

*The Kelvin Temperature Scale

In Chapter 17 we expressed the need for a temperature scale that doesn't depend on the properties of any particular material. We can now use the Carnot cycle to define such a scale. The thermal efficiency of a Carnot engine operating between two heat reservoirs at temperatures T_H and T_C is independent of the nature of the working substance and depends only on the temperatures. From Eq. (20.4), this thermal efficiency is

$$e = \frac{Q_H + Q_C}{Q_H} = 1 + \frac{Q_C}{Q_H}$$

Therefore the ratio Q_C/Q_H is the same for *all* Carnot engines operating between two given temperatures T_H and T_C .

Kelvin proposed that we *define* the ratio of the temperatures, T_C/T_H , to be equal to the magnitude of the ratio Q_C/Q_H of the quantities of heat absorbed and rejected:

$$\frac{T_C}{T_H} = \frac{|Q_C|}{|Q_H|} = -\frac{Q_C}{Q_H} \quad (\text{definition of Kelvin temperature}) \quad (20.16)$$

Equation (20.16) looks identical to Eq. (20.13), but there is a subtle and crucial difference. The temperatures in Eq. (20.13) are based on an ideal-gas thermometer, as defined in Section 17.3, while Eq. (20.16) *defines* a temperature scale based on the Carnot cycle and the second law of thermodynamics and is independent of the behavior of any particular substance. Thus the **Kelvin temperature scale** is truly *absolute*. To complete the definition of the Kelvin scale, we assign, as in Section 17.3, the arbitrary value of 273.16 K to the temperature of the triple point of water. When a substance is taken around a Carnot cycle, the ratio of the heats absorbed and rejected, $|Q_H|/|Q_C|$, is equal to the ratio of the temperatures of the reservoirs *as expressed on the gas-thermometer scale* defined in Section 17.3. Since the triple point of water is chosen to be 273.16 K in both scales, it follows that *the Kelvin and ideal-gas scales are identical*.

The zero point on the Kelvin scale is called **absolute zero**. Absolute zero can be interpreted on a molecular level; at absolute zero the system has its *minimum* possible total internal energy (kinetic plus potential). Because of quantum effects, however, it is *not* true that at $T = 0$, all molecular motion ceases. There are theoretical reasons for believing that absolute zero cannot be attained experimentally, although temperatures below 10^{-7} K have been achieved. The more closely we approach absolute zero, the more difficult it is to get closer. One statement of the *third law of thermodynamics* is that it is impossible to reach absolute zero in a finite number of thermodynamic steps.

Test Your Understanding of Section 20.6 An inventor looking for financial support comes to you with an idea for a gasoline engine that runs on a novel type of thermodynamic cycle. His design is made entirely of copper and is air-cooled. He claims that the engine will be 85% efficient. Should you invest in this marvelous new engine? (*Hint:* See Table 17.4.)

20.7 Entropy

The second law of thermodynamics, as we have stated it, is rather different in form from many familiar physical laws. It is not an equation or a quantitative relationship but rather a statement of *impossibility*. However, the second law *can* be stated as a quantitative relationship with the concept of *entropy*, the subject of this section.

We have talked about several processes that proceed naturally in the direction of increasing disorder. Irreversible heat flow increases disorder because the molecules are initially sorted into hotter and cooler regions; this sorting is lost when the system comes to thermal equilibrium. Adding heat to a body increases its disorder because it increases average molecular speeds and therefore the randomness of molecular motion. Free expansion of a gas increases its disorder because the molecules have greater randomness of position after the expansion than before. Figure 20.17 shows another process in which disorder increases.

Entropy and Disorder

Entropy provides a *quantitative* measure of disorder. To introduce this concept, let's consider an infinitesimal isothermal expansion of an ideal gas. We add heat dQ and let the gas expand just enough to keep the temperature constant. Because the internal energy of an ideal gas depends only on its temperature, the internal energy is also constant; thus from the first law, the work dW done by the gas is equal to the heat dQ added. That is,

$$dQ = dW = p dV = \frac{nRT}{V} dV \quad \text{so} \quad \frac{dV}{V} = \frac{dQ}{nRT}$$

The gas is in a more disordered state after the expansion than before because the molecules are moving in a larger volume and have more randomness of position. Thus the fractional volume change dV/V is a measure of the increase in disorder, and the above equation shows that it is proportional to the quantity dQ/T . We introduce the symbol S for the entropy of the system, and we define the infinitesimal entropy change dS during an infinitesimal reversible process at absolute temperature T as

$$dS = \frac{dQ}{T} \quad (\text{infinitesimal reversible process}) \quad (20.17)$$

If a total amount of heat Q is added during a reversible isothermal process at absolute temperature T , the total entropy change $\Delta S = S_2 - S_1$ is given by

$$\Delta S = S_2 - S_1 = \frac{Q}{T} \quad (\text{reversible isothermal process}) \quad (20.18)$$

Entropy has units of energy divided by temperature; the SI unit of entropy is 1 J/K.

We can see how the quotient Q/T is related to the increase in disorder. Higher temperature means greater randomness of motion. If the substance is initially cold, with little molecular motion, adding heat Q causes a substantial fractional increase in molecular motion and randomness. But if the substance is already hot, the same quantity of heat adds relatively little to the greater molecular motion already present. So the quotient Q/T is an appropriate characterization of the increase in randomness or disorder when heat flows into a system.

Example 20.5 Entropy change in melting

One kilogram of ice at 0°C is melted and converted to water at 0°C . Compute its change in entropy, assuming that the melting is done reversibly. The heat of fusion of water is $L_f = 3.34 \times 10^5 \text{ J/kg}$.

SOLUTION

IDENTIFY: The melting occurs at a constant temperature of 0°C , so this is a reversible isothermal process.

20.17 When firecrackers explode, disorder increases: The neatly packaged chemicals within each firecracker are dispersed in all directions, and the stored chemical energy is converted to random kinetic energy of the fragments.



Continued

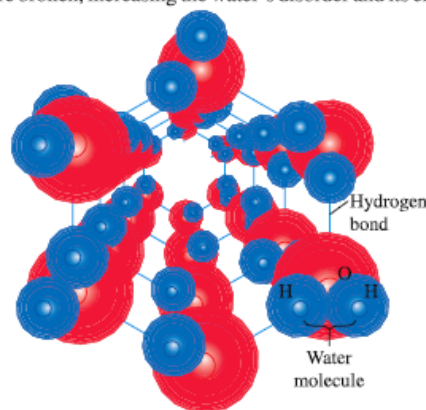
EXECUTE: The heat needed to melt the ice is $Q = mL_f = 3.34 \times 10^5 \text{ J}$. From Eq. (20.18) the increase in entropy of the system is

$$\Delta S = S_2 - S_1 = \frac{Q}{T} = \frac{3.34 \times 10^5 \text{ J}}{273 \text{ K}} = 1.22 \times 10^3 \text{ J/K}$$

EVALUATE: This increase corresponds to the increase in disorder when the water molecules go from the highly ordered state of a crystalline solid to the much more disordered state of a liquid (Fig. 20.18).

In any *isothermal* reversible process, the entropy change equals the heat transferred divided by the absolute temperature. When we refreeze the water, Q has the opposite sign, and the entropy change of the water is $\Delta S = -1.22 \times 10^3 \text{ J/K}$. The water molecules rearrange themselves into a crystal to form ice, so disorder and entropy both decrease.

20.18 Water molecules are arranged in a regular, ordered way in an ice crystal. When the ice melts, the hydrogen bonds between molecules are broken, increasing the water's disorder and its entropy.



Entropy in Reversible Processes

We can generalize the definition of entropy change to include *any* reversible process leading from one state to another, whether it is isothermal or not. We represent the process as a series of infinitesimal reversible steps. During a typical step, an infinitesimal quantity of heat dQ is added to the system at absolute temperature T . Then we sum (integrate) the quotients dQ/T for the entire process; that is,

$$\Delta S = \int_1^2 \frac{dQ}{T} \quad (\text{entropy change in a reversible process}) \quad (20.19)$$

The limits 1 and 2 refer to the initial and final states.

Because entropy is a measure of the disorder of a system in any specific state, it must depend only on the current state of the system, not on its past history. We will show later that this is indeed the case. When a system proceeds from an initial state with entropy S_1 to a final state with entropy S_2 , the change in entropy $\Delta S = S_2 - S_1$ defined by Eq. (20.19) does not depend on the path leading from the initial to the final state but is the same for *all possible* processes leading from state 1 to state 2. Thus the entropy of a system must also have a definite value for any given state of the system. We recall that *internal energy*, introduced in Chapter 19, also has this property, although entropy and internal energy are very different quantities.

Since entropy is a function only of the state of a system, we can also compute entropy changes in *irreversible* (nonequilibrium) processes for which Eqs. (20.17) and (20.19) are not applicable. We simply invent a path connecting the given initial and final states that *does* consist entirely of reversible equilibrium processes and compute the total entropy change for that path. It is not the actual path, but the entropy change must be the same as for the actual path.

As with internal energy, the above discussion does not tell us how to calculate entropy itself, but only the change in entropy in any given process. Just as with internal energy, we may arbitrarily assign a value to the entropy of a system in a specified reference state and then calculate the entropy of any other state with reference to this.

Example 20.6 Entropy change in a temperature change

One kilogram of water at 0°C is heated to 100°C. Compute its change in entropy.

SOLUTION

IDENTIFY: In practice, the process described would be done irreversibly, perhaps by setting a pan of water on an electric range whose cooking surface is maintained at 100°C. But the entropy change of the water depends only on the initial and final states of the system, and is the same whether the process is reversible or irreversible.

SET UP: We can imagine that the temperature of the water is increased reversibly in a series of infinitesimal steps, in each of which the temperature is raised by an infinitesimal amount dT . We then use Eq. (20.19) to integrate over all these steps and calculate the entropy change for the total process.

EXECUTE: From Eq. (17.14) the heat required to carry out each such infinitesimal step is $dQ = mc dT$. Substituting this into Eq. (20.19) and integrating, we find

$$\begin{aligned}\Delta S &= S_2 - S_1 = \int_1^2 \frac{dQ}{T} = \int_{T_1}^{T_2} mc \frac{dT}{T} = mc \ln \frac{T_2}{T_1} \\ &= (1.00 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \left(\ln \frac{373 \text{ K}}{273 \text{ K}} \right) \\ &= 1.31 \times 10^3 \text{ J/K}\end{aligned}$$

EVALUATE: The entropy change is positive, as it must be for a process in which the system absorbs heat.

In this calculation we assumed that the specific heat c doesn't depend on temperature. That's a pretty good approximation, since c for water increases by only 1% between 0°C and 100°C.

CAUTION When $\Delta S = Q/T$ can (and cannot) be used In solving this problem you might be tempted to avoid doing an integral by using the simpler expression in Eq. (20.18), $\Delta S = Q/T$. This would be incorrect, however, because Eq. (20.18) is applicable only to *isothermal* processes, and the initial and final temperatures in our example are *not* the same. The *only* correct way to find the entropy change in a process with different initial and final temperatures is to use Eq. (20.19). ■

Conceptual Example 20.7 A reversible adiabatic process

A gas expands adiabatically and reversibly. What is its change in entropy?

SOLUTION

In an adiabatic process, no heat enters or leaves the system. Hence $dQ = 0$ and there is *no* change in entropy in this reversible

process: $\Delta S = 0$. Every *reversible* adiabatic process is a constant-entropy process. (For this reason, reversible adiabatic processes are also called *isentropic* processes.) The increase in disorder resulting from the gas occupying a greater volume is exactly balanced by the decrease in disorder associated with the lowered temperature and reduced molecular speeds.

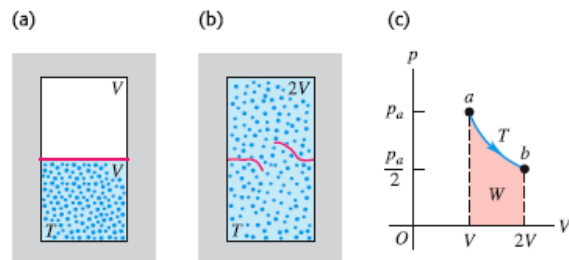
Example 20.8 Entropy change in a free expansion

A thermally insulated box is divided by a partition into two compartments, each having volume V (Fig. 20.19). Initially, one compartment contains n moles of an ideal gas at temperature T , and the other compartment is evacuated. We then break the partition, and the gas expands to fill both compartments. What is the entropy change in this free-expansion process?

SOLUTION

IDENTIFY: For this process, $Q = 0$, $W = 0$, $\Delta U = 0$, and therefore (because the system is an ideal gas) $\Delta T = 0$. We might think that the entropy change is zero because there is no heat exchange. But Eq. (20.19) can be used to calculate entropy changes for *reversible* processes only; this free expansion is *not* reversible, and there *is* an entropy change. The process is adiabatic because $Q = 0$, but it is not isentropic because $\Delta S \neq 0$. As we mentioned

20.19 (a,b) Free expansion of an insulated ideal gas. (c) The free-expansion process doesn't pass through equilibrium states from a to b . However, the entropy change $S_b - S_a$ can be calculated by using the isothermal path shown or *any* reversible path from a to b .



Continued

at the beginning of this section, entropy increases in a free expansion because the positions of the molecules are more random than before the expansion.

SET UP: To calculate ΔS , we recall that the entropy change depends only on the initial and final states. We can devise a *reversible* process having the same endpoints, use Eq. (20.19) to calculate its entropy change, and thus determine the entropy change in the original process. An appropriate reversible process in this case is an isothermal expansion from V to $2V$ at temperature T . The gas does work W during this substitute expansion, so an equal amount of heat Q must be supplied to keep the internal energy constant. We find the entropy change for this reversible isothermal process using Eq. (20.18); the entropy change for the free expansion will be the same.

EXECUTE: We found in Example 19.1 (Section 19.2) that the work done by n moles of ideal gas in an isothermal expansion from V_1 to V_2 is $W = nRT \ln(V_2/V_1)$. Using $V_1 = V$ and $V_2 = 2V$, we have

$$Q = W = nRT \ln \frac{2V}{V} = nRT \ln 2$$

Thus the entropy change is

$$\Delta S = \frac{Q}{T} = nR \ln 2$$

which is also the entropy change for the free expansion with the same initial and final states. For 1 mole,

$$\Delta S = (1 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(\ln 2) = 5.76 \text{ J/K}$$

EVALUATE: The entropy change is positive, as we predicted. The factor $(\ln 2)$ in our answer is a result of the volume having increased by a factor of 2. Can you show that if the volume had increased in the free expansion from V to xV , where x is an arbitrary number, the entropy change would have been $\Delta S = nR \ln x$?

Example 20.9 Entropy and the Carnot cycle

For the Carnot engine in Example 20.2 (Section 20.6), find the total entropy change in the engine during one cycle.

SOLUTION

IDENTIFY: All four steps in the Carnot cycle are reversible (see Fig. 20.13), so we can use the expression for the change in entropy in a reversible process.

SET UP: We find the entropy change ΔS for each step and then add the entropy changes to get the total ΔS for the cycle as a whole.

EXECUTE: There is no entropy change during the adiabatic expansion or adiabatic compression. During the isothermal expansion at $T_H = 500 \text{ K}$ the engine takes in 2000 J of heat, and its entropy change, from Eq. (20.18), is

$$\Delta S_H = \frac{Q_H}{T_H} = \frac{2000 \text{ J}}{500 \text{ K}} = 4.0 \text{ J/K}$$

During the isothermal compression at $T_C = 350 \text{ K}$ the engine gives off 1400 J of heat, and its entropy change is

$$\Delta S_C = \frac{Q_C}{T_C} = \frac{-1400 \text{ J}}{350 \text{ K}} = -4.0 \text{ J/K}$$

The total entropy change in the engine during one cycle is $\Delta S_{\text{total}} = \Delta S_H + \Delta S_C = 4.0 \text{ J/K} + (-4.0 \text{ J/K}) = 0$.

EVALUATE: The result $\Delta S_{\text{total}} = 0$ tells us that when the Carnot engine completes a cycle, it has the same entropy as it did at the beginning of the cycle. We'll explore this result in the following subsection.

What is the total entropy change of the engine's *environment* during this cycle? The hot (500 K) reservoir gives off 2000 J of heat during the reversible isothermal expansion, so its entropy change is $(-2000 \text{ J})/(500 \text{ K}) = -4.0 \text{ J/K}$; the cold (350 K) reservoir absorbs 1400 J of heat during the reversible isothermal compression, so its entropy change is $(+1400 \text{ J})/(350 \text{ K}) = +4.0 \text{ J/K}$. Thus each individual reservoir has an entropy change; however, the sum of these changes—that is, the total entropy change of the system's environment—is zero.

These results apply to the special case of the Carnot cycle, for which *all* of the processes are reversible. In this case we find that the total entropy change of the system and the environment together is zero. We will see that if the cycle includes irreversible processes (as is the case for the Otto cycle or Diesel cycle of Section 20.3), the total entropy change of the system and the environment *cannot* be zero, but rather must be positive.

Entropy in Cyclic Processes

Example 20.9 showed that the total entropy change for a cycle of a particular Carnot engine, which uses an ideal gas as its working substance, is zero. This result follows directly from Eq. (20.13), which we can rewrite as

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0 \quad (20.20)$$

The quotient Q_H/T_H equals ΔS_H , the entropy change of the engine that occurs at $T = T_H$. Likewise, Q_C/T_C equals ΔS_C , the (negative) entropy change of the

engine that occurs at $T = T_C$. Hence Eq. (20.20) says that $\Delta S_H + \Delta S_C = 0$; that is, there is zero net entropy change in one cycle.

What about Carnot engines that use a different working substance? According to the second law, *any* Carnot engine operating between given temperatures T_H and T_C has the same efficiency $e = 1 - T_C/T_H$ [Eq. (20.14)]. Combining this expression for e with Eq. (20.4), $e = 1 + Q_C/Q_H$, just reproduces Eq. (20.20). So Eq. (20.20) is valid for any Carnot engine working between these temperatures, whether its working substance is an ideal gas or not. We conclude that *the total entropy change in one cycle of any Carnot engine is zero*.

This result can be generalized to show that the total entropy change during *any* reversible cyclic process is zero. A reversible cyclic process appears on a pV -diagram as a closed path (Fig. 20.20a). We can approximate such a path as closely as we like by a sequence of isothermal and adiabatic processes forming parts of many long, thin Carnot cycles (Fig. 20.20b). The total entropy change for the full cycle is the sum of the entropy changes for each small Carnot cycle, each of which is zero. So **the total entropy change during any reversible cycle is zero**:

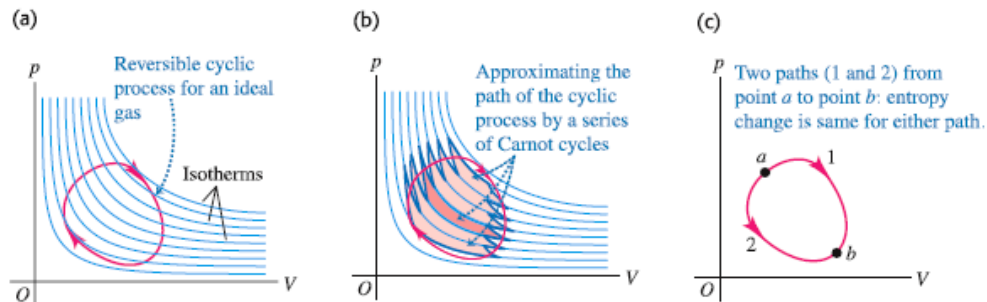
$$\int \frac{dQ}{T} = 0 \quad (\text{reversible cyclic process}) \quad (20.21)$$

It follows that when a system undergoes a reversible process leading from any state a to any other state b , *the entropy change of the system is independent of the path* (Fig. 20.20c). If the entropy change for path 1 were different from the change for path 2, the system could be taken along path 1 and then backward along path 2 to the starting point, with a nonzero net change in entropy. This would violate the conclusion that the total entropy change in such a cyclic process must be zero. Because the entropy change in such processes is independent of path, we conclude that in any given state, the system has a definite value of entropy that depends only on the state, not on the processes that led to that state.

Entropy in Irreversible Processes

In an idealized, reversible process involving only equilibrium states, the total entropy change of the system and its surroundings is zero. But all *irreversible* processes involve an increase in entropy. Unlike energy, *entropy is not a conserved quantity*. The entropy of an isolated system *can* change, but as we shall see, it can never decrease. The free expansion of a gas, described in Example 20.8, is an irreversible process in an isolated system in which there is an entropy increase.

20.20 (a) A reversible cyclic process for an ideal gas is shown as a red closed path on a pV -diagram. Several ideal-gas isotherms are shown in blue. (b) We can approximate the path in (a) by a series of long, thin Carnot cycles; one of these is highlighted in gold. The total entropy change is zero for each Carnot cycle and for the actual cyclic process. (c) The entropy change between points a and b is independent of the path.



Example 20.10 An irreversible process

Suppose 1.00 kg of water at 100°C is placed in thermal contact with 1.00 kg of water at 0°C. What is the total change in entropy? Assume that the specific heat of water is constant at 4190 J/kg · K over this temperature range.

SOLUTION

IDENTIFY: This process involves irreversible heat flow because of the temperature differences.

SET UP: Since there are equal masses of 0°C water and 100°C water, the final temperature is the average of these two temperatures, or 50°C. Although the processes are irreversible, we can calculate the entropy changes for the (initially) hot water and the (initially) cold water in the same way as in Example 20.6 by assuming that the process occurs reversibly. We must use Eq. (20.19) to calculate ΔS for each substance because the temperatures change in the process.

EXECUTE: The final temperature is 50°C = 323 K. The entropy change of the hot water is

$$\begin{aligned}\Delta S_{\text{hot}} &= mc \int_{T_1}^{T_2} \frac{dT}{T} = (1.00 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \int_{373 \text{ K}}^{323 \text{ K}} \frac{dT}{T} \\ &= (4190 \text{ J/K}) \left(\ln \frac{323 \text{ K}}{373 \text{ K}} \right) = -603 \text{ J/K}\end{aligned}$$

The entropy change of the cold water is

$$\Delta S_{\text{cold}} = (4190 \text{ J/K}) \left(\ln \frac{323 \text{ K}}{273 \text{ K}} \right) = +705 \text{ J/K}$$

The total entropy change of the system is

$$\Delta S_{\text{total}} = \Delta S_{\text{hot}} + \Delta S_{\text{cold}} = (-603 \text{ J/K}) + 705 \text{ J/K} = +102 \text{ J/K}$$

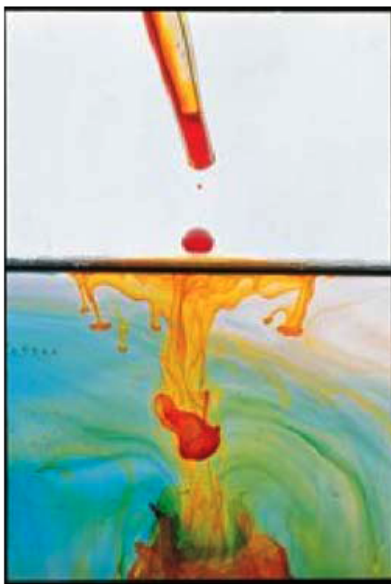
EVALUATE: An irreversible heat flow in an isolated system is accompanied by an increase in entropy. We could have reached the same end state by simply mixing the two quantities of water. This, too, is an irreversible process; because the entropy depends only on the state of the system, the total entropy change would be the same, 102 J/K.

It's worth noting that the entropy of the system increases *continuously* as the two quantities of water come to equilibrium. For example, the first 4190 J of heat transferred cools the hot water to 99°C and warms the cold water to 1°C. The net change in entropy for this step is approximately

$$\Delta S = \frac{-4190 \text{ J}}{373 \text{ K}} + \frac{4190 \text{ J}}{273 \text{ K}} = +4.1 \text{ J/K}$$

Can you show in a similar way that the net entropy change is positive for *any* one-degree temperature change leading to the equilibrium condition?

20.21 The mixing of colored ink and water starts from a state of relative order (low entropy) in which each fluid is separate and distinct from the other. The final state after mixing is more disordered (has greater entropy). Spontaneous unmixing of the ink and water, a process in which there would be a net decrease in entropy, is never observed.



Entropy and the Second Law

The results of Example 20.10 about the flow of heat from a higher to a lower temperature, or the mixing of substances at different temperatures, are characteristic of *all* natural (that is, irreversible) processes. When we include the entropy changes of all the systems taking part in the process, the increases in entropy are always greater than the decreases. In the special case of a *reversible* process, the increases and decreases are equal. Hence we can state the general principle: **When all systems taking part in a process are included, the entropy either remains constant or increases.** In other words: **No process is possible in which the total entropy decreases, when all systems taking part in the process are included.** This is an alternative statement of the second law of thermodynamics in terms of entropy. Thus it is equivalent to the “engine” and “refrigerator” statements discussed earlier. Fig. 20.21 shows a specific example of this general principle.

The increase of entropy in every natural, irreversible process measures the increase of disorder or randomness in the universe associated with that process. Consider again the example of mixing hot and cold water (Example 20.10). We *might* have used the hot and cold water as the high- and low-temperature reservoirs of a heat engine. While removing heat from the hot water and giving heat to the cold water, we could have obtained some mechanical work. But once the hot and cold water have been mixed and have come to a uniform temperature, this opportunity to convert heat to mechanical work is lost irretrievably. The lukewarm water will *never unmix* itself and separate into hotter and colder portions. No decrease in *energy* occurs when the hot and cold water are mixed. What has been lost is not *energy*, but *opportunity*, the opportunity to convert part of the heat from the hot water into mechanical work. Hence when entropy increases, energy becomes less *available*, and the universe becomes more random or “run down.”

Test Your Understanding of Section 20.7 Suppose 2.00 kg of water at 50°C spontaneously changes temperature, so that half of the water cools to 0°C while the other half spontaneously warms to 100°C. (All of the water remains liquid, so it doesn't freeze or boil.) What would be the entropy change of the water? Is this process possible? (Hint: See Example 20.10.)

*20.8 Microscopic Interpretation of Entropy

We described in Section 19.4 how the internal energy of a system could be calculated, at least in principle, by adding up all the kinetic energies of its constituent particles and all the potential energies of interaction among the particles. This is called a *microscopic* calculation of the internal energy. We can also make a microscopic calculation of the entropy S of a system. Unlike energy, however, entropy is not something that belongs to each individual particle or pair of particles in the system. Rather, entropy is a measure of the disorder of the system as a whole. To see how to calculate entropy microscopically, we first have to introduce the idea of *macroscopic* and *microscopic* states.

Suppose you toss N identical coins on the floor, and half of them show heads and half show tails. This is a description of the large-scale or **macroscopic state** of the system of N coins. A description of the **microscopic state** of the system includes information about each individual coin: Coin 1 was heads, coin 2 was tails, coin 3 was tails, and so on. There can be many microscopic states that correspond to the same macroscopic description. For instance, with $N = 4$ coins there are six possible states in which half are heads and half are tails (Fig. 20.22). The number of microscopic states grows rapidly with increasing N ; for $N = 100$ there are $2^{100} = 1.27 \times 10^{30}$ microscopic states, of which 1.01×10^{29} are half heads and half tails.






The least probable outcomes of the coin toss are the states that are either all heads or all tails. It is certainly possible that you could throw 100 heads in a row, but don't bet on it; the probability of doing this is only 1 in 1.27×10^{30} . The most probable outcome of tossing N coins is that half are heads and half are tails. The reason is that this *macroscopic* state has the greatest number of corresponding *microscopic* states, as shown in Fig. 20.22.

To make the connection to the concept of entropy, note that N coins that are all heads constitute a completely ordered macroscopic state; the description "all heads" completely specifies the state of each one of the N coins. The same is true if the coins are all tails. But the macroscopic description "half heads, half tails" by itself tells you very little about the state (heads or tails) of each individual coin. We say that the system is *disordered* because we know so little about its microscopic state. Compared to the state "all heads" or "all tails," the state "half heads, half tails" has a much greater number of possible microscopic states, much greater disorder, and hence much greater entropy (which is a quantitative measure of disorder).

Now instead of N coins, consider a mole of an ideal gas containing Avogadro's number of molecules. The macroscopic state of this gas is given by its pressure p , volume V , and temperature T ; a description of the microscopic state involves stating the position and velocity for each molecule in the gas. At a given pressure, volume, and temperature, the gas may be in any one of an astronomically large number of microscopic states, depending on the positions and velocities of its 6.02×10^{23} molecules. If the gas undergoes a free expansion into a greater volume, the range of possible positions increases, as does the number of possible microscopic states. The system becomes more disordered, and the entropy increases as calculated in Example 20.8 (Section 20.7).

We can draw the following general conclusion: **For any system, the most probable macroscopic state is the one with the greatest number of corresponding microscopic states, which is also the macroscopic state with the greatest disorder and the greatest entropy.**

20.22 All possible microscopic states of four coins. There can be several possible microscopic states for each macroscopic state.

Macroscopic state	Corresponding microscopic states
Four heads	
Three heads, one tail	
Two heads, two tails	
One head, three tails	
Four tails	

Calculating Entropy: Microscopic States

Let w represent the number of possible microscopic states for a given macroscopic state. (For the four coins shown in Fig. 20.22 the state of four heads has $w = 1$, the state of three heads and one tails has $w = 4$, and so on.) Then the entropy S of a macroscopic state can be shown to be given by

$$S = k \ln w \quad (\text{microscopic expression for entropy}) \quad (20.22)$$

where $k = R/N_A$ is the Boltzmann constant (gas constant per molecule) introduced in Section 18.3. As Eq. (20.22) shows, increasing the number of possible microscopic states w increases the entropy S .

What matters in a thermodynamic process is not the absolute entropy S but the *difference* in entropy between the initial and final states. Hence an equally valid and useful definition would be $S = k \ln w + C$, where C is a constant, since C cancels in any calculation of an entropy difference between two states. But it's convenient to set this constant equal to zero and use Eq. (20.22). With this choice, since the smallest possible value of w is unity, the smallest possible value of S for any system is $k \ln 1 = 0$. Entropy can *never* be negative.

In practice, calculating w is a difficult task, so Eq. (20.22) is typically used only to calculate the absolute entropy S of certain special systems. But we can use this relationship to calculate *differences* in entropy between one state and another. Consider a system that undergoes a thermodynamic process that takes it from macroscopic state 1, for which there are w_1 possible microscopic states, to macroscopic state 2, with w_2 associated microscopic states. The change in entropy in this process is

$$\Delta S = S_2 - S_1 = k \ln w_2 - k \ln w_1 = k \ln \frac{w_2}{w_1} \quad (20.23)$$

The *difference* in entropy between the two macroscopic states depends on the *ratio* of the numbers of possible microscopic states.

As the following example shows, using Eq. (20.23) to calculate a change in entropy from one macroscopic state to another gives the same results as considering a reversible process connecting those two states and using Eq. (20.19).

Example 20.11 A microscopic calculation of entropy change

Use Eq. (20.23) to calculate the entropy change in the free expansion of n moles of gas at temperature T described in Example 20.8 (Fig. 20.23).

SOLUTION

IDENTIFY: We are asked to calculate the entropy change using the number of microstates in the initial macroscopic state (Fig. 20.23a) and in the final macroscopic state (Fig. 20.23b).

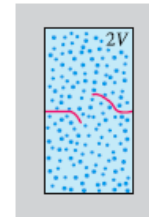
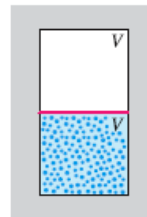
SET UP: When the partition is broken, the velocities of the molecules are unaffected, since no work is done. But each molecule now has twice as much volume in which it can move and hence has twice the number of possible positions. This is all we need to calculate the entropy change using Eq. (20.23).

EXECUTE: Let w_1 be the number of microscopic states of the system as a whole when the gas occupies volume V (Fig. 20.23a). The

20.23 In a free expansion of N molecules in which the volume doubles, the number of possible microscopic states increases by 2^N .

(a) Gas occupies volume V ; number of microstates = w_1 .

(b) Gas occupies volume $2V$; number of microstates = $w_2 = 2^N w_1$.



number of molecules is $N = nN_A$, and each molecule has twice as many possible states after the partition is broken. Hence the number w_2 of microscopic states when the gas occupies volume $2V$ (Fig. 20.23b) is greater by a factor of 2^N ; that is, $w_2 = 2^N w_1$.

The change in entropy in this process is

$$\begin{aligned}\Delta S &= k \ln \frac{w_2}{w_1} = k \ln \frac{2^N w_1}{w_1} = k \ln 2^N \\ &= Nk \ln 2\end{aligned}$$

Since $N = nN_A$ and $k = R/N_A$, this becomes

$$\Delta S = (nN_A)(R/N_A) \ln 2 = nR \ln 2$$

EVALUATE: We have found the same result as in Example 20.8, but without any reference to the thermodynamic path taken.

Microscopic States and the Second Law

The relationship between entropy and the number of microscopic states gives us new insight into the entropy statement of the second law of thermodynamics, that the entropy of a closed system can never decrease. From Eq. (20.22) this means that a closed system can never spontaneously undergo a process that decreases the number of possible microscopic states.

An example of such a forbidden process would be if all of the air in your room spontaneously moved to one half of the room, leaving a vacuum in the other half. Such a “free compression” would be the reverse of the free expansion of Examples 20.8 and 20.11. This would decrease the number of possible microscopic states by a factor of 2^N . Strictly speaking, this process is not impossible! The probability of finding a given molecule in one half of the room is $\frac{1}{2}$, so the probability of finding all of the molecules in one half of the room at once is $(\frac{1}{2})^N$. (This is exactly the same as the probability of having a tossed coin come up heads N times in a row.) This probability is *not* zero. But lest you worry about suddenly finding yourself gasping for breath in the evacuated half of your room, consider that a typical room might hold 1000 moles of air, and so $N = 1000N_A = 6.02 \times 10^{26}$ molecules. The probability of all the molecules being in the same half of the room is therefore $(\frac{1}{2})^{6.02 \times 10^{26}}$. Expressed as a decimal, this number has more than 10^{26} zeros to the right of the decimal point!

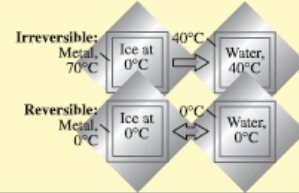
Because the probability of such a “free compression” taking place is so vanishingly small, it has almost certainly never occurred anywhere in the universe since the beginning of time. We conclude that for all practical purposes the second law of thermodynamics is never violated.

Test Your Understanding of Section 20.8 A quantity of N molecules of an ideal gas initially occupies volume V . The gas then expands to volume $2V$. The number of microscopic states of the gas increases in this expansion. Under which of the following circumstances will this number increase the most? (i) if the expansion is reversible and isothermal; (ii) if the expansion is reversible and adiabatic; (iii) the number will change by the same amount for both circumstances.



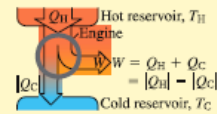
CHAPTER 20 SUMMARY

Reversible and irreversible processes: A reversible process is one whose direction can be reversed by an infinitesimal change in the conditions of the process, and in which the system is always in or very close to thermal equilibrium. All other thermodynamic processes are irreversible.



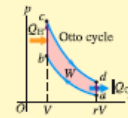
Heat engines: A heat engine takes heat Q_H from a source, converts part of it to work W , and discards the remainder $|Q_C|$ at a lower temperature. The thermal efficiency e of a heat engine measures how much of the absorbed heat is converted to work. (See Example 20.1)

$$e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \left| \frac{Q_C}{Q_H} \right| \quad (20.4)$$



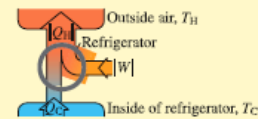
The Otto cycle: A gasoline engine operating on the Otto cycle has a theoretical maximum thermal efficiency e that depends on the compression ratio r and the ratio of heat capacities γ of the working substance.

$$e = 1 - \frac{1}{r^{\gamma-1}} \quad (20.6)$$

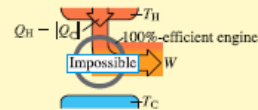


Refrigerators: A refrigerator takes heat Q_C from a colder place, has a work input $|W|$, and discards heat $|Q_H|$ at a warmer place. The effectiveness of the refrigerator is given by its coefficient of performance K .

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|} \quad (20.9)$$

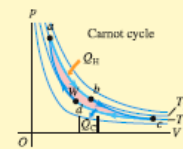


The second law of thermodynamics: The second law of thermodynamics describes the directionality of natural thermodynamic processes. It can be stated in several equivalent forms. The *engine* statement is that no cyclic process can convert heat completely into work. The *refrigerator* statement is that no cyclic process can transfer heat from a colder place to a hotter place with no input of mechanical work.



The Carnot cycle: The Carnot cycle operates between two heat reservoirs at temperatures T_H and T_C and uses only reversible processes. Its thermal efficiency depends only on T_H and T_C . An additional equivalent statement of the second law is that no engine operating between the same two temperatures can be more efficient than a Carnot engine. (See Examples 20.2 and 20.3.)

$$e_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \quad (20.14)$$



A Carnot engine run backward is a Carnot refrigerator. Its coefficient of performance depends only on T_H and T_C . Another form of the second law states that no refrigerator operating between the same two temperatures can have a larger coefficient of performance than a Carnot refrigerator. (See Example 20.4.)

$$K_{\text{Carnot}} = \frac{T_C}{T_H - T_C} \quad (20.15)$$

Entropy: Entropy is a quantitative measure of the disorder of a system. The entropy change in any reversible process depends on the amount of heat flow and the absolute temperature T . Entropy depends only on the state of the system, and the change in entropy between given initial and final states is the same for all processes leading from one state to the other. This fact can be used to find the entropy change in an irreversible process. (See Examples 20.5–20.10)

$$\Delta S = \int_1^2 \frac{dQ}{T} \quad (20.19)$$

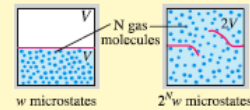
(reversible process)



An important statement of the second law of thermodynamics is that the entropy of an isolated system may increase but can never decrease. When a system interacts with its surroundings, the total entropy change of system and surroundings can never decrease. When the interaction involves only reversible processes, the total entropy is constant and $\Delta S = 0$; when there is any irreversible process, the total entropy increases and $\Delta S > 0$.

Entropy and microscopic states: When a system is in a particular macroscopic state, the particles that make up the system may be in any of w possible microscopic states. The greater the number w , the greater the entropy. (See Example 20.11.)

$$S = k \ln w \quad (20.22)$$



Key Terms

irreversible process, 673
 reversible process, 674
 equilibrium process, 674
 heat engine, 675
 working substance, 675
 cyclic process, 675
 thermal efficiency, 676

compression ratio, 678
 Otto cycle, 678
 Diesel cycle, 680
 refrigerator, 680
 coefficient of performance, 680
 energy efficiency rating, 681–682
 heat pump, 682

second law of thermodynamics, 682
 Carnot cycle, 684
 Kelvin temperature scale, 690
 absolute zero, 690
 entropy, 691
 macroscopic state, 697
 microscopic state, 697

Answer to Chapter Opening Question

Yes. That's what a refrigerator does: It makes heat flow from the cold interior of the refrigerator to the warm outside. The second law of thermodynamics says that heat cannot *spontaneously* flow from a cold body to a hot one. A refrigerator has a motor that does work on the system to *force* the heat to flow in that way.

Answers to Test Your Understanding Questions

20.1 Answer: (ii) Like sliding a book across a table, rubbing your hands together uses friction to convert mechanical energy into heat. The (impossible) reverse process would involve your hands spontaneously getting colder, with the released energy forcing your hands to move rhythmically back and forth!

20.2 Answer: (iii), (i), (ii) From Eq. (20.4) the efficiency is $e = W/Q_H$, and from Eq. (20.2) $W = Q_H + Q_C = |Q_H| - |Q_C|$. For engine (i) $Q_H = 5000 \text{ J}$ and $Q_C = -4500 \text{ J}$, so $W = 5000 \text{ J} + (-4500 \text{ J}) = 500 \text{ J}$ and $e = (500 \text{ J})/(5000 \text{ J}) = 0.100$. For engine (ii) $Q_H = 25,000 \text{ J}$ and $W = 2000 \text{ J}$, so $e = (2000 \text{ J})/(25,000 \text{ J}) = 0.080$. For engine (iii) $W = 400 \text{ J}$ and

$Q_C = -2800 \text{ J}$, so $Q_H = W - Q_C = 400 \text{ J} - (-2800 \text{ J}) = 3200 \text{ J}$ and $e = (400 \text{ J})/(3200 \text{ J}) = 0.125$.

20.3 Answer: (i), (ii) Doubling the amount of fuel burned per cycle means that Q_H is doubled, so the resulting pressure increase from b to c in Fig. 20.6 is greater. The compression ratio and hence the efficiency remain the same, so $|Q_C|$ (the amount of heat rejected to the environment) must increase by the same factor as Q_H . Hence the pressure drop from d to a in Fig. 20.6 is also greater. The volume V and the compression ratio r don't change, so the horizontal dimensions of the pV -diagram don't change.

20.4 Answer: no A refrigerator uses an input of work to transfer heat from one system (the refrigerator's interior) to another system (its exterior, which includes the house in which the refrigerator is installed). If the door is open, these two systems are really the *same* system and will eventually come to the same temperature. By the first law of thermodynamics, all of the work input to the refrigerator motor will be converted into heat and the temperature in your house will actually *increase*. To cool the house you need a system that will transfer heat from it to the outside world, such as an air conditioner or heat pump.

20.5 Answers: no, no Both the 100%-efficient engine of Fig. 20.11a and the workless refrigerator of Fig. 20.11b return to the same state at the end of a cycle as at the beginning, so the net change in internal energy of each system is zero ($\Delta U = 0$). For the 100%-efficient engine, the net heat flow into the engine equals the net work done, so $Q = W$, $Q - W = 0$, and the first law ($\Delta U = Q - W$) is obeyed. For the workless refrigerator, no net work is done (so $W = 0$) and as much heat flows into it as out (so $Q = 0$), so again $Q - W = 0$ and $\Delta U = Q - W$ in accordance with the first law. It is the second law of thermodynamics that tells us that both the 100%-efficient engine and the workless refrigerator are impossible.

20.6 Answer: no The efficiency can be no better than that of a Carnot engine running between the same two temperature limits, $e_{\text{Carnot}} = 1 - (T_C/T_H)$ [Eq. (20.14)]. The temperature T_C of the cold reservoir for this air-cooled engine is about 300 K (ambient temperature), and the temperature T_H of the hot reservoir cannot exceed the melting point of copper, 1356 K (see Table 17.4). Hence the maximum possible Carnot efficiency is $e = 1 - (300 \text{ K})/(1356 \text{ K}) = 0.78$, or 78%. The temperature of any real engine would be less than this, so it would be impossible

for the inventor's engine to attain 85% efficiency. You should invest your money elsewhere.

20.7 Answers: -102 J/K, no The process described is exactly the opposite of the process used in Example 20.10. The result violates the second law of thermodynamics, which states that the entropy of an isolated system cannot decrease.

20.8 Answer: (i) For case (i), we saw in Example 20.8 (Section 20.7) that for an ideal gas, the entropy change in a free expansion is the same as in an isothermal expansion. From Eq. (20.23), this implies that the ratio of the number of microscopic states after and before the expansion, w_2/w_1 , is also the same for these two cases. From Example 20.11, $w_2/w_1 = 2^N$, so the number of microscopic states increases by a factor 2^N . For case (ii), in a reversible expansion the entropy change is $\Delta S = \int dQ/T = 0$; if the expansion is adiabatic there is no heat flow, so $\Delta S = 0$. From Eq. (20.23), $w_2/w_1 = 1$ and there is *no* change in the number of microscopic states. The difference is that in an adiabatic expansion the temperature drops and the molecules move more slowly, so they have fewer microscopic states available to them than in an isothermal expansion.

PROBLEMS

For instructor-assigned homework, go to www.masteringphysics.com



Discussion Questions

Q20.1. A pot is half-filled with water, and a lid is placed on it, forming a tight seal so that no water vapor can escape. The pot is heated on a stove, forming water vapor inside the pot. The heat is then turned off and the water vapor condenses back to liquid. Is this cycle reversible or irreversible? Why?

Q20.2. Give two examples of reversible processes and two examples of irreversible processes in purely mechanical systems, such as blocks sliding on planes, springs, pulleys, and strings. Explain what makes each process reversible or irreversible.

Q20.3. What irreversible processes occur in a gasoline engine? Why are they irreversible?

Q20.4. Suppose you try to cool the kitchen of your house by leaving the refrigerator door open. What happens? Why? Would the result be the same if you left open a picnic cooler full of ice? Explain the reason for any differences.

Q20.5. A member of the U.S. Congress proposed a scheme to produce energy as follows. Water molecules (H_2O) are to be broken apart to produce hydrogen and oxygen. The hydrogen is then burned (that is, combined with oxygen), releasing energy in the process. The only product of this combustion is water, so there is no pollution. In light of the second law of thermodynamics, what do you think of this energy-producing scheme?

Q20.6. Is it a violation of the second law of thermodynamics to convert mechanical energy completely into heat? To convert heat completely into work? Explain your answers.

Q20.7. Imagine a special air filter placed in a window of a house. The tiny holes in the filter allow only air molecules moving faster than a certain speed to exit the house, and allow only air molecules moving slower than that speed to enter the house from outside. Explain why such an air filter would cool the house, and why the second law of thermodynamics makes building such a filter an impossible task.

Q20.8. An electric motor has its shaft coupled to that of an electric generator. The motor drives the generator, and some current from

the generator is used to run the motor. The excess current is used to light a home. What is wrong with this scheme?

Q20.9. When a wet cloth is hung up in a hot wind in the desert, it is cooled by evaporation to a temperature that may be 20°C or so below that of the air. Discuss this process in light of the second law of thermodynamics.

Q20.10. Compare the pV -diagram for the Otto cycle in Fig. 20.6 with the diagram for the Carnot heat engine in Fig. 20.13. Explain some of the important differences between the two cycles.

Q20.11. If no real engine can be as efficient as a Carnot engine operating between the same two temperatures, what is the point of developing and using Eq. (20.14)?

Q20.12. The efficiency of heat engines is high when the temperature difference between the hot and cold reservoirs is large. Refrigerators, on the other hand, work better when the temperature difference is small. Thinking of the mechanical refrigerator cycle shown in Fig. 20.9, explain in physical terms why it takes less work to remove heat from the working substance if the two reservoirs (the inside of the refrigerator and the outside air) are at nearly the same temperature, than if the outside air is much warmer than the interior of the refrigerator.

Q20.13. What would be the efficiency of a Carnot engine operating with $T_H = T_C$? What would be the efficiency if $T_C = 0 \text{ K}$ and T_H were any temperature above 0 K ? Interpret your answers.

Q20.14. Real heat engines, like the gasoline engine in a car, always have some friction between their moving parts, although lubricants keep the friction to a minimum. Would a heat engine with completely frictionless parts be 100% efficient? Why or why not? Does the answer depend on whether or not the engine runs on the Carnot cycle? Again, why or why not?

Q20.15. Does a refrigerator full of food consume more power if the room temperature is 20°C than if it is 15°C ? Or is the power consumption the same? Explain your reasoning.

Q20.16. In Example 20.4, a Carnot refrigerator requires a work input of only 230 J to extract 346 J of heat from the cold reservoir.