of the material that fills the thermometer, the temperature measurements recorded on the traditional scales are recognized nowadays as *empirical temperatures.*

The temperature scales in use today are all based on the concept of *thermodynamic temperature* defined in terms of the Second Law of Thermody-

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[†] Gabriel Daniel Fahrenheit (1686–1736), German instrument maker native of Danzig (today, Gdansk) and long-time resident of Holland, invented the mercury-in-glass thermometer in 1714. He assigned the number 0 to the mercury level corresponding to the thermal equilibrium of a mixture of ice and common salt and assigned the number 96 to the level corresponding to the temperature of the human body. He found that on the same scale, the freezing and boiling points of water correspond to numbers 32 and 212, respectively.

[‡] René Antoine Ferchault de Réaumur (1683–1757) was a leading physicist, engineer, and naturalist. In thermodynamics, he is remembered for inventing in 1731 the alcohol thermometer and the Réaumur temperature scale, on which the freezing point of water is 0 degrees and the boiling point 80 degrees. His fascinating career included the study of gold-bearing rivers, turquoise mines, forests, insects, crayfish, Chinese porcelain, opaque glass, the composition and manufacture of iron and steel, and methods for tinning iron.

[§] Anders Celsius (1701–1744), professor of astronomy at the University of Uppsala, proposed in 1742 the centigrade scale on which the freezing and boiling of water at atmospheric pressure occur at 100°C and 0°C, respectively. The present Celsius system has the scale reversed; it was introduced in 1747.

namics. Following the Tenth General Conference on Weights and Measures (1954), we use the four thermodynamic temperature scales shown in Fig. 1.6. These scales are based on only one fiducial point, the triple point of water: On the Kelvin scale, the numerical value assigned to this point is 273.16. More on the reasoning behind these scales and the distinction between, on the one hand, the *absolute temperatures* recorded on the Kelvin and Rankine scales, and on the other, the temperatures of the new, one-point Celsius and Fahrenheit scales is given in Chapter 2. Of problem-solving interest are the relations that effect the conversion of one thermodynamic temperature into another:

$$\begin{aligned} T(^\circ\mathrm{C}) &= T(\mathrm{K}) - 273.15 \\ T(\mathrm{R}) &= \tfrac{9}{5}T(\mathrm{K}) \\ T(^\circ\mathrm{F}) &= T(\mathrm{R}) - 459.67 \\ T(^\circ\mathrm{C}) &= \tfrac{5}{9}[T(^\circ\mathrm{F}) - 32] \end{aligned} \tag{1.9}$$

The relative sizes of the divisions of these scales are also shown in Fig. 1.6:

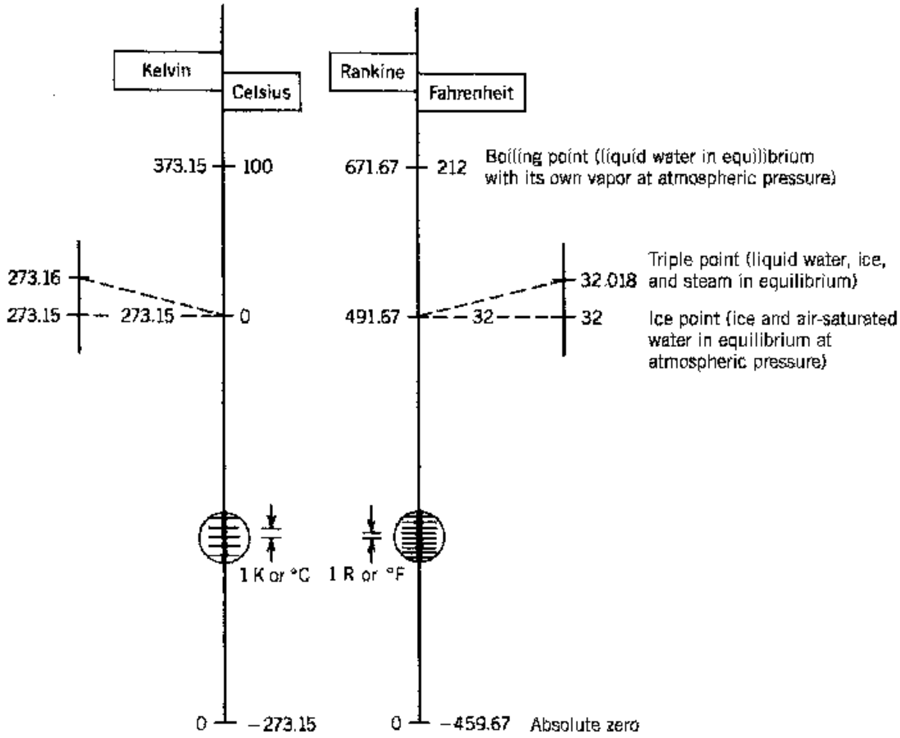

Figure 1.6 The four thermodynamic temperature scales.

$$1 \text{ R or } 1°\text{F} = \tfrac{5}{9}(1 \text{ K or } 1°\text{C}) \tag{1.10}$$

Returning now to the concept of heat interaction, the method of engineering thermodynamics relies on two additional words, *adiabatic* and *diathermal,* that effectively do away with the concept of time and, consequently, build a wall between thermodynamics and heat transfer. The word *adiabatic*[†] describes the boundary for which

$$\dot{Q} = 0 \tag{1.11}$$

regardless of the magnitude of the temperature gradient in the direction normal to the boundary. This concept was introduced by Laplace in caloric theory [6, p. 61; however, in engineering thermodynamics, it was made popular by Rankine's book [21] and the creative use of adiabatic lines in the graphic description of steam-engine cycles. The second word, *diathermal,*[‡] refers to a boundary across which the temperature gradient is zero even in the presence of heat transfer. If n is the direction normal to the boundary, for a diathermal boundary we can write

$$\frac{\partial T}{\partial n} = 0 \tag{1.12}$$

The adiabatic boundary model does not invalidate the boundary definition rule discussed in connection with Fig. 1.2: The temperature varies continuously across the boundary surface; however, the thermal conductivity of the local material is so low, or the time of observation is so short, that $\dot{Q} = 0$ is a very good approximation of the energy transferred as heat across the boundary.

To model a boundary as adiabatic or diathermal means to compare the time scale of the process executed by the system with the time that elapses if the system and its environment are allowed to reach thermal equilibrium. If the process time scale is considerably shorter than the time to thermal equilibrium, the boundary can be modeled as adiabatic. In the opposite extreme, the boundary approaches the diathermal model.

1.5 ENERGY CHANGE

The right side of eq. (1.1) is shorthand for a general expression whose terms distinguish between macroscopically identifiable forms of energy storage and the form that cannot be identified macroscopically (which for this reason is called *internal energy*):

[†] From the Greek word *adiabatos* (not to be passed; impossible to pass).

[‡] From the Greek words *dia* (through) and *therme* (hot), or *thermotis* (heat).

$$\underbrace{E_2 - E_1}_{\substack{\text{Energy}\\ \text{change}}} = \underbrace{U_2 - U_1}_{\substack{\text{Internal}\\ \text{energy}}} + \underbrace{\tfrac{1}{2}mV_2^2 - \tfrac{1}{2}mV_1^2}_{\text{Kinetic energy}} + \underbrace{mgz_2 - mgz_1}_{\substack{\text{Gravitational}\\ \text{potential}\\ \text{energy}}} + \underbrace{(E_2 - E_1)}_{\substack{\text{Other}\\ \text{macroscopic}\\ \text{forms of}\\ \text{energy storage}\\ \text{(Table 1.1)}}} \tag{1.13}$$

Whether all these terms have to be included in the composition of $E_2 - E_1$ depends on the system selected for analysis. In the thermodynamics of power and refrigeration systems, the three components that usually enter the analysis are the internal energy, the kinetic energy, and the gravitational potential energy. In thermostatics—the study of finite-size batches of substances or mixtures of substances in equilibrium—only the internal energy change term is relevant.

The term that accounts for forms of macroscopic energy storage, $(E_2 - E_1)_i$, depends on the constitution of the system. A list of the simplest possible expressions for such terms is compiled in Table 1.1, which is based on examples drawn from mechanical and electrical engineering. Each of the expressions listed for $(E_2 - E_1)_i$ is based on assuming the existence of a particular *constitutive relation.* The examples listed in Table 1.1 are by far the simplest because the cited constitutive relations are independent of one another, and each energy storage term $(E_2 - E_1)_i$ can be increased or decreased only through a characteristic energy interaction listed in the δW column. Such energy interactions and forms of energy storage can be described as *uncoupled.* Not listed in Table 1.1 are examples of *coupling:* that is, the existence of two or more energy interactions that can affect the same mode of energy storage. Energy-conversion systems are primary examples of coupled behavior: For example, the electromechanical energy of an electric motor can be changed through shaft work transfer, electrical work transfer, and a combination of shaft work transfer and electrical work transfer. In the systems encountered regularly in power and refrigeration engineering, the existence of the internal energy U as a thermodynamic property is a sign of coupled thermodynamic behavior, because the system's internal energy can be changed through work transfer, heat transfer, and a combination of work and heat transfer.

The general decomposition of energy change revealed by eq. (1.13) is also a hint of the historical development of the concept of energy and its terminology. It was Leibnitz who first discussed the conservation of the sum of the kinetic and potential energies, using the name *vis viva* (live force) for mV^2 and *vis mortua* (dead force) for mgz. The same conservation idea was implicit in Galileo Galilei's earlier formula for the velocity of a free-falling body, $V = (2gs)^{1/2}$, where s is the travel measured downward from the position of rest. The *vis viva* theory entered the realm of fluid mechanics in 1738 through

Daniel Bernoulli's famous treatise on hydrodynamics [22] and in an isolated earlier instance, through Torricelli's 1644 formula for the discharge velocity of a fluid driven by its own weight through an orifice. The *internal energy* term and the symbol U come from Clausius [16,23] and Rankine [21], although the terms *inner work, internal work,* and *intrinsic energy* were also used by their engineering contemporaries (e.g., Zeuner [17]). The term *energy,* which in thermodynamics was proposed by William Thomson in 1852, had been coined in 1807 by Thomas Young, the discoverer of the phenomenon of optical interference [24]. Additional highlights of the history of first-law concepts are given in Table 1.2 and in the closing sections of this chapter.

Example 1.1. Consider a rigid and evacuated container (bottle) of volume V that is surrounded by the atmosphere (T_0, P_0). At some point in time, the neck valve of the bottle opens, and atmospheric air gradually flows in. The wall of the bottle is thin and conductive enough so that the trapped air and the atmosphere eventually reach thermal equilibrium. In the end, the trapped air and the atmosphere are also in mechanical equilibrium, because the neck valve remains open.

Determine the net heat interaction that takes place through the wall of the bottle during the entire filling process. The challenge consists of solving the problem using the first-law statement for *closed systems* [eq. (1.1)]. As the closed system in this example, we identify the total airmass that eventually rests inside the bottle:

$$m = \frac{P_0 V}{RT_0} \tag{a}$$

The final state of the system is represented by the properties (T_0, P_0, V). Next, we visualize the position of the airmass m in the beginning of the process: That mass resides outside the bottle, and its temperature and pressure are atmospheric. Using eq. (a) and the $PV = mRT$ equation of state, we learn that the original volume occupied by m outside the bottle is also equal to V.

Using 1 and 2 for the beginning and the end of the process by which the closed system m moves inside the bottle, the first law provides the equation with which to calculate the unknown Q_{1-2}:

$$Q_{1-2} - W_{1-2} = U_2 - U_1 \tag{b}$$

Since we are treating the airmass as an ideal gas in which $T_1 = T_2 = T_0$, we note that $U_2 - U_1 = mc_v(T_2 - T_1) = 0$; that is,

$$Q_{1-2} = W_{1-2} \tag{c}$$

Finally, we calculate the work interaction by noting that *two* portions of the boundary of system m move during the process: first, the interface between m and the rest of the atmosphere, and second, the interface between m and the evacuated space. The pressure along these two surfaces are P_0 and 0, respectively, which means that work transfer is associated only with the movement of the first interface:

$$W_{1-2} = \int_1^2 P\,dV = P_0 \int_1^2 dV \tag{d}$$

The volume integral $\int_1^2 dV$ represents the volume swept by the interface as it is being pushed inward by the atmosphere. The size of the volume integral is $-V$, where the V comes from the volume originally occupied by m outside the bottle (note that V must be swept by the interface entirely if m is to end up in the bottle) and the $-$ comes from the fact that the interface moves in the direction of the forces applied by the ambient on the moving boundary [review the work transfer definition (1.7)]. In conclusion,

$$Q_{1-2} = -P_0 V < 0 \tag{e}$$

In other words, the physical sense of the heat transfer through the bottle wall is such that the atmosphere acts as heat sink. In absolute terms, the heat transfer rejected to the atmosphere matches the work done by the atmosphere for the purpose of "extruding" m through the neck valve. We consider this problem again in Example 1.2.

1.6 THE FIRST LAW FOR OPEN SYSTEMS

In engineering thermodynamics we rely most often on a generalization of the first-law statement that in Section 1.5 was reviewed in the context of closed systems. The generalization is almost as old as the statement of the first law for closed systems: It consists of allowing for mass flow across certain portions of the system boundary and writing the equivalent of eq. (1.1) or (1.5) for an open system (control volume).

Figure 1.7 shows the main features of an open system: heat interactions per unit time, $\dot{Q}$; work interactions per unit time, $\dot{W}$; and portions of the boundary that are crossed by the flow of mass. For simplicity, the figure shows

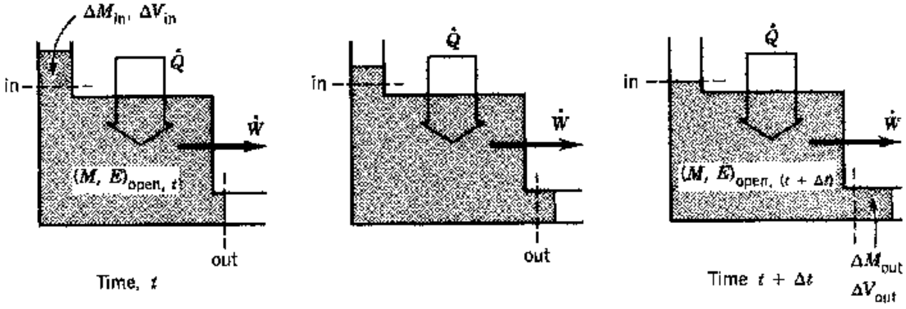

Figure 1.7 Flow of a closed system (shaded area) through the space occupied by an open system, and the conversion of the first law for closed systems into a statement valid for open systems.

only one of each type of boundary crossing, one inlet port labeled "in," and one outlet port labeled "out." The open system, or the control volume, is the region contained between the inlet and outlet ports; in other words, the stationary dashed lines labeled "in" and "out" belong to the boundary of the open system. The work transfer rate $\dot{W}$ refers to any mode or combination of work modes, $P\,dV/dt$, $\dot{W}_{\text{sh}}$, $\dot{W}_{\text{electrical}}$, $\dot{W}_{\text{magnetic}}$, and so on.

Since the first-law statement (1.1) applies strictly to closed systems, we seek a system with a fixed mass inventory that is related to the open system of interest. If M_{open} is the mass inventory of the open system at a certain point in time t, we can think of the fixed mass inventory M_{closed} that at time t "flows" through the control volume. According to Fig. 1.7, the relationship between M_{open} and M_{closed} is

$$M_{\text{closed}}\ (\text{constant}) = M_{\text{open},t} + \Delta M_{\text{in}} = M_{\text{open},(t+\Delta t)} + \Delta M_{\text{out}} \tag{1.14}$$

For the process from state 1 (time t) to state 2 (time $t + \Delta t$) executed by the closed system, the First Law of Thermodynamics (1.1) reads

$$E_{\text{closed},(t+\Delta t)} - E_{\text{closed},t} = \dot{Q}\,\Delta t - \dot{W}\,\Delta t + (P\,\Delta V)_{\text{in}} - (P\,\Delta V)_{\text{out}} \tag{1.15}$$

The last two terms on the right side account for the $P\,dV$ type of work transfer associated with the deformation of the closed system from time t to time $t + \Delta t$. Note that in each term, P is the local pressure: that is, the pressure in the immediate vicinity of the port. Relations similar to eqs. (1.14) express the relative size of the energy inventories of the closed and open systems:

$$E_{\text{closed},t} = E_{\text{open},t} + \Delta E_{\text{in}} \tag{1.16}$$

$$E_{\text{closed},(t+\Delta t)} = E_{\text{open},(t+\Delta t)} + \Delta E_{\text{out}} \tag{1.17}$$

Furthermore, the ΔE's and ΔV's can be rewritten in terms of their per-unit-mass counterparts e and v as

$$(\Delta E)_{\text{in,out}} = (e\,\Delta M)_{\text{in,out}} \quad \text{and} \quad (\Delta V)_{\text{in,out}} = (v\,\Delta M)_{\text{in,out}} \tag{1.18}$$

Like the port pressure P, the specific energy and volume (e and v, respectively) are properties of the intensive state of the fluid that crosses the boundary at time t. Combining eqs. (1.15)–(1.17) for the purpose of eliminating the terms that refer to the energy inventory of the closed system (E_{closed}), we obtain

$$\frac{1}{\Delta t}\left(E_{\text{open},(t+\Delta t)} - E_{\text{open},t}\right) = \dot{Q} - \dot{W} + \left[(e + Pv)\frac{\Delta M}{\Delta t}\right]_{\text{in}} - \left[(e + Pv)\frac{\Delta M}{\Delta t}\right]_{\text{out}} \tag{1.19}$$

Invoking the limit $\Delta t \rightarrow 0$, writing $\dot{m}$ for the mass flow rate $\Delta M/\Delta t$, dropping the subscript "open" from the energy inventory of the control volume, and assuming that more than one inlet port and outlet port exist, we arrive at the most general statement of the First Law of Thermodynamics for an open system:

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum_{\text{in}} \dot{m}(e + Pv) - \sum_{\text{out}} \dot{m}(e + Pv) \tag{1.20}$$

What makes this statement more general than the per-unit-time first law for closed systems [eq. (1.5)], are the terms $\dot{m}(e + Pv)$: These terms represent the energy transfer associated with the flow of mass across the system boundary. Finally, in the absence of macroscopic forms of energy storage other than kinetic and gravitational, the specific energy e can be decomposed into $(u + \frac{1}{2}V^2 + gz)$ [eq. (1.13)]. The result of this decomposition is that the specific *enthalpy*

$$h = u + Pv \tag{1.21}$$

shows up explicitly in the terms accounting for energy transfer via mass flow:

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum_{\text{in}} \dot{m}(h + \tfrac{1}{2}V^2 + gz) - \sum_{\text{out}} \dot{m}(h + \tfrac{1}{2}V^2 + gz) \tag{1.22}$$

In the fields of gas dynamics and compressible fluid mechanics, the group $(h + \frac{1}{2}V^2)$ is recognized as the local *stagnation enthalpy* of the flowing fluid. Kestin proposed an engineering generalization of the enthalpy concept under the name *methalpy* (symbol h°) [25, p. 223]:

$$h^\circ = e + Pv = h + \tfrac{1}{2}V^2 + gz \tag{1.23}$$

which is intended to mean "beyond enthalpy" or "transcending enthalpy" [note the Greek word *meta* (beyond)].

Following a procedure that is analogous to the transformation from closed system to open system illustrated in Fig. 1.7, the first-law statement (1.22) can be generalized further by considering the class of open systems where the inflows and the outflows are not restricted to penetrating discrete patches (ports) on the control surface. If $\mathscr{A}$ is the closed control surface that contains the control volume $\mathscr{V}$, the First Law of Thermodynamics reads

$$\int_{\mathscr{V}} \frac{\partial(\rho e)}{\partial t}\, d\mathscr{V} = -\int_{\mathscr{A}} \mathbf{q} \cdot \mathbf{n}\, d\mathscr{A} - \dot{W} - \int_{\mathscr{A}} \rho h^\circ \mathbf{v} \cdot \mathbf{n}\, d\mathscr{A} \tag{1.24}$$

In this expression, $\mathbf{q}$ and $\mathbf{v}$ represent the heat-flux vector and the velocity vector, respectively, at the points that make up the control surface. The unit vector **n** is normal to the control surface and points outward. The specific energy e and methalpy h° are local properties of the material that resides inside the volume element $d\mathscr{V}$ and along the area element $d\mathscr{A}$.

The first-law statement for a control volume of point size situated inside $\mathscr{V}$ is obtained by transforming the surface integrals of eq. (1.24) into volume integrals via the divergence theorem:

$$\frac{\partial}{\partial t}(\rho e) = -\nabla \cdot \mathbf{q} - \nabla \cdot (\rho h^\circ \mathbf{v}) - w''' \tag{1.25}$$

Or, using the mass-continuity statement shown later [eq. (1.29)], we obtain

$$\rho \frac{\partial e}{\partial t} + \rho \mathbf{v} \cdot \nabla e = -\nabla \cdot \mathbf{q} - \nabla \cdot (P\mathbf{v}) - w''' \tag{1.26}$$

In these expressions, w''' represents the contribution made by the point-size system to the overall work transfer rate $\dot{W}$ delivered by the finite-size control volume $\mathscr{V}$ in other words, $\dot{W} = \int_{\mathscr{V}} w''' \, d\mathscr{V}$ (note the definition of positive $\dot{W}$) (Fig. 1.3). In the continua studied in the field of conduction heat transfer, w''' usually accounts for the negative of the volumetric rate of electrical power dissipation q''' [26]. In the fluid media encountered in convective heat transfer, w''' accounts for both $-q'''$ and the negative of the work done via viscous forces on the point-size control volume [1].

The $\Delta t \rightarrow 0$ limit can be invoked in connection with the second of eqs. (1.14) to yield the *mass-conservation* statement:

$$\frac{dM}{dt} = \sum_{\text{in}} \dot{m} - \sum_{\text{out}} \dot{m} \tag{1.27}$$

This equation spells out the difference between open systems and closed systems (in the latter, the $\dot{m}$ values are all zero and the mass inventory M is a constant). In the language of eq. (1.24)—that is, for a control volume $\mathscr{V}$ enclosed by a permeable control surface $\mathscr{A}$—the mass-conservation equation is

$$\int_{\mathscr{V}} \frac{\partial \rho}{\partial t} \, d\mathscr{V} = -\int_{\mathscr{A}} \rho \mathbf{v} \cdot \mathbf{n} \, d\mathscr{A} \tag{1.28}$$

The corresponding statement for a control volume of point size is

$$\frac{D\rho}{Dt} = -\rho \nabla \cdot \mathbf{v} \tag{1.29}$$

Important in engineering applications is a special class of open systems whose inventories of mass (M), energy (E), and entropy (S), (Chapter 2) are time independent. Such systems are said to operate in the *steady-state* or *stationary regime.* The equations that govern their operation are simpler because time derivatives such as dE/dt and dM/dt in eqs. (1.22) and (1.27) vanish. The constancy of the M, E, and S inventories in time does not mean that the mass, energy, and entropy are distributed uniformly through the space occupied by the open system. The steady state should not be confused with the spatial uniformity of the intensive state.

The First Law of Thermodynamics for open systems and its enthalpy-based presentation illustrate admirably the aging of engineering thermodynamics into a discipline that threatens to lose sight of its origins. The first law for open systems was first formulated by Gustav Zeuner as part of the analysis of flow systems that operate in the steady state. He made this result known primarily through his technical thermodynamics treatise, whose first German edition was published in 1859 [17, pp. 225–231]. Equally impressive is that Zeuner saw and stressed the important role played by the first law in fluid mechanics next to the other equations that in his time were recognized as the pillars of fluid and gas dynamics [27]. Zeuner's name never made it into fluid mechanics vocabulary; more surprising is that it disappeared from engineering thermodynamics beginning with the turn of the century.[†] The most recent reference I can find in connection with "Zeuner's formula" is in Stodola's treatise on steam turbines, first published in German in 1903 [28]. Zeuner's statement of the first law for steady flow and the argument on which its derivation was based are present in virtually every engineering thermodynamics treatise of the twentieth century.

Another example of death and forgetting in the world of engineering thermodynamics is the invention of the word *enthalpy.* The widespread use of this term was triggered by the work of another professor from the old University of Dresden, Richard Mollier (the other influential Dresden figure had been Gustav Zeuner). Mollier recognized the importance of the group $u + Pv$ in the first-law analysis of steam turbines, next to entropy (s) in second-law analysis. He presented graphically and in tabular form the properties of

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[†] About the forget-first-the-engineer syndrome, Rankine wrote in 1859:

> . . . the improvers of the mechanical arts were neglected by biographers and historians, from a mistaken prejudice against practice, as being inferior in dignity to contemplation; and even in the case of men such as Archytas [an ancient Greek philosopher] and Archimedes, who combined practical skill with scientific knowledge, the records of their labours that have reached our time give but vague and imperfect accounts of their mechanical inventions, which are treated as matters of trifling importance in comparison with their philosophical speculations. The same prejudice, prevailing with increased strength during the middle ages, and aided by the prevalence of the belief in sorcery, rendered the records of the progress of practical mechanics, until the end of the fifteenth century, almost a blank. Those remarks apply, with peculiar force, to the history of those machines called PRIME MOVERS . . .. [21, p. xv]

Which is why Rankine—the engineer and cofounder of classical thermodynamics (next to Clausius and Kelvin)—is almost never mentioned by the philosophers.

steam as the now famous enthalpy–entropy chart (the Mollier chart, h–s) [29]. Mollier referred to the group $u + Pv$ as "heat contents" and "total heat" and labeled it "*i*." The symbol *i* was used until about 40 years ago in the engineering thermodynamics taught in German, Russian, and the languages of Central and Eastern Europe. Mollier's contribution is not the discovery of the group $u + Pv$—this group was already known as Gibbs' "heat function for constant pressure" (symbol χ) [14, p. 92]—rather, it is the invention of an important graphical tool whose impact on the efficiency of slide-rule calculations in thermal design is beyond question. The term *enthalpy*[†] was coined by Kamerlingh-Onnes [30], professor at the University of Leiden, otherwise famous for having been the first to liquefy helium and to discover the phenomena of superconductivity and superfluidity. Part of the mystery that persists in the wake of Kamerlingh-Onnes' innovations is due to the limited circulation enjoyed by his original writings, for which he used Dutch as language and the bulletin of his own low-temperature laboratory as journal [31].

Example 1.2. Consider again the problem stated in Example 1.1, this time in the context of *open systems*: This phenomenon is the common "filling" process. The object is to determine the heat interaction that occurs across the bottle wall during the filling process.

As open system, we choose the space contained by the bottle. The system has one inlet port (the neck valve), and the operation of the system is unsteady (the system accumulates mass during the process). The mass-conservation equation and the first law require at any instant that

$$\frac{dM}{dt} = \dot{m} \tag{a}$$

$$\frac{dU}{dt} = \dot{Q} + \dot{m}h_0 \tag{b}$$

where M and U are the instantaneous inventories of mass and internal energy of the system. Symbols $\dot{Q}$, $\dot{m}$, and h_0 stand for the instantaneous heat transfer rate into the system, the instantaneous inlet flow rate, and the enthalpy of atmospheric air, $h_0(T_0, P_0) =$ constant. The unknown is the integral

$$Q_{1-2} = \int_1^2 \dot{Q}\,dt \tag{c}$$

where 1 and 2 denote the start and finish of the filling operation, respectively.

Combining eqs. (a)–(c), it is easy to show that

$$Q_{1-2} = U_2 - U_1 - h_0(M_2 - M_1) \tag{d}$$

[†] Accent on the second syllable; from the Greek word *enthalpein* (to heat).

or since the open system is initially evacuated ($U_1 = 0$, $M_1 = 0$),

$$Q_{1-2} = U_2 - M_2 h_0 \tag{e}$$

Finally, we note that $U_2 = M_2 u_0$, where u_0 is the specific internal energy of air at T_0 and P_0 (recall that $T_2 = T_0$ and $P_2 = P_0$). Combining eq. (e) with the definition of enthalpy, we obtain

$$h_0 = u_0 + P_0 v_0 \tag{f}$$

and noting that $V = M_2 v_0$, we arrive at the same answer as in Example 1.1:

$$Q_{1-2} = -P_0 M_2 v_0 = -\ P_0 V \tag{g}$$

Comparing the two methods of deriving this answer, my impression is that the open-system analysis of Example 1.2 is more direct. However, the closed-system approach used in Example 1.1 reveals not only the size and sign of Q_{1-2}, but also the physical meaning of the expression P_0V. We discuss this physical meaning again in Example 2.2.

The combined message of Examples 1.1 and 1.2 is that there is more than one way in which to pursue the solution to a given problem. The researcher is *free to choose the method* [1, p. 53].

1.7 HISTORICAL BACKGROUND

The review presented so far emphasized the main concepts associated with the first law and those items that are most likely to lead to confusion in the process of analyzing an engineering problem. I was unable to discuss these points without drawing attention to their historical background: I believe that the effort to understand the pioneers (their personality, research methodology, fights, victories, and disappointments en route to “making it”) deserves emphasis. If we are to speak exotic words such as *energy, enthalpy,* and *entropy,* the best teachers of this language can only be its inventors.

We develop a better understanding of the meaning of the first law by looking at its position against the development of engineering science in general. A number of highlights are presented in Table 1.2 by recording first a new concept or discovery, the person responsible for it, and the time frame (usually, the year of publication of the innovator’s main opus). The historic record is so vast that any condensation of the type exhibited here reflects first the writer’s bias and incomplete knowledge of history. In the present display, an engineering bias was used intentionally to organize these events in two columns (or “currents”) whose confluence is marked by the emergence of thermodynamics in the mid-1800s.

On the practical side, the “work” line refers to human preoccupation with (1) mechanisms that *transmit* the mechanical power derived from animal, hydraulic, aeolian, or combustible origins, and (2) machines that *produce* mechanical power while consuming fuel (atmospheric-pumping engines, steam engines). On the practical side of the preoccupation with hotness (the “heat” line), (Table 1.2), we recall the measurement of temperature, quantity of heat, and in more recent times the rate of heat propagation (heat transfer).

One practical contribution of the “heat” line was the recording of the changes undergone by various substances under the influence of heating and cooling: for example, the dilation of thermometric fluids and “permanent gases.” Through such experiments, it was discovered that the state of a batch is determined by *two independent properties* in addition to the mass of the batch that was being studied. It is this early work that provides the empirical foundation for what we now call *state principle* and for the analytical and tabular summaries known as *equations of state* (Chapter 4).

The confluence of the “work” and “heat” lines was accompanied on a theoretical level by the coexistence of two views on the nature of hotness: (1) the mechanical theory, holding that heat is the manifestation of motion (live force) at the molecular level, and (2) the material or caloric theory, maintaining that the caloric fluid contained in a substance is uniquely defined if the state is specified. A key word in describing the evolution of these two views is *coexistence,* which means that the mechanical and caloric theories were not mutually exclusive and that they were accepted together as complementary. Note that the success and wide acceptance of the newer theory (the caloric theory) was the result of the great service that this theory rendered to the quantitative fields of thermochemistry and “heat engineering.”

No theory is perfect and forever. One respect in which the caloric theory failed—the generation of heat through friction—was well known in the 1700s and was certainly known by Lavoisier and Laplace. This particular limitation of the caloric theory was assaulted in a series of papers started in 1798 by Count Rumford [32,33] based on exhaustive and otherwise approximate observations of the heat generated by a drill during the boring of a cannon.[†]

[†] Count Rumford’s 1798 paper begins with advice to all researchers to keep their eyes open:

> It frequently happens, that in the ordinary affairs and occupations of life, opportunities present themselves of contemplating some of the most curious operations of nature; and very interesting philosophical experiments might often be made, almost without trouble or expence, by means of machinery contrived for the mere mechanical purposes of the arts and manufacturer.
>
> I have frequently had occasion to make this observation; and am persuaded, that a habit of keeping the eyes open to every thing that is going on in the ordinary course of the business of life has oftener led, as it were by accident, or in the playful excursions of the imagination, put into action by contemplating the most common appearances, to useful doubts and sensible schemes for investigating and improvement, than all the more intense meditations of philosophers, in the hours expressly set apart for study. [32, p. 80] (*continued on p. 30*)

TABLE 1.2 Highlights in the Conceptual Development of Classical Thermodynamics

The *Work* Line	The *Heat* Line
Machines	*Thermometry*
The 12th century: Gunpowder is brought from China to Europe, marking the beginning of the technology of firearms. From Manchester, which as an intellectual environment had played a leading role in the birth of thermodynamics, Osborne Reynolds remarked that "the combustion, in the form of the cannon, is the oldest form of heat engine." A similar view had been advocated earlier by Amontons and Daniel Bernoulli. The 13th, 14th, and 15th centuries: the proliferation of water-driven machines, air bellows, water pumps, irrigation, and the draining of mines. The technology and study of pumps (Stevinus, 1586; della Porta, 1601). The use of mathematical analysis in mechanics, the motion under the influence of gravity, the first instrument for measuring temperature (Galilei, 1623; see also "thermometry" in the adjacent column). The barometer, the orifice velocity of a fluid driven by its own weight (Torricelli, 1644). A basic understanding of the origins of atmospheric pressure (Pascal, 1648). The invention, demonstration, and popularization of the air (vacuum) pump (Otto von Guericke, 1654 and later). Noteworthy is his 1672 book in which he makes popular the idea that the weight of the atmosphere can be put to work: The famous woodcut known as the "Magdeburg hemispheres" shows two eight-horse teams trying to pull apart two 36-cm-diameter hemispheres from which the air had been evacuated—an exaggerated image that invited the work on atmospheric-pumping engines (e.g., Huygens, 1657). Captain Thomas Savery builds the first atmospheric engine (1698): The development of heat engines in the prethermodynamics era continues in Fig. 2.1.	Galilei's barothermoscope (1592): a glass bulb filled with air and having a downward stem dipped into a pool of mercury. Sealed-stem thermometers filled with alcohol; stem calibrated in thousandths parts of bulb volume (Grand Duke Ferdinand II of Tuscany, 1654). The air thermometer: a volume of air confined by a column of mercury as indicator (Amontons, late 1600s). The mercury-in-glass thermometer (Fahrenheit, 1714; the empirical Fahrenheit, Réaumur, and Celsius scales are described on p. 18).
From Mechanics to Machine Science	*Calorimetry*
The *vis viva* theory or the conservation of live force, the method of infinitesimal calculus along with the system of notation that was universally adopted (Leibnitz, 1684; Newton's calculus was published three years later). The law of universal gravitation, the three laws of motion, calculus presented in geometric terms (Newton, 1687). The conservation of live force in hydraulics, the kinetic-molecular theory of gases (Daniel Bernoulli, 1738).	The elasticity of a gas, PV = constant at constant T (Boyle, 1660; Mariotte, 1679; both preceded by Towneley, Boyle's student). The phlogiston theory: Phlogiston is a substance without weight, odor, color, or taste that is contained by all flammable bodies and is given off during burning (advanced by Becher; extended and made popular by Stahl in the late 1600s). The constancy of temperature during phase change (Newton, 1701; observed also by Amontons). The foundations of quantitative calorimetry; the concepts of "quantity of heat" and "latent heat"; the discovery of CO_2, called "fixed air" (Black, late 1700s). The discovery of oxygen by Priestley (1774), who called it "dephlogisticated air" (later it was named "oxygen" by Lavoisier, who, by explaining combustion, discredited the phlogiston theory; Priestley also discovered sulfur dioxide and ammonia). The latent heat of fusion of ice and the concept of "specific heat" (Wilcke, 1772, 1781). Lavoisier and Laplace publish *Memoire sur la chaleur* (1783): a systematic foundation for the science of calorimetry, the heat conservation axiom ("all variations in heat, real or apparent, which a system of bodies undergoes in changing state are reproduced in inverse order when the system returns to its final state"), the calorimetric measurement of specific heat, heat of reaction, and so on. In 1789, Lavoisier publishes "*Traité élémentaire de chimie*": a system of chemistry in which the caloric fluid (*calorique*) is chosen as one of the simple substances or elements. The material or caloric theory of heat becomes established.

<table>
<tr>
<td colspan="2">The mathematical foundations of inviscid fluid flow (Euler, 1755).
The gravitational field theory, the mathematics of thermal diffusion (Laplace, 1785 and later).
The law governing friction (Coulomb, in a 1781 prize-winning paper).
The equations of analytical mechanics (Lagrange, 1788).
The foundations of descriptive geometry (Monge, 1795).
The beginnings of a science of machines (mechanisms); the “Carnot principle” of avoiding shocks, percussion, and turbulent flow in order to achieve maximum efficiency or continuity in the transmission of mechanical power (Lazare Carnot, 1783; he also defines the concept of “moment of activity,” which in 1829 was named “work,” independently by Coriolis and Poncelet).
The <i>École Polytechnique</i> is established in 1795: under its influence and through the teachings of some of its first graduates, the study of machines becomes central to engineering education everywhere (e.g., courses by Navier, 1826; Coriolis, 1829; Poncelet, 1829).
The “dynamic unit” or “dynamode,” as the work required to raise 1 kilogram to a height of 1 meter (Hachette, 1811); the “calorie” was defined as the quantity of heat required to raise the temperature of 1 kilogram of water by 1°C (Clément, 1826).</td>
<td>The gas law $V \sim T$ at constant P (Gay-Lussac, 1802; he also discovered that $\Delta U = 0$ at constant T in gases).
The law of partial pressures in gas mixtures (Dalton, 1805); Avogadro’s law (1811).
The discovery of “critical temperature” (Cagnard Latour, 1810s).
The approximate character of Boyle’s law for real gases; the careful measurement of the specific heat and thermal expansion coefficient of gases, liquids, and solids (Regnault, mid-1800s).

<i>Heat Transfer</i>

The proportionality between cooling rate and body-surroundings temperature difference (Newton, 1701).
Comparative measurement of thermal conductivity (Ingen Housz, 1785, 1789; Count Rumford, 1786 and later).
Convection as a principal heat transfer mechanism through clothing (Rumford, 1797; the word <i>convection</i> was coined by Prout in 1834).
The proportionality between heat transfer rate and temperature gradient (Biot, 1804); also the distinction between the thermal conductivity and the heat transfer coefficient (Fourier, 1807).
Fourier formulates the partial differential equation for time-dependent heat conduction (1807): In today’s language, this ranks as the first analytical formulation of the first law (in the context of zero-work processes, Table 1.3). The field of heat transfer continues to develop along the pure “heat” line into the late 1900s, when it is reunited with the field of engineering thermodynamics in 1982 [11].</td>
</tr>
<tr>
<td>The assault on the conservation of caloric doctrine (Count Rumford, 1798 and later; Sir Humphry Davy, 1799).</td>
<td>The “heat” equivalent of “work,” or, traditionally, the “mechanical equivalent of heat” (the theoretical line: Mayer, 1842 and later; also Séguin, 1839; Holtzmann, 1845; the experimental line: Joule, 1843 and later; enriched by Violle, 1870; Rowland, 1879; Hirn; and others).</td>
<td>The “first law” as an integral part of the new science of “thermodynamics” (Clausius, 1850 and later; Rankine, 1850 and later; Kelvin, 1851 and later).</td>
</tr>
</table>

This theme was also advocated by Sir Humphry Davy, who communicated that he was able to induce the melting of two blocks of ice by rubbing them against each other. Although the correctness of Davy's communication has been questioned [34], and despite the view expressed by some that Rumford had a gift for exaggeration, the vociferous attack on one shortcoming of the caloric theory played an important role in the developments that were to take place in the 1840s and 1850s. The Rumford–Davy theme did not win many converts at the turn of the century; however, it was used conveniently and successfully by the founders of thermodynamics (Joule even attributed to Rumford the honor of having first measured the heat equivalent of work—this, in order to draw the establishment's attention to his own measurements [35]).

The Rumford–Davy line of questioning contributed to preparing an audience for the theory that was to arrive. Note Sadi Carnot's *Manuscript Notes* papers, which were saved and revealed first in 1871 by Sadi's brother Hippolyte and which had probably been written around the time of his 1824 memoir [36]. In these notes we find that Sadi Carnot had questioned the conservation of caloric doctrine and decided, "Heat is nothing more than motive power, or, in other words, the motion that has changed form. Wherever motive force is produced, there is always production of heat in a quantity precisely proportional to the quantity of motive power destroyed. Conversely: Wherever there is destruction of heat, there is production of motive power." He concludes that "one can state as a general thesis that the motive power is an invariable quantity in nature and that it is never, properly speaking, produced or destroyed. In fact, it changes form; that is, it produces sometimes one kind of motion, sometimes another, but it is never exhausted" [18, p. 51;

About the experiment in which water boiled as a result of frictional heating, he wrote:

> At 2 hours 20 minutes it was at 200°(F); and at 2 hours 30 minutes it ACTUALLY BOILED!
>
> It would be difficult to describe the surprise and astonishment expressed by the countenances of the by-standers, on seeing so large a quantity of cold water heated, and actually made to boil, without any fire.
>
> Though there was, in fact, nothing that could justly be considered as surprising in this event, yet I acknowledge fairly that it afforded me a degree of childish pleasure, which, were I ambitious of the reputation of a *grave philosopher,* I ought most certainly rather to hide than to discover. [32, p. 92]

His final and famous conclusion on the origin of the observed heating effect was as follows:

> It is hardly necessary to add, that any thing which any *insulated* body, or system of bodies, can continue to furnish *without limitation,* cannot possibly be a *material substance:* and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of any thing, capable of being excited, and communicated, in the manner the heat was excited and communicated in these experiments, except it be MOTION. [32, p. 99]

my translation]. After this unambiguous statement of the future principle of the conservation of energy (the first law), he reports an estimate of the heat equivalent of one unit of motive power, which today amounts to 3.7 joules/calorie—that is, only 12 percent below the modern value of 4.186 joules/calorie.

Sadi Carnot's unpublished notes do not in any way detract from the credit that Mayer and Joule deserve for publishing similar views, and for *fighting the battle to have them accepted.* The notes show, however, that Sadi Carnot's thinking was well ahead of the views expressed in his published memoir and, quite possibly, that the conservation of caloric doctrine was losing ground among some of his peers. One of these, Emile Clapeyron, wrote in 1834 that "a quantity of mechanical action and a quantity of heat which can pass from a hot body to a cold body are quantities of the same nature, and that it is possible to replace the one by the other—in the same manner as in mechanics a body which is able to fall from a certain height and a mass moving with a certain velocity are quantities of the same order, which can be transformed one into the other by physical means" [4, pp. 36–51].

The first clear-cut theory expressing that "heat" and "work" are equivalent and that their respective units are convertible was published independently by Mayer in May 1842 [37] and Joule in August 1843 [38]. This dual approach to such a great step is a perfect example of how differently two people can think, and it is a very strong case for free access to the marketplace of ideas as the best recipe for scientific progress. An important item in the history of the first law is the fact that both Mayer and Joule had difficulty in getting their papers published and in being taken seriously by their established contemporaries.

Mayer was the theoretician, the man obsessed by the idea: He conceived it in circumstances that even today appear removed from the thermodynamics scene (more on this shortly), and then he relied on the contemporary state of knowledge to support its validity. Joule, on the other hand, was the ultimate experimentalist: He first discovered in his measurements that the heat generated by electrical resistances is proportional to the mechanical power required to generate the electrical power. He then recognized the importance of this proportionality and drew the revolutionary conclusion that a *universal* proportionality must exist between the two effects (work and heat). Only to polish this idea and to convince the skeptics (e.g., the Royal Society), he produced a series of nakedly simple experiments whose message proved impossible to refute. From the point of view of mechanical engineers, the most memorable among these experiments was the heating of a pool of water by an array of paddle wheels driven by falling weights.

Mayer's entrance on this controversial stage was considerably different. A medical doctor by training, he was serving as surgeon on a ship sailing through the East Indies when he observed that the blood of European sailors showed a brighter color of red: that is, a smaller rate of oxidation. This was in July 1840. He attributed this observation to the high temperatures near the equator: that is, to the lower metabolic rate that is needed to maintain the body temperature. Mayer, however, went beyond the connection between the chemical energy contained in food and the rejection of body heat to the ambient: He saw the energy of food as the common source of both body heat and muscular work; in other words, he saw intuitively that heat and work have similar origins and are interconvertible.

It was pointed out by Epstein [39] that the field of physiology had already seen a connection between heat and work in the form of an outmoded theory of respiration that claimed that body heat is generated by the friction of air in the air passages of the lungs. The theory was being displaced at the time by Lavoisier's conclusive theory of oxidation. Epstein's research of the physiology literature and of the healthy intellectual milieu of Manchester (of which Cardwell [7] writes so well) goes on to suggest that the physiologists' connection between heat and work was also known to Joule.[†]

Mayer was very clear about the meaning of his theory: "We must find out how high a particular weight must be raised above the surface of the earth in order that its falling power may be equivalent to the heating of an equal weight of water from 0° to 1°C" [37, p. 240]. He reasoned that an amount of gas has to be heated more at constant pressure than at constant volume, because at constant pressure it is free to dilate and do work against the atmosphere; in today's notation we would write $mc_P\,\Delta T - mc_v\,\Delta T = P_{\text{atm}}\,\Delta V$, where ΔV is the volume increment associated with ΔT and $P = P_{\text{atm}}$. Using the c_P and c_P/c_v constants known in his time, he estimated the left side of the equation in calories, while the right side was known in mechanical units. He established the equivalence between these units numerically by listing "365 m" as the answer to the question quoted earlier in this paragraph (this number corresponds to 3.58 joules/calorie; that is, it is nearly the same as Sadi Carnot's estimate on p. 31). Worth noting is that if we use *Clapeyron's equation* $Pv = RT$ in Mayer's argument previously, we arrive at "$c_P - c_v = R$": This classical relation between the specific heats of an ideal gas is recognized as *Mayer's equation*.

Most, if not all, of the credit for convincing the skeptics and putting the heat/work equivalence on the books belongs to Joule, whose experiments

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[†] Revealing is Tisza's one-sentence dismissal of the suggestion that Joule's work and ideas may have had something to do with physiology and Count Rumford [8, p. 25]: This is just one of the many subtle attempts to banish the thought that the pioneers might have been something other than physicists: namely, engineers (Sadi Carnot, Clapeyron, Séguin, Rankine, and the many engine builders of Scotland and Cornwall) (Fig. 2.1), medical doctors (Mayer, Helmholtz), public servants (Fourier, Lazare Carnot), and—we should not forget—military men (Lazare and Sadi Carnot, Count Rumford, Helmholtz). The symbol of this diverse group is Joule himself, a man who received no formal education: that is, a veritable amateur.

found a strong and very influential supporter in William Thomson.† Mayer received recognition for his theoretical contribution later, thanks to the efforts of Tyndall, Helmholtz, and, among engineers, Zeuner. Helmholtz's letter to Tait on behalf of Mayer [41,42] is, in retrospect, an important statement on scientific progress and a discoverer's troubles with the establishment in general:

> I must say that to me the discoveries of Kirchhoff in this area (radiation and absorption) appear to be one of the most instructive cases in the history of science, precisely because so many others had previously been so close to making the same discoveries. Kirchhoff's predecessors in this field were related to him in roughly the same way in which, with respect to the conservation of force, Robert Mayer, Colding, and Seguin were related to Joule and William Thomson.
>
> With respect to Robert Mayer, I can, of course, understand the position you have taken in opposition to him; I cannot, however, let this opportunity pass without stating that I am not completely of the same opinion. The progress of the natural sciences depends always upon new inductions being formed out of available facts, and upon the consequence of these inductions, insofar as they refer to new facts, being compared with reality through the use of experiments. There can be no doubt concerning the necessity of this second undertaking. This part of science often requires a large amount of work and great ingenuity, and we are obligated in the highest degree to those who do it well. The fame of discovery, however, remains with those who have found the new idea; the later experimental verification is quite a mechanical occupation. Further, we cannot demand unconditionally that the person who discovers a new idea also be obligated to carry out the second part of the work. If this were the case, we would have to reject the greatest part of the work of all mathematical physicists. William Thomson, for example, produced a number of theoretical papers concerning Carnot's law and its consequences before he performed a single experiment, and it would not occur to any one of us to treat these lightly.
>
> Robert Mayer was not in a position to conduct experiments; he was repulsed by the physicists with whom he was acquainted (this also happened to me several

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† In a note dated 1885, Joule wrote:

> It was in the year 1843 that I read a paper "On the Calorific Effects of Magneto-Electricity and the Mechanical Value of Heat" to the Chemical Section of the British Association assembled at Cork. With the exception of some eminent men . . . the subject did not excite much general attention; so that when I brought it forward again at the meeting in 1847, the chairman suggested that . . . I should not read my paper, but confine myself to a short verbal description of my experiments. This I endeavoured to do, and discussion not being invited, the communication would have passed without comment if a young man had not risen in the section, and by his intelligent observation created a lively interest in the new theory. The young man was William Thomson, who had two years previously passed the University of Cambridge with the highest honour, and is now probably the foremost scientific authority of the age . . .. [40]

> years later); it was only with difficulty that he could find space for the publication of his first condensed formulation of this principle. You must know that as a result of this rejection he at last became mentally ill. It is now difficult to set oneself back into the modes of thought of that period, and to make clear to oneself how absolutely new the whole idea seemed at that time. I should imagine that Joule too must have fought for a long time in order to gain recognition for his discovery.
>
> Thus, although no one can deny that Joule did much more than Mayer, and although one must admit that in the first publications of Mayer there were many things that were unclear, still I believe that one must accept that Mayer formulated this idea, which determined the most important recent progress in the natural sciences, independently and completely. His reward should not be lessened because at the same time another man in another country and under other conditions made the same discovery and, to be sure, carried it through afterwards better than he did.

1.8 THE STRUCTURED PRESENTATION OF THE FIRST LAW

The objective of this chapter has been to review the various concepts of the first law. We end the chapter by reviewing several ways of streamlining and structuring the presentation of the first law (Table 1.3). Each formulation reveals the same structure, which begins with the selection of the smallest number of understandable notions that serve as primary concepts for the remainder of the scheme. Additional concepts are later defined using the primary concepts and an appropriate statement of the first law.

1.8.1 Poincaré's Scheme

The first structured presentation of this kind was made by Poincaré [18]. As primary concepts, he chose the heat transfer, the temperature, and the experience condensed in the Zeroth Law of Thermodynamics. For the definition of the concept of heat transfer (heat, in the thermodynamics language of the late 1800s), he relied heavily on the science of calorimetry, which—it is worth noting—is a science that serves us well to this day despite the celebrated failure of certain aspects of the caloric theory. Heat transfer was defined as the system–environment interaction made possible by the inequality of temperatures between the two systems. The size of the heat interaction was measured by counting the number of auxiliary standard systems that must be placed in thermal communication with the system of interest. The function of the standard system is to undergo a temperature excursion between two standard temperature levels under the influence of the heat interaction that is to be measured.

As foundation for the first law, Poincaré chose the numerous measurements of the mechanical equivalent of heat pioneered by Joule and continued by Rowland, Violle, and Hirn, and then he stated that the work transfer equals the heat transfer during a complete cycle. Finally, Poincaré defined the dif-

TABLE 1.3 Alternatives for the Structured Presentation of the First Law and Its Concepts

Structure	Poincaré [18]	Carrathéodory [44]	Keenan and Shapiro’s Second Method [43]
Primary concepts	Work transfer Temperature Heat transfer	Work transfer Adiabatic boundary	Temperature Heat transfer Zero-work boundary
The first law	$\oint \delta W = \oint \delta Q$	$\int_1^2 \delta W_{\text{adiabatic}} = f(1, 2)$	$\int_1^2 \delta Q_{\text{zero-work}} = f(1, 2)$
Definition of the infinitesimal change in property *E*	$\delta Q - \delta W$	$-\delta W_{\text{adiabatic}}$	$\delta Q_{\text{zero-work}}$
Derived definition of heat transfer	—	$\delta W - \delta W_{\text{adiabatic}}$	—
Derived definition of work transfer	—	—	$\delta Q - \delta Q_{\text{zero-work}}$
Other derived concepts	Adiabatic boundary Zero-work boundary	Heat transfer Temperature Zero-work boundary	Work transfer Adiabatic boundary

Source: After Ref. 43.

ference between heat transfer and work transfer as a new quantity called internal energy, and he relied on the first law to prove that the internal energy is a thermodynamic property.

1.8.2 Carathéodory's Scheme

The third column of Table 1.3 shows another approach, which relies on the concepts of work transfer and adiabatic boundary as primary concepts [44]. The work transfer is defined by reference to the mechanical concept of work. While avoiding any reference to thermal concepts that would certainly sound more appealing and natural, the adiabatic wall is defined by the special feature that the "equilibrium of a body enclosed by (this wall) is not disturbed by any external process as long as no part of the wall is moved (distance forces being excluded in the whole consideration)" [45].

The next step in the Carathéodory structure is the first-law statement that the work transfer experienced by a closed system surrounded by an adiabatic boundary depends only on the end states of the process. One consequence of this statement is that the adiabatic work transfer is a thermodynamic property—hence the definition of the property E:

$$dE = -\delta W_{\text{adiabatic}} \tag{1.30}$$

Under the Carathéodory scheme, the heat transfer becomes a derived concept, as δQ is defined simply as the sum $dE + \delta W$. The temperature also becomes a derived concept: Two bodies are said to have the same temperature when the heat transfer δQ (or $dE + \delta W$) is zero in the absence of an adiabatic wall.

1.8.3 Keenan and Shapiro's Second Scheme

Although the Poincaré and Carathéodory presentations cover very well the range from the most successful to the most abstract, they do not represent all the possibilities of introducing the first law and its concepts. Keenan and Shapiro [43] proposed two alternate routes, the second of which is summarized in the fourth column of Table 1.3. The primary concepts are the temperature, the heat transfer, and the zero-work boundary. The temperature and the heat transfer are defined in the same way as Poincaré's method. The concept of zero-work boundary, on the other hand, is an instrument required to get to the first law while avoiding any reference to work transfer (note here the relationship between this idea and Carathéodory's). In Keenan and Shapiro's definition, "a zero-work wall is a wall which is motionless (except in the absence of force at the wall) and through which pass no moving force fields and no electrical currents."

The first law amounts to the statement that the heat transfer experienced by a system surrounded by a zero-work boundary depends only on the end states of the process. Energy, then, is the name given to this thermodynamic property:

$$dE = \delta Q_{\text{zero-work}} \tag{1.31}$$

As a derived concept, the work interaction is defined as the difference $\delta Q - dE$, or

$$\delta W = \delta Q - \delta Q_{\text{zero-work}} \tag{1.32}$$

Finally, the adiabatic boundary is the one for which we can write $\delta Q = 0$.

Keenan and Shapiro's second scheme draws attention to a very special set of circumstances in which "heat" is indeed "conserved" [eq. (1.31)]. This observation begs us to look back at what preceded modern thermodynamics and to appreciate a little more the *legitimacy* of the caloric theory [46] as a milestone in man's search for truth and in the development of his language. Of course, no theory is perfect and forever, which is why there is something rotten in the contemporary trend of portraying the caloric thinking as the equivalent of "failure" and "bad thermodynamics." A theory that was created by the minds of Lavoisier and Laplace—the theory that was misused so creatively by Sadi Carnot—couldn't have been all bad!

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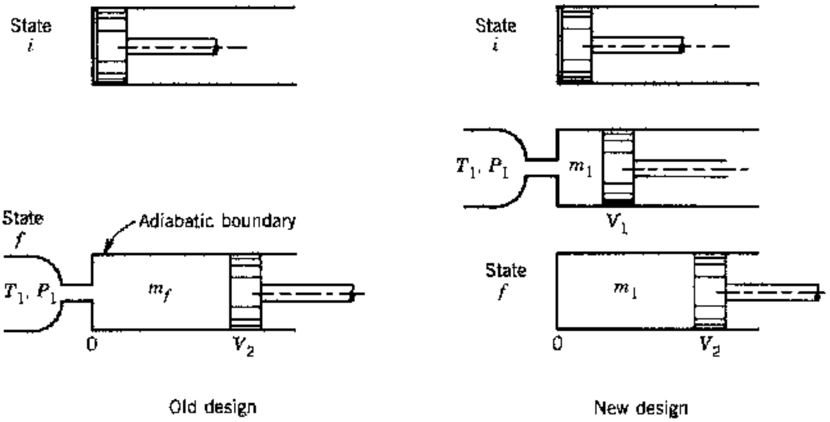
PROBLEMS

1.1 One invention that revolutionized the design of the early steam engine was the *principle of expansive operation* (see Hornblower and Watt, Fig. 2.1). According to the "old design," high-pressure steam was admitted from the boiler throughout the work-producing stroke of the piston, i–f. During this process, the cylinder pressure remained practically con-



Old design

New design

Figure P1.1

stant and equal to the steam supply pressure, P_1. Before the piston could be returned to its original position (i), the high-pressure steam that filled the V_2 volume had to be exhausted into the atmosphere.

The "new design" consisted of cutting off the admission of steam at some intermediate volume V_1 and allowing the gas m_1 trapped inside the cylinder to work "expansively" (i.e., to expand as a closed system) as the piston completed its work-producing stroke. The purpose of the steam cutoff feature was to lower the final cylinder pressure to the atmospheric level to avoid the costly discharge of high-pressure steam.

Evaluate the relative goodness of the new design, where "goodness" can be measured as the work produced during one full stroke W_{i-f} divided by the total amount of (T_1, P_1) gas drawn from the gas supply to execute that stroke. To develop an answer analytically, make the following simplifying assumptions:

- Instead of steam, the fluid that enters and expands in the cylinder is an ideal gas with known constants R and c_v.
- Initially, the piston touches the bottom of the cylinder, $V_i = 0$.
- The heat transfer through the wall of the cylinder is negligible.

(a) Consider first the old design and calculate in order:

  (1) The work delivered during one stroke, W_{i-f}

  (2) The final temperature inside the cylinder, T_f

  (3) The final gas mass m_f admitted into the cylinder at state f

  (4) The goodness ratio W_{i-f}/m_f

(b) Consider next the new design, where the connection between the gas supply and the cylinder stays open only between $V = 0$ and

$V = V_1$. The expansion from $V = V_1$ to $V = V_2$ can be modeled as reversible and adiabatic. Calculate in order:

- **(1)** The ideal gas mass m_1 trapped in the cylinder at $V = V_1$ and later
- **(2)** The work delivered during one stroke, W_{i-f}
- **(3)** The goodness ratio W_{i-f}/m_1

(c) Show that the goodness ratio of the new design is greater than the goodness ratio of the old design.

1.2 One kilogram of H_2O (the "system") is being heated in a rigid container. In the initial state, the system is a mixture of liquid water and steam of temperature $T_1 = 100°\text{C}$ and vapor quality $x_1 = 0.5$. The total heat transfer experienced by the system from state 1 to state 2 is $Q_{1-2} = 2199.26$ kJ.

(a) Draw the path of the process on a P–v diagram.

(b) Pinpoint the final state 2; that is, determine *two* independent properties of the system at state 2.

(c) Determine T_2 and P_2.

(d) Comment on the dependence of the system's internal energy on temperature at states near state 2. For example, can H_2O be modeled as an ideal gas in the vicinity of state 2?

1.3 An amount of ideal gas m (with known constants R and c_v) is confined by means of two rigid and diathermal diaphragms and one floating piston in three compartments, as shown in Fig. P1.3. Each compartment contains one-third of the amount of ideal gas; however, the pressure differs from one compartment to the next (pressures P_{1A}, P_{1B}, and P_{1C} are known). The three compartments are initially in thermal equilibrium at temperature T_1.

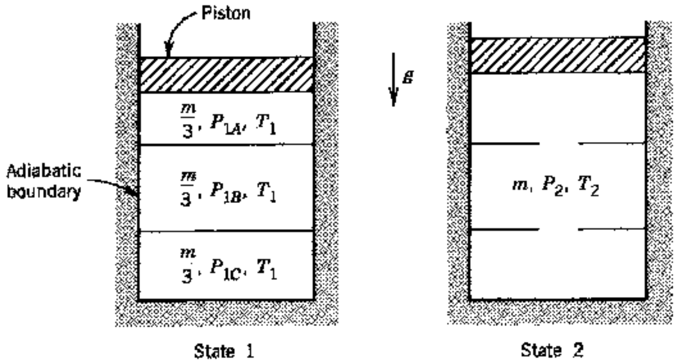


Figure P1.3

Consider next the adiabatic process 1 → 2 triggered when the two diaphragms are punctured. In the end (at state 2), the ideal gas is characterized by a unique pressure P_2 and a unique temperature T_2. Determine the final temperature T_2 and show that your conclusion can be shaped as follows:

$$\frac{T_2}{T_1} = \text{function}\left(\frac{R}{c_v}, \frac{P_{1A}}{P_{1B}}, \frac{P_{1A}}{P_{1C}}\right)$$

1.4 During its warm-up phase and before the pressure-release safety valve opens, a pressure cooker can be modeled as a constant-volume rigid container that is being heated at a rate $\dot{Q}$. Let m be the mass of the liquid–water vapor mixture at some point in time t when the quality of the mixture is x and the pressure is P. Assuming that $\dot{Q}$, x, and P are known, determine analytically the rate of pressure increase in the pressure cooker (dP/dt) as a function of $\dot{Q}$, m, x, and various properties of the saturated states f (liquid) and g (gas) that correspond to pressure P.

1.5 The air from a glass tube has been evacuated completely before the tip of the tube was fused and sealed. You are invited to break the tip of the tube, wait a second or two, and dip the open end of the tube into a beaker containing some water. Do you expect the water to rise into the glass tube, or do you expect air bubbles to come out of the tube into the water? Explain the basis for your expectations [47].

1.6 A rigid container with volume V is originally filled with water of temperature T_1. A hose is then connected to an inlet port and hotter water of temperature T_2 is pumped into the container at a mass flow rate $\dot{m}_{\text{in}}$, while another venting port allows the displaced water to flow out, the pressure being constant.

Assume that inside the container the incoming hot water mixes quickly with the water inside, so that the temperature is to a good approximation uniform. The water can be viewed as an incompressible liquid with constant specific volume v_w and with $du = c\,dT$, where the specific heat c is given.

(a) Treating the container as an open system, derive an expression for the temperature T inside the container as a function of time. Neglect effects due to gravity and kinetic energy.

(b) Suppose that the container has a volume of 1 m^3 and $v_w = 10^{-3}$ m^3/kg. If $T_1 = 10°C$ and $T_2 = 40°C$, what hot water mass must be pumped into the container to raise the inside temperature from 10°C to 20°C?

1.7 A rigid and well-insulated container holds 1 kg of dry saturated steam at $P_1 = 5$ MPa. At some point in time, a tiny crack develops in the

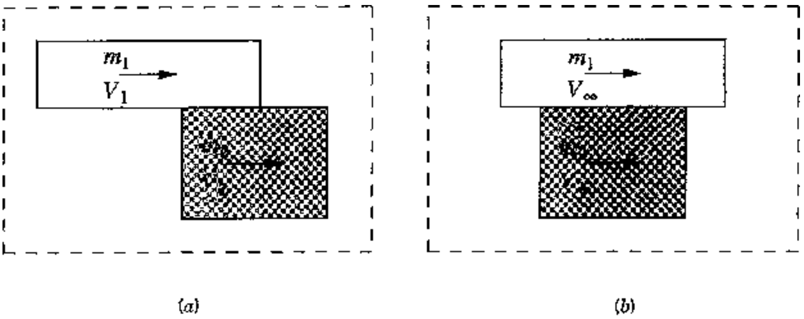


Figure P1.8

uppermost region of the container. Through this crack, some of the H_2O escapes slowly into the atmosphere until the pressure inside the container falls to $P_2 = 1.5$ MPa. This leakage process is slow enough so that at any instant the H_2O inventory is in a state of equilibrium. Any liquid that forms during this process accumulates at the bottom of the container, whereas the escaping H_2O is always gaseous.

(a) Calculate the vapor quality at the final equilibrium state (2). Note that between 5 and 1.5 MPa, the specific enthalpy of dry saturated steam is practically constant, $h_g \cong 2800$ kJ/kg.

(b) Calculate the ratio of the volumes occupied by vapor and liquid in the final state.

1.8 Two masses (m_1, m_2) travel in the same direction at different velocities (V_1, V_2). They happen to touch and rub against each other, and after a sufficiently long time they acquire the same velocity (V_∞). Consider the system composed of m_1 and m_2, and also consider the process (a)–(b) illustrated in Fig. P1.8. There are no forces between the system and its environment. Determine the ratio $\eta = \text{KE}_b/\text{KE}_a$ as a function of m_2/m_1 and V_2/V_1, where KE is the kinetic energy inventory of the system. Show that $\eta < 1$ when $V_2 \neq V_1$ and that η is of order 1 when m_2/m_1 is of order 1. Next, assume that the masses m_1 and m_2 are incompressible substances and that (a) and (b) are states of thermal equilibrium with the ambient of temperature T_0. Determine an expression for the heat transfer between the system and the environment.