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Thermodynamic entropy

1.1 Thermodynamics and entropy

The existence of entropy follows inevitably from the first and second laws of thermodynamics. However, our purpose is not to reproduce this deduction, but rather to focus on the concept of entropy, its meaning and its applications. Entropy is a central concept for many reasons, but its chief function in thermodynamics is to *quantify the irreversibility of a thermodynamic process.* Each term in this phrase deserves elaboration. Here we define *thermodynamics* and *process*; in subsequent sections we take up *irreversibility*. We will also learn how entropy or, more precisely, differences in entropy tell us which processes of an isolated system are possible and which are not.

Thermodynamics is the science of macroscopic objects composed of many parts. The very size and complexity of thermodynamic systems allow us to describe them simply in terms of a mere handful of *equilibrium* or *thermodynamic variables*, for instance, pressure, volume, temperature, mass or mole number, internal energy, and, of course, entropy. Some of these variables are related to others via *equations of state* in ways that differently characterize different kinds of systems, whether gas, liquid, solid, or composed of magnetized parts.

A thermodynamic system undergoes a *thermodynamic process* when the variables that describe the system change from one set of values to another, that is, change from one *thermodynamic state* to another. Thus, we describe a thermodynamic process by specifying an initial state, a final state, and specific conditions under which the change occurs. Specific conditions include: *iso-energetically*, that is, with constant energy as would occur when the system is completely isolated; *adiabatically*, that is, within a thermally insulating boundary; and *quasistatically*, that is, so slowly the system occupies a continuous sequence of thermodynamic states each one of which is characterized by thermodynamic variables. Thermodynamics *per se* says nothing about the rate at which a process unfolds.

The laws of thermodynamics also limit the ways in which a thermodynamic system may proceed from one state to another. The *first law of thermodynamics* is the law of conservation of energy applied to the internal energy of a thermodynamic system. The *internal energy* excludes the energy of the position or motion of the system as a whole. According to the first law there are only two ways to change the internal energy of a given thermodynamic system: (1) heating or cooling the system and (2) working on the system or arranging for the system to work on its surroundings. Quantitatively the first law is

$$\Delta E = Q + W \tag{1.1}$$

where $\Delta E \left[= E_f - E_i\right]$ is the increment in the internal energy E of a thermodynamic system as it transitions from an initial state with energy E_i to a final state with energy E_f. The quantity Q is the energy absorbed by the system when heated, and W is the work done on the system during the transition. These are signed quantities so that when $Q < 0$, the system is cooled rather than heated, and when $W < 0$, work is done *by* rather than *on* the system. (Note that some texts use the symbol W in the opposite way so that when $W < 0$, work is done *on* rather than *by* the system. In this case the first law of thermodynamics is $\Delta E = Q - W$ instead of (1.1).)

When these changes are indefinitely small the first law becomes

$$dE = \delta Q + \delta W. \tag{1.2}$$

Here the different notations, dE versus δQ and δW, emphasize that while E is a variable that describes the state of a system, Q and W are not. The heat quantities, Q and δQ, and their work correlatives, W and δW, merely indicate the amount of energy transferred to or from a system in these ways. (We have no standard way of distinguishing between a differential of a state variable and an equivalently small infinitesimal that is not the differential of a state variable. Here I use d to signal the first as in dE and δ to signal the second and as in δQ and δW. Other texts adopt other solutions to this notational problem.) Thus, a thermodynamic system contains energy but does not, indeed cannot, contain heat or work, as suggested in Figure 1.1.

1.2 Reversible and irreversible processes

All interactions among fundamental particles are *reversible*. The simplest interaction is a collision between two fundamental particles. One particle approaches another; they interact via gravitational, electromagnetic, or nuclear

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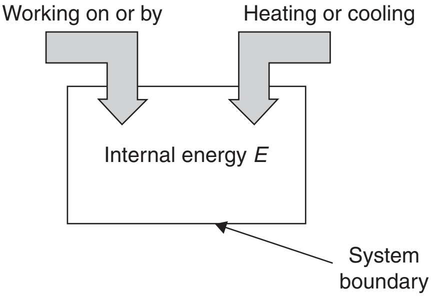

Figure 1.1 The internal energy E of a thermodynamic system can be changed in only two ways: (1) heating or cooling and (2) working.

forces; then they recede from each other. Interestingly, a film of such a collision would make as much physical sense proceeding backwards as proceeding forwards. It may help us to think of a white cue ball striking a colored billiard ball, the latter initially at rest. While some care may be required to set both balls in motion with reversed velocities in such a way that the colored billiard ball strikes the cue ball and both recover their initial states of rest and motion, it can be done. And certainly this reversal can be imagined without supposing the violation of any of Newton's laws of motion. For there is nothing in the laws of motion or in the way fundamental particles interact that prefers one direction of time over the other. We say that interactions among fundamental particles are *time reversible*.

The same cannot be said of the processes of a thermodynamic system composed, as it is, of many parts. Thermodynamic processes are, in fact, typically *irreversible*. A cup of hot coffee sitting on the kitchen table always cools down. We never observe a cup of initially room-temperature coffee extracting energy from the air and heating up. When a hot object and a cold one are in thermal contact, the hot object always cools and the cold object always heats until both reach an intermediate temperature. We never observe these processes occurring in reverse order. A backwards-running video of a thermodynamically irreversible process appears implausible.

Thermodynamic reversibility

There is, however, a special sense in which a thermodynamic process can meaningfully be reversed. If making only an indefinitely small change in the system or its environment reverses the direction of the process, the process is thermodynamically reversible. Sadi Carnot (1796–1832) invented the concept of *thermodynamic reversibility* in order to articulate and prove what is now called *Carnot's theorem*: *The most efficient heat engine is one that operates reversibly*.

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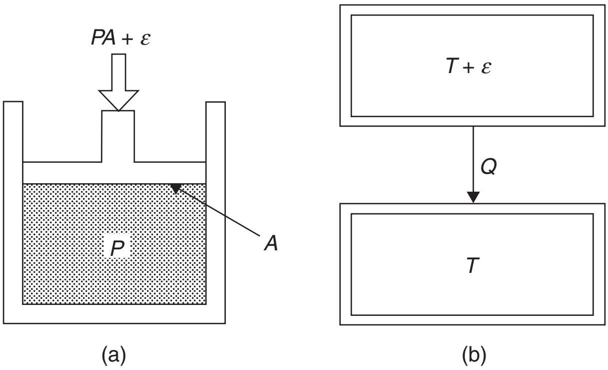

Figure 1.2 (a) A frictionless piston reversibly compresses a fluid. (b) Two systems with an infinitesimal temperature difference heat and cool each other reversibly.

A reversible thermodynamic process must be (1) quasistatic, that is, indefinitely slow, and (2) without friction or dissipation (internal friction). Consider, for instance, the piston compressing the fluid illustrated in Figure 1.2a. The piston quasistatically and frictionlessly compresses the fluid when the force the piston exerts on the fluid, $PA + \varepsilon$, is an indefinitely small amount ε larger than the force PA the fluid of pressure P exerts on the piston head of area A. When, instead, the force exerted by the piston on the fluid is infinitesimally less than PA, that is, $PA - \varepsilon$, the fluid expands quasistatically. Thus, these are thermodynamically reversible changes because their direction can be reversed by an infinitesimal change in either the system or its environment. In similar fashion, the heating or cooling of one system by another is reversible when an infinitesimal temperature difference is maintained between the two as shown in Figure 1.2b. Clearly, thermodynamic reversibility is an ideal that can be approached but never fully realized. All actual thermodynamic processes are irreversible.

To summarize: all fundamental processes are reversible because one can imagine reversing their direction of change without violating a law of physics. On the other hand, all non-idealized thermodynamic processes are irreversible. Thermodynamic processes, in practice, always proceed in one direction.

Loschmidt's paradox

Yet if, as is widely assumed, a thermodynamic system is composed of many fundamental particles and a thermodynamic process is composed of many fundamental interactions, why are not all thermodynamic processes reversible? Johann Loschmidt (1821–1895) asked this question in 1876. We still have no fully satisfactory answer. That many reversible fundamental processes do not necessarily compose a reversible thermodynamic process is

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known as *Loschmidt's paradox* or the *reversibility paradox*. Our failure to resolve Loschmidt's paradox suggests that the laws governing the interactions of fundamental particles do not form a complete picture of nature and need to be supplemented with additional physics equivalent to the second law of thermodynamics.

Example 1.1 Reversible or irreversible?

Problem: A piston quasistatically compresses a gas enclosed in a chamber. In order to compress the gas the piston must overcome a force of 0.01 N caused by the piston head rubbing against the sides of the piston chamber. Is the work performed on the gas reversible or irreversible?

Solution: This work is performed quasistatically but not without friction. Therefore, the work is irreversible. Alternatively, in order to change the quasistatic compression into a quasistatic expansion the force exerted on the piston must change by the finite amount of 2×0.01 N.

1.3 The second law of thermodynamics

There are a number of logically equivalent versions of the second law. Perhaps not surprisingly, the earliest versions are the most readily grasped. Rudolph Clausius (1822–1888) was the first, in 1850, to identify a version of the second law of thermodynamics. For this purpose Clausius elevated everyday observations about heating and cooling to the status of a general law: *A cooler object never heats a hotter object*.

By *heating (cooling) an object* we mean transferring energy to (from) the object without doing work. And by *cooler object* we mean one with lower temperature and by *hotter object* we mean one with higher temperature. We will discuss *temperature* in more detail later. For now it suffices to consider temperature as the degree of hotness measured on some scale.

Heat reservoirs

Clausius's and other versions of the second law of thermodynamics are most conveniently expressed in terms of *heat reservoirs*. By definition, a heat reservoir maintains the same temperature regardless of how much heating or cooling it experiences. Thus a heat reservoir has infinite heat capacity just as if it were indefinitely large. In the language of heat reservoirs Clausius's second law is: *A process whose only result is to cause one heat reservoir with temperature* T_C *to lose energy* Q *through cooling and a hotter heat reservoir with temperature* $T_H > T_C$ *to gain energy* Q *through heating never occurs.*

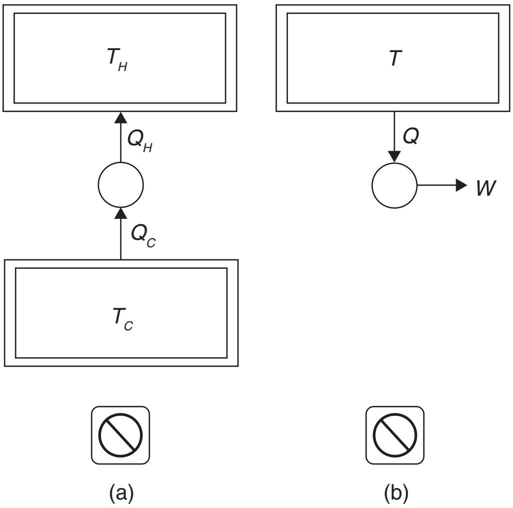

Figure 1.3 (a) A process whose only result is to cause one heat reservoir with temperature T_c to lose energy Q_C through cooling and cause a hotter heat reservoir with temperature $T_H > T_C$ to gain energy Q_H through heating is forbidden by Clausius's version of the second law, in this case $\mathrm{Q_H = Q_C}$. (b) A heat engine whose only result is to cause a single heat reservoir to lose energy Q through cooling and perform an equal amount of work $W[=Q]$ is forbidden by Kelvin's version of the second law.

In 1851 William Thomson (1824–1907), later known as Lord Kelvin, formulated a verbally distinct version of the second law. Kelvin's second law concerns the operation of a *heat engine*, that is, a device that uses a temperature difference to produce work. According to Kelvin's second law: *A heat engine whose only result is to cause a single heat reservoir to lose energy Q through cooling and perform an equal amount of work W [$= Q$] is impossible.*

Given the first law, Kelvin's version of the second law is logically equivalent to Clausius's. The version one favors is a matter of taste and convenience. If one wants a second law in the language of natural phenomena, one adopts Clausius's second law. If one wants a second law in the language of technology, one adopts Kelvin's. We illustrate these impossible processes in terms of which these versions of the second law are framed in Figure 1.3 and label them with a symbol ⊘ that proclaims, "forbidden by the second law."

The second law and irreversibility

The second law of thermodynamics can also be expressed in terms of the language of irreversible processes. Recall that an irreversible thermodynamic

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process cannot be completely reversed. Therefore, another way to say that a particular process is forbidden is to say that the forbidden process is the result of reversing a thermodynamically irreversible process. In these terms Clausius's second law becomes: *A process whose only result is to cool a hotter reservoir and heat a colder one cannot be completely reversed*. Likewise, Kelvin's second law becomes: *A process whose only result is to dissipate work into a single heat reservoir cannot be completely reversed*. Every time our coffee cools and every time we shuffle across the floor we experience or create necessarily irreversible processes. In the next two sections we focus on the first of these, a hotter reservoir heating a colder one, in order to introduce the measure of irreversibility we call entropy and to reformulate the second law in terms of that measure.

1.4 Entropy and irreversibility

Imagine a thermodynamic system that can exist in many different thermodynamic states. We represent each of these states by a point in a multi-dimensional thermodynamic state space. The variables that define the state space will, of course, depend upon the nature of the system. For instance, because only two variables completely determine the state of a *simple fluid*, the state space of a simple fluid is a plane whose points are defined by locating values on two axes: one labeled, say, energy E and the other volume V. Now, choose any two points representing two different states in our thermodynamic state space and a path through the state space that connects these two points as in Figure 1.4. Each point on this path necessarily represents a thermodynamic state and the complete path necessarily represents a quasistatic process that connects the two endpoint states.

Of course, non-quasistatic, for example, turbulent or explosively rapid, processes can also transform a system from one thermodynamic state to another. But non-quasistatic processes are not composed of a continuous sequence of thermodynamic states and cannot be represented by a path in thermodynamic state space.

Therefore, a path in thermodynamic state space necessarily represents a quasistatic process. And quasistatic processes come in only two kinds: reversible processes that proceed without friction or dissipation and irreversible ones that proceed with friction or dissipation. Recall that a completely reversible process is also one for which the system and its environment can, with only infinitesimal adjustments, evolve along a path in state space in either direction, and an irreversible process is one for which the system and its environment would require finite adjustments to proceed along a path in either direction. A piston that very slowly compresses a gas while overcoming friction between

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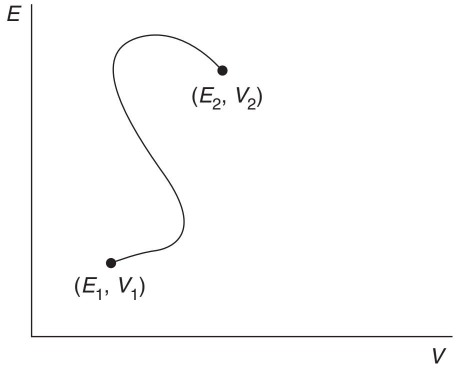

Figure 1.4 Thermodynamic state space, two states, denoted (E_1,V_1) and (E_2,V_2), and a path connecting the two states.

the piston head and the sides of the piston chamber is an example of an irreversible, quasistatic process that can be represented by a path in state space. To summarize: every segment of a path in state space represents a quasistatic process that, in turn, represents either a reversible or an irreversible process.

Entropy difference

We seek a quantitative measure of the irreversibility of a quasistatic process. Rudolph Clausius was, in 1865, able to construct such a measure by discovering a state variable of an isolated system that monotonically changes along a path representing an irreversible process and remains the same along a path representing a reversible process. Thus, two states of an isolated system connected by a reversible path have the same value of this state variable and two states of an isolated system connected by an irreversible path have different values of this state variable. Clausius's discovery of this state variable required an elaborate deduction from the first and second laws of thermodynamics. I will not reproduce that deduction.

Clausius coined the word *entropy* for this state variable – a word parallel in structure, sound, and spelling to the word *energy* – and adopted S for its symbol. Clausius derived the word *entropy* from the Greek root *tropy* meaning "turn" and a prefix *en* meaning *in*. Thus *entropy* literally means "in turn" or "turn in." It seems that Clausius sought a name for a concept that, in part, characterizes how physical systems *turn*, that is, how they *change*, *evolve,* or *proceed*. Clausius himself interpreted the word *entropy* metaphorically as *transformation content*. We will in time discover more suggestive metaphors for the concept of entropy.

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In a thermodynamics based on the first and second laws the only purpose of Clausius's state variable *entropy* is to provide comparisons between two states. For example, if the path connecting states 1 and 2 of an isolated system as illustrated in Figure 1.4 represents an irreversible process, then either $S_2 > S_1$ or $S_1 > S_2$. Alternatively, if the path illustrated represents a reversible process of an isolated system, then $S_2 = S_1$.

The absolute entropy of a single state is much like the absolute energy of a single state. The first and second laws of thermodynamics sanction neither absolute energy nor absolute entropy but assign meaning only to energy and entropy differences. The third law of thermodynamics does, indeed, allow us to assign a meaning to the concept of absolute entropy. But before we explore the third law we determine, in the next several sections, how the entropy difference between two states of an isolated system quantifies the irreversibility of a process connecting those two states.

1.5 Quantifying irreversibility

The key to quantifying the irreversibility of an isolated system's evolution is to require that the entropy increment ΔS of a composite system be additively distributed over its parts. Symbolically stated,

$$\Delta S = \sum_j \left(S_{f,j} - S_{i,j}\right) = \sum_j \Delta S_j \tag{1.3}$$

where $S_{f,j}$ is the final entropy of the system's jth part, $S_{i,j}$ is the initial entropy of the system's jth part, and $\Delta S_j \left[= S_{f,j} - S_{i,j}\right]$ is the entropy increment of the system's jth part. In this way, and as illustrated in Figure 1.5, the entropy increment of a composite system ΔS is the sum of the entropy increments of its parts.

To proceed further we apply these ideas to a particular process: a heat reservoir with temperature T is heated by absorbing energy Q. If, alternatively, the heat reservoir is cooled, then $Q < 0$. Therefore, if the heat reservoir increments its entropy, that increment ΔS can be a function of only two quantities: the reservoir temperature T and the heat Q where the sign of Q indicates whether energy is absorbed through heating $[Q > 0]$ or rejected through cooling $[Q < 0]$. [The noun *heat* here refers to the energy absorbed or rejected by heating or cooling.] The equation

$$\Delta S = f(T, Q) \tag{1.4}$$

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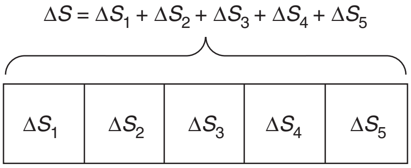

Figure 1.5 The entropy increment ΔS is additive over the parts of a composite system.

states this relation. Note that we have imposed no special restrictions on the system or on this heating or cooling process. In particular the heating or cooling described in Eq. (1.4) may be either reversible or irreversible.

Applying additivity

The additive property (1.3) severely restricts the form of the function $f(T,Q)$. For instance, if we divide a single-temperature T heat reservoir that absorbs heat Q into two identical parts, each still has temperature T and each absorbs half the heat $Q/2$. Since the entropy increment of the composite system is the sum of the entropy increments of its parts: $f\left(T, Q\right) = f\left(T, Q/2\right) + f(T, Q/2)$ or, equivalently, $f(T, Q) = 2f(T, Q/2)$. If instead of dividing the heat reservoir into two identical parts we divide it into n identical parts, then

$$f\left(T, Q\right) = nf\left(T, \frac{Q}{n}\right). \tag{1.5}$$

There is only one non-trivial solution to (1.5) and that is

$$f(T, Q) = g(T)Q, \tag{1.6}$$

where $g(T)$ is an as yet undetermined function of the temperature T. (One can derive (1.6) by taking the partial derivative of (1.5) with respect to n, and solving the resulting partial differential equation.) Accordingly, the entropy of a heat reservoir with temperature T changes by

$$\Delta S = g(T)Q \tag{1.7}$$

when the reservoir absorbs or rejects energy Q through, respectively, cooling or heating another object.

Entropy generation in a two-reservoir, isolated system

Next we apply these ideas to a composite, two-reservoir, isolated system that experiences the following irreversible process: a hotter reservoir directly heats