PUZZLER

The purpose of a refrigerator is to keep its contents cool. Beyond the attendant increase in your electricity bill, there is another good reason you should not try to cool the kitchen on a hot day by leaving the refrigerator door open. What might this reason be?
(Charles D. Winters)

chapter

22

Heat Engines, Entropy, and the Second Law of Thermodynamics

Chapter Outline

The first law of thermodynamics, which we studied in Chapter 20, is a statement of conservation of energy, generalized to include internal energy. This law states that a change in internal energy in a system can occur as a result of energy transfer by heat or by work, or by both. As was stated in Chapter 20, the law makes no distinction between the results of heat and the results of work—either heat or work can cause a change in internal energy. However, an important distinction between the two is not evident from the first law. One manifestation of this distinction is that it is impossible to convert internal energy completely to mechanical energy by taking a substance through a thermodynamic cycle such as in a *heat engine,* a device we study in this chapter.

Although the first law of thermodynamics is very important, it makes no distinction between processes that occur spontaneously and those that do not. However, we find that only certain types of energy-conversion and energy-transfer processes actually take place. The *second law of thermodynamics,* which we study in this chapter, establishes which processes do and which do not occur in nature. The following are examples of processes that proceed in only one direction, governed by the second law:

- When two objects at different temperatures are placed in thermal contact with each other, energy always flows by heat from the warmer to the cooler, never from the cooler to the warmer.
- A rubber ball dropped to the ground bounces several times and eventually comes to rest, but a ball lying on the ground never begins bouncing on its own.
- An oscillating pendulum eventually comes to rest because of collisions with air molecules and friction at the point of suspension. The mechanical energy of the system is converted to internal energy in the air, the pendulum, and the suspension; the reverse conversion of energy never occurs.

All these processes are *irreversible*—that is, they are processes that occur naturally in one direction only. No irreversible process has ever been observed to run backward—if it were to do so, it would violate the second law of thermodynamics.[1]

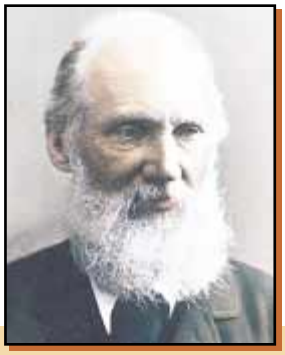
From an engineering standpoint, perhaps the most important implication of the second law is the limited efficiency of heat engines. The second law states that a machine capable of continuously converting internal energy completely to other forms of energy in a cyclic process cannot be constructed.

22.1 HEAT ENGINES AND THE SECOND LAW OF THERMODYNAMICS

A **heat engine** is a device that converts internal energy to mechanical energy. For instance, in a typical process by which a power plant produces electricity, coal or some other fuel is burned, and the high-temperature gases produced are used to convert liquid water to steam. This steam is directed at the blades of a turbine, setting it into rotation. The mechanical energy associated with this rotation is used to drive an electric generator. Another heat engine—the internal combustion engine in an automobile—uses energy from a burning fuel to perform work that results in the motion of the automobile.

[1] Although we have never *observed* a process occurring in the time-reversed sense, it is *possible* for it to occur. As we shall see later in the chapter, however, such a process is highly improbable. From this viewpoint, we say that processes occur with a vastly greater probability in one direction than in the opposite direction.

Figure 22.1 This steam-driven locomotive runs from Durango to Silverton, Colorado. It obtains its energy by burning wood or coal. The generated energy vaporizes water into steam, which powers the locomotive. (This locomotive must take on water from tanks located along the route to replace steam lost through the funnel.) Modern locomotives use diesel fuel instead of wood or coal. Whether old-fashioned or modern, such locomotives are heat engines, which extract energy from a burning fuel and convert a fraction of it to mechanical energy.



Lord Kelvin **British physicist and mathematician (1824–1907)** Born William Thomson in Belfast, Kelvin was the first to propose the use of an absolute scale of temperature. The Kelvin temperature scale is named in his honor. Kelvin's work in thermodynamics led to the idea that energy cannot pass spontaneously from a colder body to a hotter body. *(J. L. Charmet/SPL/Photo Researchers, Inc.)*

A heat engine carries some working substance through a cyclic process during which (1) the working substance absorbs energy from a high-temperature energy reservoir, (2) work is done by the engine, and (3) energy is expelled by the engine to a lower-temperature reservoir. As an example, consider the operation of a steam engine (Fig. 22.1), in which the working substance is water. The water in a boiler absorbs energy from burning fuel and evaporates to steam, which then does work by expanding against a piston. After the steam cools and condenses, the liquid water produced returns to the boiler and the cycle repeats.

It is useful to represent a heat engine schematically as in Figure 22.2. The engine absorbs a quantity of energy Q_h from the hot reservoir, does work W, and then gives up a quantity of energy Q_c to the cold reservoir. Because the working substance goes through a cycle, its initial and final internal energies are equal, and so $\Delta E_{\text{int}} = 0$. Hence, from the first law of thermodynamics, $\Delta E_{\text{int}} = Q - W$, and with no change in internal energy, **the net work W done by a heat engine is equal to the net energy Q_{net} flowing through it.** As we can see from Figure 22.2, $Q_{\text{net}} = Q_h - Q_c$; therefore,

$$W = Q_h - Q_c \tag{22.1}$$

In this expression and in many others throughout this chapter, to be consistent with traditional treatments of heat engines, we take both Q_h and Q_c to be positive quantities, even though Q_c represents energy leaving the engine. In discussions of heat engines, we shall describe energy leaving a system with an explicit minus sign,

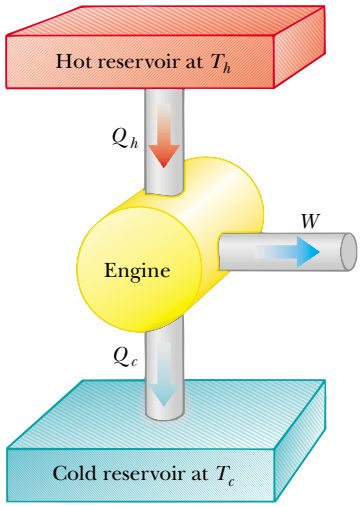


Figure 22.2 Schematic representation of a heat engine. The engine absorbs energy Q_h from the hot reservoir, expels energy Q_c to the cold reservoir, and does work W.

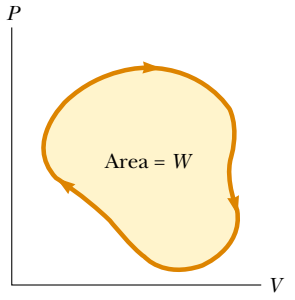


Figure 22.3 *PV* diagram for an arbitrary cyclic process. The value of the net work done equals the area enclosed by the curve.

as in Equation 22.1. Also note that we model the energy input and output for the heat engine as heat, as it often is; however, the energy transfer could occur by another mechanism.

The net work done in a cyclic process is the area enclosed by the curve representing the process on a *PV* diagram. This is shown for an arbitrary cyclic process in Figure 22.3.

The **thermal efficiency** e of a heat engine is defined as the ratio of the net work done by the engine during one cycle to the energy absorbed at the higher temperature during the cycle:

$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} \qquad \textbf{(22.2)}$$

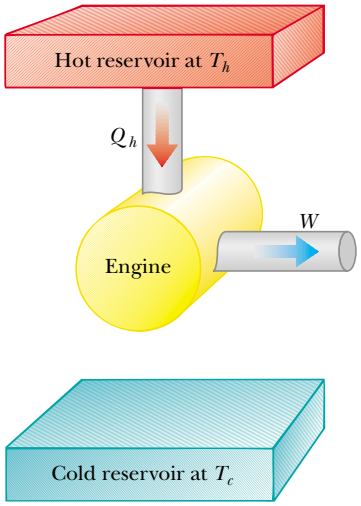
We can think of the efficiency as the ratio of what you get (mechanical work) to what you give (energy transfer at the higher temperature). In practice, we find that all heat engines expel only a fraction of the absorbed energy as mechanical work and that consequently the efficiency is less than 100%. For example, a good automobile engine has an efficiency of about 20%, and diesel engines have efficiencies ranging from 35% to 40%.

Equation 22.2 shows that a heat engine has 100% efficiency ($e = 1$) only if $Q_c = 0$—that is, if no energy is expelled to the cold reservoir. In other words, a heat engine with perfect efficiency would have to expel all of the absorbed energy as mechanical work. On the basis of the fact that efficiencies of real engines are well below 100%, the **Kelvin–Planck** form of the **second law of thermodynamics** states the following:

Kelvin–Planck statement of the second law of thermodynamics

It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the absorption of energy from a reservoir and the performance of an equal amount of work.

This statement of the second law means that, during the operation of a heat engine, W can never be equal to Q_h, or, alternatively, that some energy Q_c must be



The impossible engine

Figure 22.4 Schematic diagram of a heat engine that absorbs energy Q_h from a hot reservoir and does an equivalent amount of work. It is impossible to construct such a perfect engine.

rejected to the environment. Figure 22.4 is a schematic diagram of the impossible "perfect" heat engine.

The first and second laws of thermodynamics can be summarized as follows: The first law specifies that **we cannot get more energy out of a cyclic process by work than the amount of energy we put in,** and the second law states that **we cannot break even because we must put more energy in, at the higher temperature, than the net amount of energy we get out by work.**

EXAMPLE 22.1 The Efficiency of an Engine

Find the efficiency of a heat engine that absorbs 2 000 J of energy from a hot reservoir and exhausts 1 500 J to a cold reservoir.

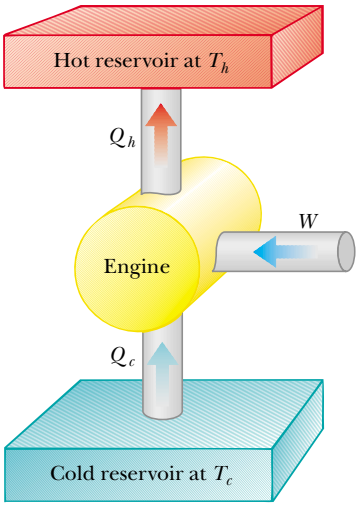
Solution To calculate the efficiency of the engine, we use Equation 22.2:

$$e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{1\,500\ \text{J}}{2\,000\ \text{J}} = 0.25, \text{ or } 25\%$$

Refrigerators and Heat Pumps

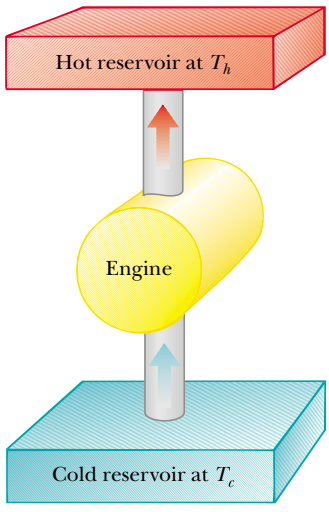
Refrigerators and **heat pumps** are heat engines running in reverse. Here, we introduce them briefly for the purposes of developing an alternate statement of the second law; we shall discuss them more fully in Section 22.5.

In a refrigerator or heat pump, the engine absorbs energy Q_c from a cold reservoir and expels energy Q_h to a hot reservoir (Fig. 22.5). This can be accomplished only if work is done *on* the engine. From the first law, we know that the energy given up to the hot reservoir must equal the sum of the work done and the energy absorbed from the cold reservoir. Therefore, the refrigerator or heat pump transfers energy from a colder body (for example, the contents of a kitchen refrigerator or the winter air outside a building) to a hotter body (the air in the kitchen or a room in the building). In practice, it is desirable to carry out this process with a minimum of work. If it could be accomplished without doing any work, then the refrigerator or heat pump would be "perfect" (Fig. 22.6). Again, the existence of



Refrigerator

Figure 22.5 Schematic diagram of a refrigerator, which absorbs energy Q_c from a cold reservoir and expels energy Q_h to a hot reservoir. Work W is done *on* the refrigerator. A heat pump, which can be used to heat or cool a building, works the same way.



Impossible refrigerator

Figure 22.6 Schematic diagram of an impossible refrigerator or heat pump—that is, one that absorbs energy Q_c from a cold reservoir and expels an equivalent amount of energy to a hot reservoir with $W = 0$.

such a device would be in violation of the second law of thermodynamics, which in the form of the **Clausius statement**[2] states:

Clausius statement of the second law of thermodynamics

It is impossible to construct a cyclical machine whose sole effect is the continuous transfer of energy from one object to another object at a higher temperature without the input of energy by work.

In simpler terms, **energy does not flow spontaneously from a cold object to a hot object.** For example, we cool homes in summer using heat pumps called *air conditioners*. The air conditioner pumps energy from the cool room in the home to the warm air outside. This direction of energy transfer requires an input of energy to the air conditioner, which is supplied by the electric power company.

The Clausius and Kelvin–Planck statements of the second law of thermodynamics appear, at first sight, to be unrelated, but in fact they are equivalent in all respects. Although we do not prove so here, if either statement is false, then so is the other.[3]

22.2 REVERSIBLE AND IRREVERSIBLE PROCESSES

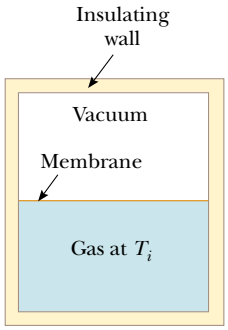


Figure 22.7 Adiabatic free expansion of a gas.

In the next section we discuss a theoretical heat engine that is the most efficient possible. To understand its nature, we must first examine the meaning of reversible and irreversible processes. In a **reversible** process, the system undergoing the process can be returned to its initial conditions along the same path shown on a *PV* diagram, and every point along this path is an equilibrium state. A process that does not satisfy these requirements is **irreversible.**

All natural processes are known to be irreversible. From the endless number of examples that could be selected, let us examine the adiabatic free expansion of a gas, which was already discussed in Section 20.6, and show that it cannot be reversible. The system that we consider is a gas in a thermally insulated container, as shown in Figure 22.7. A membrane separates the gas from a vacuum. When the membrane is punctured, the gas expands freely into the vacuum. As a result of the puncture, the system has changed because it occupies a greater volume after the expansion. Because the gas does not exert a force through a distance on the surroundings, it does no work on the surroundings as it expands. In addition, no energy is transferred to or from the gas by heat because the container is insulated from its surroundings. Thus, in this adiabatic process, the system has changed but the surroundings have not.

For this process to be reversible, we need to be able to return the gas to its original volume and temperature without changing the surroundings. Imagine that we try to reverse the process by compressing the gas to its original volume. To do so, we fit the container with a piston and use an engine to force the piston inward. During this process, the surroundings change because work is being done by an outside agent on the system. In addition, the system changes because the compression increases the temperature of the gas. We can lower the temperature of the gas by allowing it to come into contact with an external energy reservoir. Although this step returns the gas to its original conditions, the surroundings are

[2] First expressed by Rudolf Clausius (1822–1888).

[3] See, for example, R. P. Bauman, *Modern Thermodynamics and Statistical Mechanics,* New York, Macmillan Publishing Co., 1992.

again affected because energy is being added to the surroundings from the gas. If this energy could somehow be used to drive the engine that we have used to compress the gas, then the net energy transfer to the surroundings would be zero. In this way, the system and its surroundings could be returned to their initial conditions, and we could identify the process as reversible. However, the Kelvin–Planck statement of the second law specifies that the energy removed from the gas to return the temperature to its original value cannot be completely converted to mechanical energy in the form of the work done by the engine in compressing the gas. Thus, we must conclude that the process is irreversible.

We could also argue that the adiabatic free expansion is irreversible by relying on the portion of the definition of a reversible process that refers to equilibrium states. For example, during the expansion, significant variations in pressure occur throughout the gas. Thus, there is no well-defined value of the pressure for the entire system at any time between the initial and final states. In fact, the process cannot even be represented as a path on a *PV* diagram. The *PV* diagram for an adiabatic free expansion would show the initial and final conditions as points, but these points would not be connected by a path. Thus, because the intermediate conditions between the initial and final states are not equilibrium states, the process is irreversible.

Although all real processes are always irreversible, some are almost reversible. If a real process occurs very slowly such that the system is always very nearly in an equilibrium state, then the process can be approximated as reversible. For example, let us imagine that we compress a gas very slowly by dropping some grains of sand onto a frictionless piston, as shown in Figure 22.8. We make the process isothermal by placing the gas in thermal contact with an energy reservoir, and we transfer just enough energy from the gas to the reservoir during the process to keep the temperature constant. The pressure, volume, and temperature of the gas are all well defined during the isothermal compression, so each state during the process is an equilibrium state. Each time we add a grain of sand to the piston, the volume of the gas decreases slightly while the pressure increases slightly. Each grain we add represents a change to a new equilibrium state. We can reverse the process by slowly removing grains from the piston.

A general characteristic of a reversible process is that no dissipative effects (such as turbulence or friction) that convert mechanical energy to internal energy can be present. Such effects can be impossible to eliminate completely. Hence, it is not surprising that real processes in nature are irreversible.

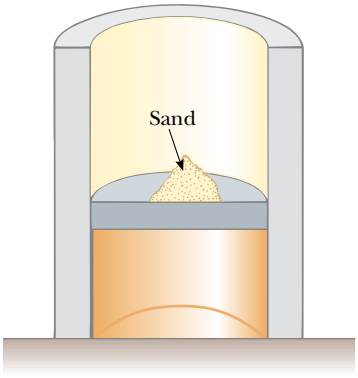
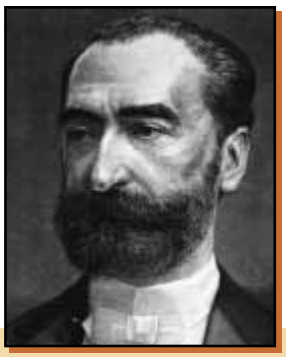


Figure 22.8 A gas in thermal contact with an energy reservoir is compressed slowly as individual grains of sand drop onto the piston. The compression is isothermal and reversible.

22.3 THE CARNOT ENGINE

10.9 In 1824 a French engineer named Sadi Carnot described a theoretical engine, now called a **Carnot engine,** that is of great importance from both practical and theoretical viewpoints. He showed that a heat engine operating in an ideal, reversible cycle—called a **Carnot cycle**—between two energy reservoirs is the most efficient engine possible. Such an ideal engine establishes an upper limit on the efficiencies of all other engines. That is, the net work done by a working substance taken through the Carnot cycle is the greatest amount of work possible for a given amount of energy supplied to the substance at the upper temperature. **Carnot's theorem** can be stated as follows:

> No real heat engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.



Sadi Carnot **French physicist (1796–1832)** Carnot was the first to show the quantitative relationship between work and heat. In 1824 he published his only work—*Reflections on the Motive Power of Heat*—which reviewed the industrial, political, and economic importance of the steam engine. In it, he defined work as "weight lifted through a height." *(FPG)*

To argue the validity of this theorem, let us imagine two heat engines operating between the *same* energy reservoirs. One is a Carnot engine with efficiency e_C, and the other is an engine with efficiency e, which is greater than e_C. We use the more efficient engine to drive the Carnot engine as a Carnot refrigerator. Thus, the output by work of the more efficient engine is matched to the input by work of the

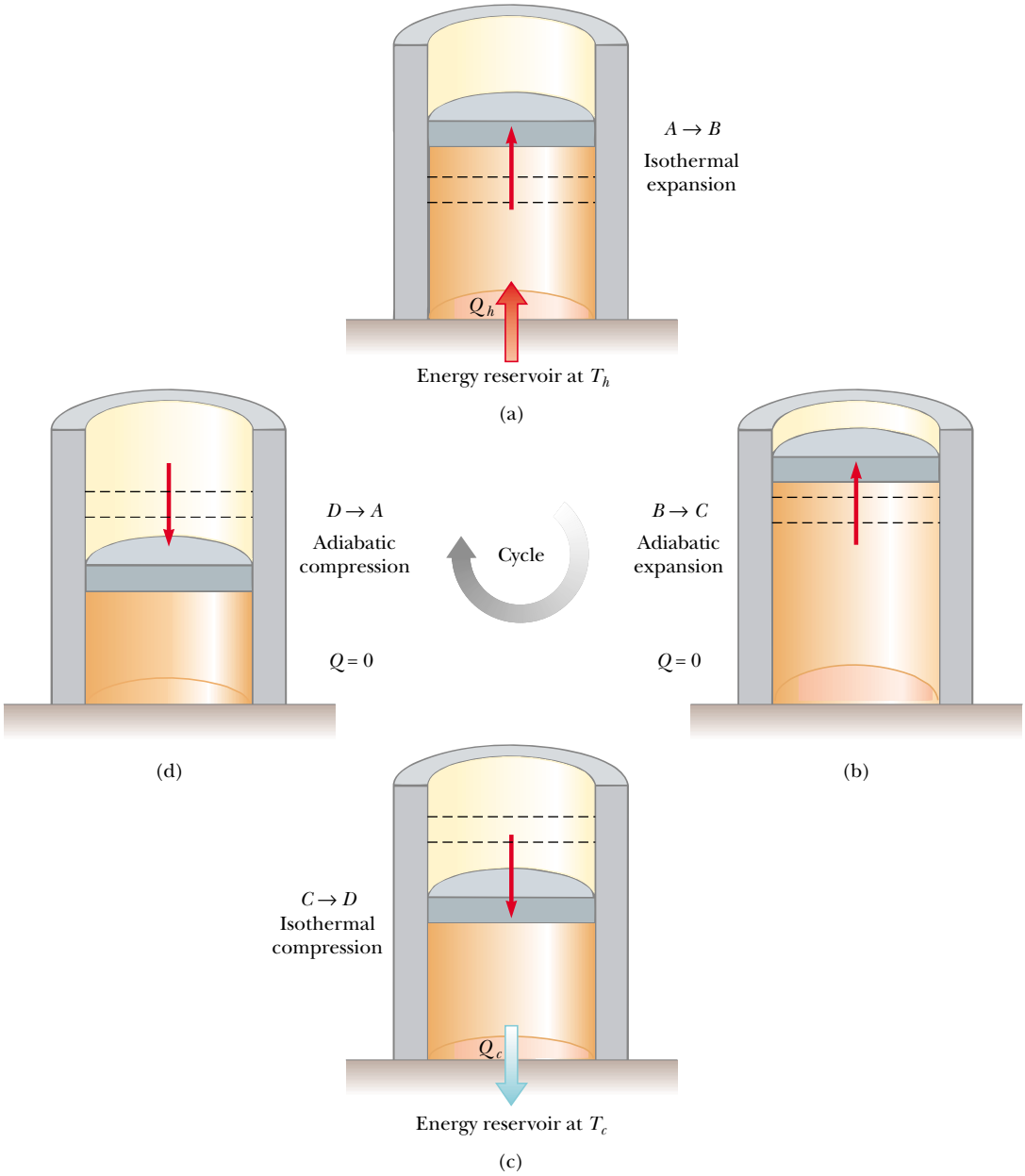


Figure 22.9 The Carnot cycle. In process $A \rightarrow B$, the gas expands isothermally while in contact with a reservoir at T_h. In process $B \rightarrow C$, the gas expands adiabatically ($Q = 0$). In process $C \rightarrow D$, the gas is compressed isothermally while in contact with a reservoir at $T_c < T_h$. In process $D \rightarrow A$, the gas is compressed adiabatically. The upward arrows on the piston indicate that weights are being removed during the expansions, and the downward arrows indicate that weights are being added during the compressions.

Carnot refrigerator. For the *combination* of the engine and refrigerator, then, no exchange by work with the surroundings occurs. Because we have assumed that the engine is more efficient than the refrigerator, the net result of the combination is a transfer of energy from the cold to the hot reservoir without work being done on the combination. According to the Clausius statement of the second law, this is impossible. Hence, the assumption that $e > e_C$ must be false. **All real engines are less efficient than the Carnot engine because they do not operate through a reversible cycle.** The efficiency of a real engine is further reduced by such practical difficulties as friction and energy losses by conduction.

To describe the Carnot cycle taking place between temperatures T_c and T_h, we assume that the working substance is an ideal gas contained in a cylinder fitted with a movable piston at one end. The cylinder's walls and the piston are thermally nonconducting. Four stages of the Carnot cycle are shown in Figure 22.9, and the *PV* diagram for the cycle is shown in Figure 22.10. The Carnot cycle consists of two adiabatic processes and two isothermal processes, all reversible:

1. Process $A \rightarrow B$ (Fig. 22.9a) is an isothermal expansion at temperature T_h. The gas is placed in thermal contact with an energy reservoir at temperature T_h. During the expansion, the gas absorbs energy Q_h from the reservoir through the base of the cylinder and does work W_{AB} in raising the piston.
2. In process $B \rightarrow C$ (Fig. 22.9b), the base of the cylinder is replaced by a thermally nonconducting wall, and the gas expands adiabatically—that is, no energy enters or leaves the system. During the expansion, the temperature of the gas decreases from T_h to T_c and the gas does work W_{BC} in raising the piston.
3. In process $C \rightarrow D$ (Fig. 22.9c), the gas is placed in thermal contact with an energy reservoir at temperature T_c and is compressed isothermally at temperature T_c. During this time, the gas expels energy Q_c to the reservoir, and the work done by the piston on the gas is W_{CD}.
4. In the final process $D \rightarrow A$ (Fig. 22.9d), the base of the cylinder is replaced by a nonconducting wall, and the gas is compressed adiabatically. The temperature of the gas increases to T_h, and the work done by the piston on the gas is W_{DA}.

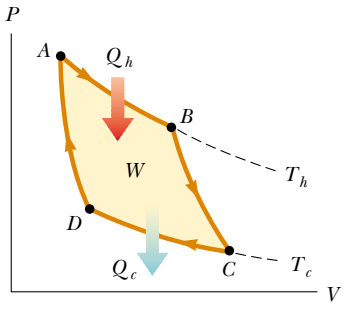


Figure 22.10 *PV* diagram for the Carnot cycle. The net work done, *W*, equals the net energy received in one cycle, $Q_h - Q_c$. Note that $\Delta E_{int} = 0$ for the cycle.

The net work done in this reversible, cyclic process is equal to the area enclosed by the path *ABCDA* in Figure 22.10. As we demonstrated in Section 22.1, because the change in internal energy is zero, the net work *W* done in one cycle equals the net energy transferred into the system, $Q_h - Q_c$. The thermal efficiency of the engine is given by Equation 22.2:

$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

In Example 22.2, we show that for a Carnot cycle

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h} \qquad (22.3)$$

Ratio of energies for a Carnot cycle

Hence, the thermal efficiency of a Carnot engine is

$$e_C = 1 - \frac{T_c}{T_h} \qquad (22.4)$$

Efficiency of a Carnot engine

This result indicates that **all Carnot engines operating between the same two temperatures have the same efficiency.**

Equation 22.4 can be applied to any working substance operating in a Carnot cycle between two energy reservoirs. According to this equation, the efficiency is zero if $T_c = T_h$, as one would expect. The efficiency increases as T_c is lowered and as T_h is raised. However, the efficiency can be unity (100%) only if $T_c = 0$ K. Such reservoirs are not available; thus, the maximum efficiency is always less than 100%. In most practical cases, T_c is near room temperature, which is about 300 K. Therefore, one usually strives to increase the efficiency by raising T_h.

EXAMPLE 22.2 Efficiency of the Carnot Engine

Show that the efficiency of a heat engine operating in a Carnot cycle using an ideal gas is given by Equation 22.4.

Solution During the isothermal expansion (process $A \rightarrow B$ in Figure 22.9), the temperature does not change. Thus, the internal energy remains constant. The work done by a gas during an isothermal expansion is given by Equation 20.13. According to the first law, this work is equal to Q_h, the energy absorbed, so that

$$Q_h = W_{AB} = nRT_h \ln \frac{V_B}{V_A}$$

In a similar manner, the energy transferred to the cold reservoir during the isothermal compression $C \rightarrow D$ is

$$Q_c = |W_{CD}| = nRT_c \ln \frac{V_C}{V_D}$$

We take the absolute value of the work because we are defining all values of Q for a heat engine as positive, as mentioned earlier. Dividing the second expression by the first, we find that

$$(1) \qquad \frac{Q_c}{Q_h} = \frac{T_c}{T_h} \frac{\ln(V_C/V_D)}{\ln(V_B/V_A)}$$

We now show that the ratio of the logarithmic quantities is unity by establishing a relationship between the ratio of volumes. For any quasi-static, adiabatic process, the pressure and volume are related by Equation 21.18:

$$(2) \qquad PV^{\gamma} = \text{constant}$$

During any reversible, quasi-static process, the ideal gas must also obey the equation of state, $PV = nRT$. Solving this expression for P and substituting into (2), we obtain

$$\frac{nRT}{V} V^{\gamma} = \text{constant}$$

which we can write as

$$TV^{\gamma - 1} = \text{constant}$$

where we have absorbed nR into the constant right-hand side. Applying this result to the adiabatic processes $B \rightarrow C$ and $D \rightarrow A$, we obtain

$$T_h V_B^{\gamma - 1} = T_c V_C^{\gamma - 1}$$

$$T_h V_A^{\gamma - 1} = T_c V_D^{\gamma - 1}$$

Dividing the first equation by the second, we obtain

$$(V_B/V_A)^{\gamma - 1} = (V_C/V_D)^{\gamma - 1}$$

$$(3) \qquad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Substituting (3) into (1), we find that the logarithmic terms cancel, and we obtain the relationship

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

Using this result and Equation 22.2, we see that the thermal efficiency of the Carnot engine is

$$e_C = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

which is Equation 22.4, the one we set out to prove.

EXAMPLE 22.3 The Steam Engine

A steam engine has a boiler that operates at 500 K. The energy from the burning fuel changes water to steam, and this steam then drives a piston. The cold reservoir's temperature is that of the outside air, approximately 300 K. What is the maximum thermal efficiency of this steam engine?

Solution Using Equation 22.4, we find that the maximum thermal efficiency for any engine operating between these temperatures is

$$e_C = 1 - \frac{T_c}{T_h} = 1 - \frac{300 \text{ K}}{500 \text{ K}} = 0.4, \text{ or } 40\%$$

You should note that this is the highest *theoretical* efficiency of the engine. In practice, the efficiency is considerably lower.

Exercise Determine the maximum work that the engine can perform in each cycle if it absorbs 200 J of energy from the hot reservoir during each cycle. ***Answer*** 80 J.

EXAMPLE 22.4 The Carnot Efficiency

The highest theoretical efficiency of a certain engine is 30%. If this engine uses the atmosphere, which has a temperature of 300 K, as its cold reservoir, what is the temperature of its hot reservoir?

Solution We use the Carnot efficiency to find T_h:

$$e_C = 1 - \frac{T_c}{T_h}$$

$$T_h = \frac{T_c}{1 - e_C} = \frac{300\ \text{K}}{1 - 0.30} = 430\ \text{K}$$

22.4 GASOLINE AND DIESEL ENGINES

In a gasoline engine, six processes occur in each cycle; five of these are illustrated in Figure 22.11. In this discussion, we consider the interior of the cylinder above the piston to be the system that is taken through repeated cycles in the operation of the engine. For a given cycle, the piston moves up and down twice. This represents a four-stroke cycle consisting of two upstrokes and two downstrokes. The processes in the cycle can be approximated by the **Otto cycle,** a *PV* diagram of which is illustrated in Figure 22.12:

1. During the *intake stroke* $O \rightarrow A$ (Fig. 22.11a), the piston moves downward, and a gaseous mixture of air and fuel is drawn into the cylinder at atmospheric pressure. In this process, the volume increases from V_2 to V_1. This is the energy input part of the cycle, as energy enters the system (the interior of the cylinder) as internal energy stored in the fuel. This is energy transfer by *mass transfer*—that is, the energy is carried with a substance. It is similar to convection, which we studied in Chapter 20.
2. During the *compression stroke* $A \rightarrow B$ (Fig. 22.11b), the piston moves upward, the air–fuel mixture is compressed adiabatically from volume V_1 to volume V_2, and the temperature increases from T_A to T_B. The work done by the gas is negative, and its value is equal to the area under the curve AB in Figure 22.12.
3. In process $B \rightarrow C$, combustion occurs when the spark plug fires (Fig. 22.11c). This is not one of the strokes of the cycle because it occurs in a very short period of time while the piston is at its highest position. The combustion represents a rapid transformation from internal energy stored in chemical bonds in the fuel to internal energy associated with molecular motion, which is related to temperature. During this time, the pressure and temperature in the cylinder increase rapidly, with the temperature rising from T_B to T_C. The volume, however, remains approximately constant because of the short time interval. As a result, approximately no work is done by the gas. We can model this process in the *PV* diagram (Fig. 22.12) as that process in which the energy Q_h enters the system. However, in reality this process is a transformation of energy already in the cylinder (from process $O \rightarrow A$) rather than a transfer.
4. In the *power stroke* $C \rightarrow D$ (Fig. 22.11d), the gas expands adiabatically from V_2 to

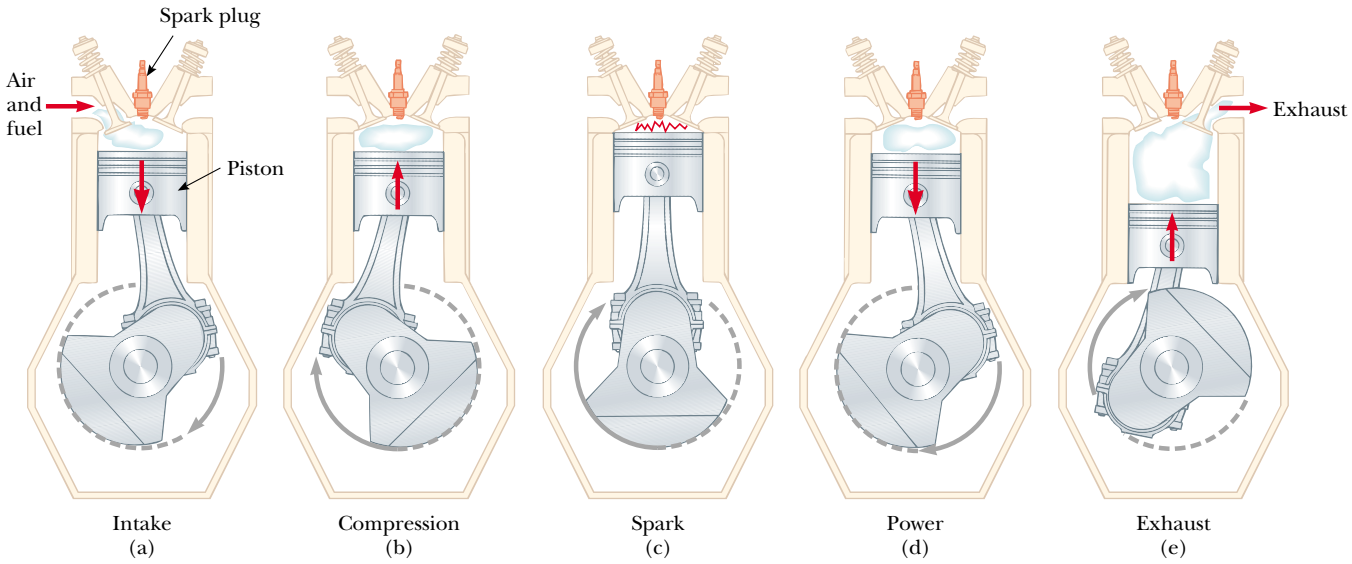


Figure 22.11 The four-stroke cycle of a conventional gasoline engine. (a) In the intake stroke, air is mixed with fuel. (b) The intake valve is then closed, and the air–fuel mixture is compressed by the piston. (c) The mixture is ignited by the spark plug, with the result that the temperature of the mixture increases. (d) In the power stroke, the gas expands against the piston. (e) Finally, the residual gases are expelled, and the cycle repeats.

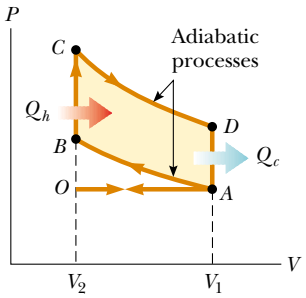


Figure 22.12 *PV* diagram for the Otto cycle, which approximately represents the processes occurring in an internal combustion engine.

V_1. This expansion causes the temperature to drop from T_C to T_D. Work is done by the gas in pushing the piston downward, and the value of this work is equal to the area under the curve *CD*.

5. In the process $D \rightarrow A$ (not shown in Fig. 22.11), an exhaust valve is opened as the piston reaches the bottom of its travel, and the pressure suddenly drops for a short time interval. During this interval, the piston is almost stationary and the volume is approximately constant. Energy is expelled from the interior of the cylinder and continues to be expelled during the next process.
6. In the final process, the *exhaust stroke* $A \rightarrow O$ (Fig. 22.11e), the piston moves upward while the exhaust valve remains open. Residual gases are exhausted at atmospheric pressure, and the volume decreases from V_1 to V_2. The cycle then repeats.

If the air–fuel mixture is assumed to be an ideal gas, then the efficiency of the Otto cycle is

Efficiency of the Otto cycle

$$e = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}} \qquad \textbf{(22.5)}$$

where γ is the ratio of the molar specific heats C_P/C_V for the fuel–air mixture and V_1/V_2 is the **compression ratio.** Equation 22.5, which we derive in Example 22.5, shows that the efficiency increases as the compression ratio increases. For a typical compression ratio of 8 and with $\gamma = 1.4$, we predict a theoretical efficiency of 56% for an engine operating in the idealized Otto cycle. This value is much greater than that achieved in real engines (15% to 20%) because of such effects as friction, energy transfer by conduction through the cylinder walls, and incomplete combustion of the air–fuel mixture.

Diesel engines operate on a cycle similar to the Otto cycle but do not employ a spark plug. The compression ratio for a diesel engine is much greater than that

for a gasoline engine. Air in the cylinder is compressed to a very small volume, and, as a consequence, the cylinder temperature at the end of the compression stroke is very high. At this point, fuel is injected into the cylinder. The temperature is high enough for the fuel–air mixture to ignite without the assistance of a spark plug. Diesel engines are more efficient than gasoline engines because of their greater compression ratios and resulting higher combustion temperatures.

EXAMPLE 22.5 Efficiency of the Otto Cycle

Show that the thermal efficiency of an engine operating in an idealized Otto cycle (see Figs. 22.11 and 22.12) is given by Equation 22.5. Treat the working substance as an ideal gas.

Solution First, let us calculate the work done by the gas during each cycle. No work is done during processes $B \rightarrow C$ and $D \rightarrow A$. The work done by the gas during the adiabatic compression $A \rightarrow B$ is negative, and the work done by the gas during the adiabatic expansion $C \rightarrow D$ is positive. The value of the net work done equals the area of the shaded region bounded by the closed curve in Figure 22.12. Because the change in internal energy for one cycle is zero, we see from the first law that the net work done during one cycle equals the net energy flow through the system:

$$W = Q_h - Q_c$$

Because processes $B \rightarrow C$ and $D \rightarrow A$ take place at constant volume, and because the gas is ideal, we find from the definition of molar specific heat (Eq. 21.8) that

$$Q_h = nC_V(T_C - T_B) \qquad \text{and} \qquad Q_c = nC_V(T_D - T_A)$$

Using these expressions together with Equation 22.2, we obtain for the thermal efficiency

$$(1) \qquad e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_D - T_A}{T_C - T_B}$$

We can simplify this expression by noting that processes $A \rightarrow B$ and $C \rightarrow D$ are adiabatic and hence obey the relationship $TV^{\gamma-1} = \text{constant}$, which we obtained in Example 22.2. For the two adiabatic processes, then,

$$A \rightarrow B: \qquad T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1}$$

$$C \rightarrow D: \qquad T_C V_C^{\gamma-1} = T_D V_D^{\gamma-1}$$

Using these equations and relying on the fact that $V_A = V_D = V_1$ and $V_B = V_C = V_2$, we find that

$$T_A V_1^{\gamma-1} = T_B V_2^{\gamma-1}$$

$$(2) \qquad T_A = T_B\left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$T_D V_1^{\gamma-1} = T_C V_2^{\gamma-1}$$

$$(3) \qquad T_D = T_C\left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

Subtracting (2) from (3) and rearranging, we find that

$$(4) \qquad \frac{T_D - T_A}{T_C - T_B} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

Substituting (4) into (1), we obtain for the thermal efficiency

$$(5) \qquad e = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}$$

which is Equation 22.5.

We can also express this efficiency in terms of temperatures by noting from (2) and (3) that

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{T_A}{T_B} = \frac{T_D}{T_C}$$

Therefore, (5) becomes

$$(6) \qquad e = 1 - \frac{T_A}{T_B} = 1 - \frac{T_D}{T_C}$$

During the Otto cycle, the lowest temperature is T_A and the highest temperature is T_C. Therefore, the efficiency of a Carnot engine operating between reservoirs at these two temperatures, which is given by the expression $e_C = 1 - (T_A/T_C)$, is *greater* than the efficiency of the Otto cycle given by (6), as expected.

APPLICATION Models of Gasoline and Diesel Engines

We can use the thermodynamic principles discussed in this and earlier chapters to model the performance of gasoline and diesel engines. In both types of engine, a gas is first compressed in the cylinders of the engine and then the fuel–air mixture is ignited. Work is done on the gas during compression, but significantly more work is done on the piston by the mixture as the products of combustion expand in the cylinder. The power of the engine is transferred from the piston to the crankshaft by the connecting rod.

Two important quantities of either engine are the **displacement volume,** which is the volume displaced by the piston as it moves from the bottom to the top of the cylinder, and the com-

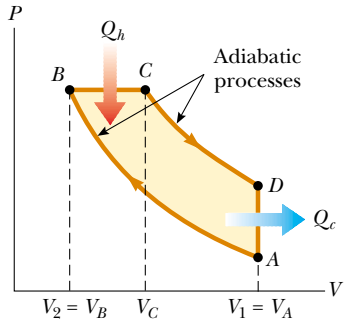


Figure 22.13 *PV* diagram for an ideal diesel engine.

pression ratio r, which is the ratio of the maximum and minimum volumes of the cylinder (see p. 680). In our notation, $r = V_A/V_B$, or V_1/V_2 in Eq. 22.5. Most gasoline and diesel engines operate with a four-cycle process (intake, compression, power, exhaust), in which the net work of the intake and exhaust cycles can be considered negligible. Therefore, power is developed only once for every two revolutions of the crankshaft.

In a diesel engine, only air (and no fuel) is present in the cylinder at the beginning of the compression. In the idealized diesel cycle of Figure 22.13, air in the cylinder undergoes an adiabatic compression from A to B. Starting at B, fuel is injected into the cylinder in such a way that the fuel–air mixture undergoes a constant-pressure expansion to an intermediate volume $V_C (B \rightarrow C)$. The high temperature of the mixture causes combustion, and the power stroke is an adiabatic expansion back to $V_D = V_A (C \rightarrow D)$. The exhaust valve is opened, and a constant-volume output of energy occurs $(D \rightarrow A)$ as the cylinder empties.

To simplify our calculations, we assume that the mixture in the cylinder is air modeled as an ideal gas. We use specific heats c instead of molar specific heats C and assume constant values for air at 300 K. We express the specific heats and the universal gas constant in terms of unit masses rather than moles. Thus, $c_V = 0.718$ kJ/kg·K, $c_P = 1.005$ kJ/kg·K, $\gamma = c_P/c_V = 1.40$, and $R = c_P - c_V = 0.287$ kJ/kg·K = 0.287 kPa·m^3/kg·K.

A 3.00-L Gasoline Engine

Let us calculate the power delivered by a six-cylinder gasoline engine that has a displacement volume of 3.00 L operating at 4 000 rpm and having a compression ratio of $r = 9.50$. The air–fuel mixture enters a cylinder at atmospheric pressure and an ambient temperature of 27°C. During combustion, the mixture reaches a temperature of 1 350°C.

First, let us calculate the work done by an individual cylinder. Using the initial pressure $P_A = 100$ kPa and the initial temperature $T_A = 300$ K, we calculate the initial volume and the mass of the air–fuel mixture. We know that the ratio of the initial and final volumes is the compression ratio,

$$\frac{V_A}{V_B} = r = 9.50$$

We also know that the difference in volumes is the displacement volume. The 3.00-L rating of the engine is the total displacement volume for all six cylinders. Thus, for one cylinder,

$$V_A - V_B = \frac{3.00 \text{ L}}{6} = \frac{3.00 \times 10^{-3} \text{ m}^3}{6} = 0.500 \times 10^{-3} \text{ m}^3$$

Solving these two equations simultaneously, we find the initial and final volumes:

$$V_A = 0.559 \times 10^{-3} \text{ m}^3 \qquad V_B = 0.588 \times 10^{-4} \text{ m}^3$$

Using the ideal gas law (in the form $PV = mRT$, because we are using the universal gas constant in terms of mass rather than moles), we can find the mass of the air–fuel mixture:

$$m = \frac{P_A V_A}{RT_A} = \frac{(100 \text{ kPa})(0.559 \times 10^{-3} \text{ m}^3)}{(0.287 \text{ kPa·m}^3/\text{kg·K})(300 \text{ K})} = 6.49 \times 10^{-4} \text{ kg}$$

Process $A \rightarrow B$ (see Fig. 22.12) is an adiabatic compression, and this means that $PV^\gamma = \text{constant}$; hence,

$$P_B V_B^\gamma = P_A V_A^\gamma$$

$$P_B = P_A \left(\frac{V_A}{V_B}\right)^\gamma = P_A (r)^\gamma = (100 \text{ kPa})(9.50)^{1.40} = 2.34 \times 10^3 \text{ kPa}$$

Using the ideal gas law, we find that the temperature after the compression is

$$T_B = \frac{P_B V_B}{mR} = \frac{(2.34 \times 10^3 \text{ kPa})(0.588 \times 10^{-4} \text{ m}^3)}{(6.49 \times 10^{-4} \text{ kg})(0.287 \text{ kPa·m}^3/\text{kg·K})} = 739 \text{ K}$$

In process $B \rightarrow C$, the combustion that transforms the internal energy in chemical bonds into internal energy of molecular motion occurs at constant volume; thus, $V_C = V_B$. Combustion causes the temperature to increase to $T_C = 1\,350°\text{C} = 1\,623$ K. Using this value and the ideal gas law, we can calculate P_C:

$$P_C = \frac{mRT_C}{V_C} = \frac{(6.49 \times 10^{-4} \text{ kg})(0.287 \text{ kPa·m}^3/\text{kg·K})(1\,623 \text{ K})}{(0.588 \times 10^{-4} \text{ m}^3)} = 5.14 \times 10^3 \text{ kPa}$$

Process $C \rightarrow D$ is an adiabatic expansion; the pressure after the expansion is

$$P_D = P_C \left(\frac{V_C}{V_D}\right)^\gamma = P_C \left(\frac{V_B}{V_A}\right)^\gamma = P_C \left(\frac{1}{r}\right)^\gamma$$

$$= (5.14 \times 10^3 \text{ kPa}) \left(\frac{1}{9.50}\right)^{1.40} = 220 \text{ kPa}$$

Using the ideal gas law again, we find the final temperature:

$$T_D = \frac{P_D V_D}{mR} = \frac{(220\ \text{kPa})(0.559 \times 10^{-3}\ \text{m}^3)}{(6.49 \times 10^{-4}\ \text{kg})(0.287\ \text{kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})} = 660\ \text{K}$$

Now that we have the temperatures at the beginning and end of each process of the cycle, we can calculate the net energy transfer and net work done by each cylinder every two cycles. From Equation 21.8, we can state

$$Q_h = Q_{\text{in}} = mc_V(T_C - T_B) = (6.49 \times 10^{-4}\ \text{kg})(0.718\ \text{kJ/kg}\cdot\text{K})(1\,623\ \text{K} - 739\ \text{K}) = 0.412\ \text{kJ}$$

$$Q_c = Q_{\text{out}} = mc_V(T_D - T_A) = (6.49 \times 10^{-4}\ \text{kg})(0.718\ \text{kJ/kg}\cdot\text{K})(660\ \text{K} - 300\ \text{K}) = 0.168\ \text{kJ}$$

$$W_{\text{net}} = Q_{\text{in}} - Q_{\text{out}} = 0.244\ \text{kJ}$$

From Equation 22.2, the efficiency is $e = W_{\text{net}}/Q_{\text{in}} = 59\%$. (We can also use Equation 22.5 to calculate the efficiency directly from the compression ratio.)

Recalling that power is delivered every other revolution of the crankshaft, we find that the net power for the six-cylinder engine operating at 4 000 rpm is

$$\mathcal{P}_{\text{net}} = 6\left(\frac{1}{2\ \text{rev}}\right)(4\,000\ \text{rev/min})\ (1\ \text{min}/60\ \text{s})\ (0.244\ \text{kJ}) = 49\ \text{kW} = 66\ \text{hp}$$

A 2.00-L Diesel Engine

Let us calculate the power delivered by a four-cylinder diesel engine that has a displacement volume of 2.00 L and is operating at 3 000 rpm. The compression ratio is $r = V_A/V_B = 22.0$, and the **cutoff ratio,** which is the ratio of the volume change during the constant-pressure process $B \rightarrow C$ in Figure 22.13, is $r_c = V_C/V_B = 2.00$. The air enters each cylinder at the beginning of the compression cycle at atmospheric pressure and at an ambient temperature of 27°C.

Our model of the diesel engine is similar to our model of the gasoline engine except that now the fuel is injected at point B and the mixture self-ignites near the end of the compression cycle $A \rightarrow B$, when the temperature reaches the ignition temperature. We assume that the energy input occurs in the constant-pressure process $B \rightarrow C$, and that the expansion process continues from C to D with no further energy transfer by heat.

Let us calculate the work done by an individual cylinder that has an initial volume of $V_A = (2.00 \times 10^{-3}\ \text{m}^3)/4 = 0.500 \times 10^{-3}\ \text{m}^3$. Because the compression ratio is quite high, we approximate the maximum cylinder volume to be the displacement volume. Using the initial pressure $P_A = 100$ kPa and initial temperature $T_A = 300$ K, we can calculate the mass of the air in the cylinder using the ideal gas law:

$$m = \frac{P_A V_A}{RT_A} = \frac{(100\ \text{kPa})(0.500 \times 10^{-3}\ \text{m}^3)}{(0.287\ \text{kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})(300\ \text{K})} = 5.81 \times 10^{-4}\ \text{kg}$$

Process $A \rightarrow B$ is an adiabatic compression, so PV^γ = constant; thus,

$$P_B V_B^\gamma = P_A V_A^\gamma$$

$$P_B = P_A\left(\frac{V_A}{V_B}\right)^\gamma = (100\ \text{kPa})(22.0)^{1.40} = 7.57 \times 10^3\ \text{kPa}$$

Using the ideal gas law, we find that the temperature of the air after the compression is

$$T_B = \frac{P_B V_B}{mR} = \frac{(7.57 \times 10^3\ \text{kPa})(0.500 \times 10^{-3}\ \text{m}^3)\left(\frac{1}{22.0}\right)}{(5.81 \times 10^{-4}\ \text{kg})(0.287\ \text{kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})} = 1.03 \times 10^3\ \text{K}$$

Process $B \rightarrow C$ is a constant-pressure expansion; thus, $P_C = P_B$. We know from the cutoff ratio of 2.00 that the volume doubles in this process. According to the ideal gas law, a doubling of volume in an isobaric process results in a doubling of the temperature, so

$$T_C = 2T_B = 2.06 \times 10^3\ \text{K}$$

Process $C \rightarrow D$ is an adiabatic expansion; therefore,

$$P_D = P_C\left(\frac{V_C}{V_D}\right)^\gamma = P_C\left(\frac{V_C}{V_B}\frac{V_B}{V_D}\right)^\gamma = P_C\left(r_c\frac{1}{r}\right)^\gamma = (7.57 \times 10^3\ \text{kPa})\left(\frac{2.00}{22.0}\right)^{1.40} = 264\ \text{kPa}$$

We find the temperature at D from the ideal gas law:

$$T_D = \frac{P_D V_D}{mR} = \frac{(264\ \text{kPa})(0.500 \times 10^{-3}\ \text{m}^3)}{(5.81 \times 10^{-4}\ \text{kg})(0.287\ \text{kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})} = 792\ \text{K}$$

Now that we have the temperatures at the beginning and the end of each process, we can calculate the net energy transfer by heat and the net work done by each cylinder every two cycles:

$$Q_h = Q_{\text{in}} = mc_P(T_C - T_B) = 0.601\ \text{kJ}$$

$$Q_c = Q_{\text{out}} = mc_V(T_D - T_A) = 0.205\ \text{kJ}$$

$$W_{\text{net}} = Q_{\text{in}} - Q_{\text{out}} = 0.396\ \text{kJ}$$

The efficiency is $e = W_{\text{net}}/Q_{\text{in}} = 66\%$.

The net power for the four-cylinder engine operating at 3 000 rpm is

$$\mathcal{P}_{\text{net}} = 4\left(\frac{1}{2\ \text{rev}}\right)(3\,000\ \text{rev/min})\ (1\ \text{min}/60\ \text{s})\ (0.396\ \text{kJ}) = 39.6\ \text{kW} = 53\ \text{hp}$$

Of course, modern engine design goes beyond this simple thermodynamic treatment, which uses idealized cycles.

22.5 HEAT PUMPS AND REFRIGERATORS

In Section 22.1 we introduced a heat pump as a mechanical device that moves energy from a region at lower temperature to a region at higher temperature. Heat pumps have long been used for cooling homes and buildings, and they are now becoming increasingly popular for heating them as well. The heat pump contains two sets of metal coils that can exchange energy by heat with the surroundings: one set on the outside of the building, in contact with the air or buried in the ground; and the other set in the interior of the building. In the heating mode, a circulating fluid flowing through the coils absorbs energy from the outside and releases it to the interior of the building from the interior coils. The fluid is cold and at low pressure when it is in the external coils, where it absorbs energy by heat from either the air or the ground. The resulting warm fluid is then compressed and enters the interior coils as a hot, high-pressure fluid, where it releases its stored energy to the interior air.

An air conditioner is simply a heat pump operating in the cooling mode, with its exterior and interior coils interchanged. Energy is absorbed into the circulating fluid in the interior coils; then, after the fluid is compressed, energy leaves the fluid through the external coils. The air conditioner must have a way to release energy to the outside. Otherwise, the work done on the air conditioner would represent energy added to the air inside the house, and the temperature would increase. In the same manner, a refrigerator cannot cool the kitchen if the refrigerator door is left open. The amount of energy leaving the external coils (Fig. 22.14) behind or underneath the refrigerator is greater than the amount of energy removed from the food or from the air in the kitchen if the door is left open. The difference between the energy out and the energy in is the work done by the electricity supplied to the refrigerator.

Figure 22.14 The coils on the back of a refrigerator transfer energy by heat to the air. The second law of thermodynamics states that this amount of energy must be greater than the amount of energy removed from the contents of the refrigerator (or from the air in the kitchen, if the refrigerator door is left open).

Figure 22.15 is a schematic representation of a heat pump. The cold temperature is T_c, the hot temperature is T_h, and the energy absorbed by the circulating fluid is Q_c. The heat pump does work W on the fluid, and the energy transferred from the pump to the building in the heating mode is Q_h.

The effectiveness of a heat pump is described in terms of a number called the **coefficient of performance** (COP). In the heating mode, the COP is defined as the ratio of the energy transferred to the hot reservoir to the work required to transfer that energy:

$$\text{COP (heating mode)} \equiv \frac{\text{Energy transferred at high temperature}}{\text{Work done by pump}} = \frac{Q_h}{W} \qquad \textbf{(22.6)}$$

Note that the COP is similar to the thermal efficiency for a heat engine in that it is a ratio of what you get (energy delivered to the interior of the building) to what you give (work input). Because Q_h is generally greater than W, typical values for the COP are greater than unity. It is desirable for the COP to be as high as possible, just as it is desirable for the thermal efficiency of an engine to be as high as possible.

If the outside temperature is 25°F or higher, then the COP for a heat pump is about 4. That is, the amount of energy transferred to the building is about four times greater than the work done by the motor in the heat pump. However, as the outside temperature decreases, it becomes more difficult for the heat pump to extract sufficient energy from the air, and so the COP decreases. In fact, the COP can fall below unity for temperatures below the midteens. Thus, the use of heat pumps that extract energy from the air, while satisfactory in moderate climates, is not appropriate in areas where winter temperatures are very low. It is possible to

use heat pumps in colder areas by burying the external coils deep in the ground. In this case, the energy is extracted from the ground, which tends to be warmer than the air in the winter.

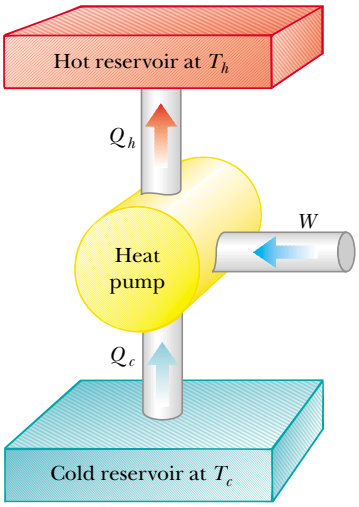


Figure 22.15 Schematic diagram of a heat pump, which absorbs energy Q_c from a cold reservoir and expels energy Q_h to a hot reservoir. Note that this diagram is the same as that for the refrigerator shown in Figure 22.5.

Quick Quiz 22.1

In an electric heater, electrical energy can be converted to internal energy with an efficiency of 100%. By what percentage does the cost of heating your home change when you replace your electric heating system with a heat pump that has a COP of 4? Assume that the motor running the heat pump is 100% efficient.

Theoretically, a Carnot-cycle heat engine run in reverse constitutes the most effective heat pump possible, and it determines the maximum COP for a given combination of hot and cold reservoir temperatures. Using Equations 22.1 and 22.3, we see that the maximum COP for a heat pump in its heating mode is

$$\text{COP}_\text{C}(\text{heating mode}) = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c} = \frac{1}{1 - \dfrac{Q_c}{Q_h}} = \frac{1}{1 - \dfrac{T_c}{T_h}} = \frac{T_h}{T_h - T_c}$$

For a heat pump operating in the cooling mode, "what you get" is energy removed from the cold reservoir. The most effective refrigerator or air conditioner is one that removes the greatest amount of energy from the cold reservoir in exchange for the least amount of work. Thus, for these devices we define the COP in terms of Q_c:

$$\text{COP (cooling mode)} = \frac{Q_c}{W} \tag{22.7}$$

A good refrigerator should have a high COP, typically 5 or 6.

The greatest possible COP for a heat pump in the cooling mode is that of a heat pump whose working substance is carried through a Carnot cycle in reverse:

$$\text{COP}_\text{C}\ (\text{cooling mode}) = \frac{T_c}{T_h - T_c}$$

As the difference between the temperatures of the two reservoirs approaches zero in this expression, the theoretical COP approaches infinity. In practice, the low temperature of the cooling coils and the high temperature at the compressor limit the COP to values below 10.

QuickLab

Estimate the COP of your refrigerator by making rough temperature measurements of the stored food and of the exhaust coils (found either on the back of the unit or behind a panel on the bottom). Use just your hand if no thermometer is available.

22.6 ENTROPY

10.10 & 10.11

The zeroth law of thermodynamics involves the concept of temperature, and the first law involves the concept of internal energy. Temperature and internal energy are both state functions—that is, they can be used to describe the thermodynamic state of a system. Another state function—this one related to the second law of thermodynamics—is **entropy** S. In this section we define entropy on a macroscopic scale as it was first expressed by Clausius in 1865.

Consider any infinitesimal process in which a system changes from one equilibrium state to another. If dQ_r is the amount of energy transferred by heat when the system follows a reversible path between the states, then the change in entropy dS is equal to this amount of energy for the reversible process divided by the absolute temperature of the system:

Clausius definition of change in entropy

$$dS = \frac{dQ_r}{T} \tag{22.8}$$

We have assumed that the temperature is constant because the process is infinitesimal. Since we have claimed that entropy is a state function, **the change in entropy during a process depends only on the end points and therefore is independent of the actual path followed.**

The subscript r on the quantity dQ_r is a reminder that the transferred energy is to be measured along a reversible path, even though the system may actually have followed some irreversible path. When energy is absorbed by the system, dQ_r is positive and the entropy of the system increases. When energy is expelled by the system, dQ_r is negative and the entropy of the system decreases. Note that Equation 22.8 defines not entropy but rather the *change* in entropy. Hence, the meaningful quantity in describing a process is the *change* in entropy.

Entropy was originally formulated as a useful concept in thermodynamics; however, its importance grew tremendously as the field of statistical mechanics developed because the analytical techniques of statistical mechanics provide an alternative means of interpreting entropy. In statistical mechanics, the behavior of a substance is described in terms of the statistical behavior of its atoms and molecules. One of the main results of this treatment is that **isolated systems tend toward disorder and that entropy is a measure of this disorder.** For example, consider the molecules of a gas in the air in your room. If half of the gas molecules had velocity vectors of equal magnitude directed toward the left and the other half had velocity vectors of the same magnitude directed toward the right, the situation would be very ordered. However, such a situation is extremely unlikely. If you could actually view the molecules, you would see that they move haphazardly in all directions, bumping into one another, changing speed upon collision, some going fast and others going slowly. This situation is highly disordered.

The cause of the tendency of an isolated system toward disorder is easily explained. To do so, we distinguish between *microstates* and *macrostates* of a system. A **microstate** is a particular description of the properties of the individual molecules of the system. For example, the description we just gave of the velocity vectors of the air molecules in your room being very ordered refers to a particular microstate, and the more likely likely haphazard motion is another microstate—one that represents disorder. A **macrostate** is a description of the conditions of the system from a macroscopic point of view and makes use of macroscopic variables such as pressure, density, and temperature. For example, in both of the microstates described for the air molecules in your room, the air molecules are distributed uniformly throughout the volume of the room; this uniform density distribution is a macrostate. We could not distinguish between our two microstates by making a macroscopic measurement—both microstates would appear to be the same macroscopically, and the two macrostates corresponding to these microstates are equivalent.

For any given macrostate of the system, a number of microstates are possible, or *accessible*. Among these microstates, it is assumed that all are equally probable. However, when all possible microstates are examined, it is found that far more of them are disordered than are ordered. Because all of the microstates are equally

probable, it is highly likely that the actual macrostate is one resulting from one of the highly disordered microstates, simply because there are many more of them. Similarly, the probability of a macrostate's forming from disordered microstates is greater than the probability of a macrostate's forming from ordered microstates.

All physical processes that take place in a system tend to cause the system and its surroundings to move toward more probable macrostates. The more probable macrostate is always one of greater disorder. If we consider a system and its surroundings to include the entire Universe, then the Universe is always moving toward a macrostate corresponding to greater disorder. Because entropy is a measure of disorder, an alternative way of stating this is **the entropy of the Universe increases in all real processes.** This is yet another statement of the second law of thermodynamics that can be shown to be equivalent to the Kelvin–Planck and Clausius statements.

In real processes, the disorder of the Universe increases

To calculate the change in entropy for a finite process, we must recognize that T is generally not constant. If dQ_r is the energy transferred by heat when the system is at a temperature T, then the change in entropy in an arbitrary reversible process between an initial state and a final state is

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T} \qquad \text{(reversible path)} \tag{22.9}$$

Change in entropy for a finite process

As with an infinitesimal process, the change in entropy ΔS of a system going from one state to another has the same value for *all* paths connecting the two states. That is, the finite change in entropy ΔS of a system depends only on the properties of the initial and final equilibrium states. Thus, we are free to choose a particular reversible path over which to evaluate the entropy in place of the actual path, as long as the initial and final states are the same for both paths.

Quick Quiz 22.2

Which of the following is true for the entropy change of a system that undergoes a reversible, adiabatic process? (a) $\Delta S < 0$. (b) $\Delta S = 0$. (c) $\Delta S > 0$.

Let us consider the changes in entropy that occur in a Carnot heat engine operating between the temperatures T_c and T_h. In one cycle, the engine absorbs energy Q_h from the hot reservoir and expels energy Q_c to the cold reservoir. These energy transfers occur only during the isothermal portions of the Carnot cycle; thus, the constant temperature can be brought out in front of the integral sign in Equation 22.9. The integral then simply has the value of the total amount of energy transferred by heat. Thus, the total change in entropy for one cycle is

$$\Delta S = \frac{Q_h}{T_h} - \frac{Q_c}{T_c}$$

where the negative sign represents the fact that energy Q_c is expelled by the system, since we continue to define Q_c as a positive quantity when referring to heat engines. In Example 22.2 we showed that, for a Carnot engine,

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

Using this result in the previous expression for ΔS, we find that the total change in

The change in entropy for a Carnot cycle is zero

entropy for a Carnot engine operating in a cycle is *zero*:

$$\Delta S = 0$$

Now let us consider a system taken through an arbitrary (non-Carnot) reversible cycle. Because entropy is a state function—and hence depends only on the properties of a given equilibrium state—we conclude that $\Delta S = 0$ for *any* reversible cycle. In general, we can write this condition in the mathematical form

$\Delta S = 0$ for any reversible cycle

$$\oint \frac{dQ_r}{T} = 0 \tag{22.10}$$

where the symbol $\oint$ indicates that the integration is over a closed path.

Quasi-Static, Reversible Process for an Ideal Gas

Let us suppose that an ideal gas undergoes a quasi-static, reversible process from an initial state having temperature T_i and volume V_i to a final state described by T_f and V_f. Let us calculate the change in entropy of the gas for this process.

Writing the first law of thermodynamics in differential form and rearranging the terms, we have $dQ_r = dE_{\text{int}} + dW$, where $dW = P\,dV$. For an ideal gas, recall that $dE_{\text{int}} = nC_V\,dT$ (Eq. 21.12), and from the ideal gas law, we have $P = nRT/V$. Therefore, we can express the energy transferred by heat in the process as

$$dQ_r = dE_{\text{int}} + P\,dV = nC_V\,dT + nRT\frac{dV}{V}$$

We cannot integrate this expression as it stands because the last term contains two variables, T and V. However, if we divide all terms by T, each of the terms on the right-hand side depends on only one variable:

$$\frac{dQ_r}{T} = nC_V\frac{dT}{T} + nR\frac{dV}{V} \tag{22.11}$$

Assuming that C_V is constant over the interval in question, and integrating Equation 22.11 from the initial state to the final state, we obtain

$$\Delta S = \int_i^f \frac{dQ_r}{T} = nC_V \ln\frac{T_f}{T_i} + nR\ln\frac{V_f}{V_i} \tag{22.12}$$

This expression demonstrates mathematically what we argued earlier—that ΔS depends only on the initial and final states and is independent of the path between the states. Also, note in Equation 22.12 that ΔS can be positive or negative, depending on the values of the initial and final volumes and temperatures. Finally, for a cyclic process ($T_i = T_f$ and $V_i = V_f$), we see from Equation 22.12 that $\Delta S = 0$. This is evidence that entropy is a state function.

EXAMPLE 22.6 Change in Entropy—Melting

A solid that has a latent heat of fusion L_f melts at a temperature T_m. (a) Calculate the change in entropy of this substance when a mass m of the substance melts.

Solution Let us assume that the melting occurs so slowly that it can be considered a reversible process. In this case the temperature can be regarded as constant and equal to T_m. Making use of Equations 22.9 and that for the latent heat of fusion $Q = mL_f$ (Eq. 20.6), we find that

$$\Delta S = \int \frac{dQ_r}{T} = \frac{1}{T_m}\int dQ = \frac{Q}{T_m} = \frac{mL_f}{T_m}$$

Note that we are able to remove T_m from the integral because the process is isothermal. Note also that ΔS is positive. This means that when a solid melts, its entropy increases because the molecules are much more disordered in the liquid state than they are in the solid state. The positive value for ΔS also means that the substance in its liquid state does not spontaneously transfer energy from itself to the surroundings and freeze because to do so would involve a spontaneous decrease in entropy.

(b) Estimate the value of the change in entropy of an ice cube when it melts.

Solution Let us assume an ice tray makes cubes that are about 3 cm on a side. The volume per cube is then (very roughly) 30 cm^3. This much liquid water has a mass of 30 g. From Table 20.2 we find that the latent heat of fusion of ice is 3.33×10^5 J/kg. Substituting these values into our answer for part (a), we find that

$$\Delta S = \frac{mL_f}{T_m} = \frac{(0.03\ \text{kg})(3.33 \times 10^5\ \text{J/kg})}{273\ \text{K}} = 4 \times 10^1\ \text{J/K}$$

We retain only one significant figure, in keeping with the nature of our estimations.

22.7 ENTROPY CHANGES IN IRREVERSIBLE PROCESSES

By definition, calculation of the change in entropy requires information about a reversible path connecting the initial and final equilibrium states. To calculate changes in entropy for real (irreversible) processes, we must remember that entropy (like internal energy) depends only on the *state* of the system. That is, entropy is a state function. Hence, the change in entropy when a system moves between any two equilibrium states depends only on the initial and final states. We can show that if this were not the case, the second law of thermodynamics would be violated.

We now calculate the entropy change in some irreversible process between two equilibrium states by devising a reversible process (or series of reversible processes) between the same two states and computing $\Delta S = \int dQ_r/T$ for the reversible process. In irreversible processes, it is critically important that we distinguish between Q, the actual energy transfer in the process, and Q_r, the energy that would have been transferred by heat along a reversible path. Only Q_r is the correct value to be used in calculating the entropy change.

As we shall see in the following examples, the change in entropy for a system and its surroundings is always positive for an irreversible process. In general, the total entropy—and therefore the disorder—always increase in an irreversible process. Keeping these considerations in mind, we can state the second law of thermodynamics as follows:

> The total entropy of an isolated system that undergoes a change can never decrease.

Furthermore, **if the process is irreversible, then the total entropy of an isolated system always increases. In a reversible process, the total entropy of an isolated system remains constant.**

When dealing with a system that is not isolated from its surroundings, remember that the increase in entropy described in the second law is that of the system *and* its surroundings. When a system and its surroundings interact in an irreversible process, the increase in entropy of one is greater than the decrease in entropy of the other. Hence, we conclude that **the change in entropy of the Universe must be greater than zero for an irreversible process and equal to zero for a reversible process.** Ultimately, the entropy of the Universe should reach a maximum value. At this value, the Universe will be in a state of uniform temperature and density. All physical, chemical, and biological processes will cease because a state of perfect disorder implies that no energy is available for doing work. This gloomy state of affairs is sometimes referred to as the heat death of the Universe.

Quick Quiz 22.3

In the presence of sunlight, a tree rearranges an unorganized collection of carbon dioxide and water molecules into the highly ordered collection of molecules we see as leaves and branches. True or false: This reduction of entropy in the tree is a violation of the second law of thermodynamics. Explain your response.

Entropy Change in Thermal Conduction

Let us now consider a system consisting of a hot reservoir and a cold reservoir in thermal contact with each other and isolated from the rest of the Universe. A process occurs during which energy Q is transferred by heat from the hot reservoir at temperature T_h to the cold reservoir at temperature T_c. Because the cold reservoir absorbs energy Q, its entropy increases by Q/T_c. At the same time, the hot reservoir loses energy Q, and so its entropy change is $-Q/T_h$. Because $T_h > T_c$, the increase in entropy of the cold reservoir is greater than the decrease in entropy of the hot reservoir. Therefore, the change in entropy of the system (and of the Universe) is greater than zero:

$$\Delta S_U = \frac{Q}{T_c} + \frac{-Q}{T_h} > 0$$

Example 22.7 **Which Way Does the Energy Flow?**

A large, cold object is at 273 K, and a large, hot object is at 373 K. Show that it is impossible for a small amount of energy—for example, 8.00 J—to be transferred spontaneously from the cold object to the hot one without a decrease in the entropy of the Universe and therefore a violation of the second law.

Solution We assume that, during the energy transfer, the two objects do not undergo a temperature change. This is not a necessary assumption; we make it only to avoid using integral calculus in our calculations. The process as described is irreversible, and so we must find an equivalent reversible process. It is sufficient to assume that the objects are connected by a poor thermal conductor whose temperature spans the range from 273 K to 373 K. This conductor transfers energy slowly, and its state does not change during the process. Under this assumption, the energy transfer to or from each object is reversible, and we may set $Q = Q_r$. The entropy change of the hot object is

$$\Delta S_h = \frac{Q_r}{T_h} = \frac{8.00\ \text{J}}{373\ \text{K}} = 0.021\ 4\ \text{J/K}$$

The cold object loses energy, and its entropy change is

$$\Delta S_c = \frac{Q_r}{T_c} = \frac{-8.00\ \text{J}}{273\ \text{K}} = -0.029\ 3\ \text{J/K}$$

We consider the two objects to be isolated from the rest of the Universe. Thus, the entropy change of the Universe is just that of our two-object system, which is

$$\Delta S_U = \Delta S_c + \Delta S_h = -0.007\ 9\ \text{J/K}$$

This decrease in entropy of the Universe is in violation of the second law. That is, **the spontaneous transfer of energy from a cold to a hot object cannot occur.**

In terms of disorder, let us consider the violation of the second law if energy were to continue to transfer spontaneously from a cold object to a hot object. Before the transfer, a certain degree of order is associated with the different temperatures of the objects. The hot object's molecules have a higher average energy than the cold object's molecules. If energy spontaneously flows from the cold object to the hot object, then, over a period of time, the cold object will become colder and the hot object will become hotter. The difference in average molecular energy will become even greater; this would represent an increase in order for the system and a violation of the second law.

In comparison, the process that does occur naturally is the flow of energy from the hot object to the cold object. In this process, the difference in average molecular energy decreases; this represents a more random distribution of energy and an increase in disorder.

Exercise Suppose that 8.00 J of energy is transferred from a hot object to a cold one. What is the net entropy change of the Universe?

Answer $+0.007\ 9$ J/K.

Entropy Change in a Free Expansion

Let us again consider the adiabatic free expansion of a gas occupying an initial volume V_i (Fig. 22.16). A membrane separating the gas from an evacuated region is broken, and the gas expands (irreversibly) to a volume V_f. Let us find the changes in entropy of the gas and of the Universe during this process.

The process is clearly neither reversible nor quasi-static. The work done by the gas against the vacuum is zero, and because the walls are insulating, no energy is transferred by heat during the expansion. That is, $W = 0$ and $Q = 0$. Using the first law, we see that the change in internal energy is zero. Because the gas is ideal, E_{int} depends on temperature only, and we conclude that $\Delta T = 0$ or $T_i = T_f$.

To apply Equation 22.9, we cannot use $Q = 0$, the value for the irreversible process, but must instead find Q_r; that is, we must find an equivalent reversible path that shares the same initial and final states. A simple choice is an isothermal, reversible expansion in which the gas pushes slowly against a piston while energy enters the gas by heat from a reservoir to hold the temperature constant. Because T is constant in this process, Equation 22.9 gives

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \frac{1}{T}\int_i^f dQ_r$$

For an isothermal process, the first law of thermodynamics specifies that $\int_i^f dQ_r$ is equal to the work done by the gas during the expansion from V_i to V_f, which is given by Equation 20.13. Using this result, we find that the entropy change for the gas is

$$\Delta S = nR \ln \frac{V_f}{V_i} \tag{22.13}$$

Because $V_f > V_i$, we conclude that ΔS is positive. This positive result indicates that both the entropy and the disorder of the gas increase as a result of the irreversible, adiabatic expansion.

Because the free expansion takes place in an insulated container, no energy is transferred by heat from the surroundings. (Remember that the isothermal, reversible expansion is only a *replacement* process that we use to calculate the entropy change for the gas; it is not the *actual* process.) Thus, the free expansion has no effect on the surroundings, and the entropy change of the surroundings is zero. Thus, the entropy change for the Universe is positive; this is consistent with the second law.

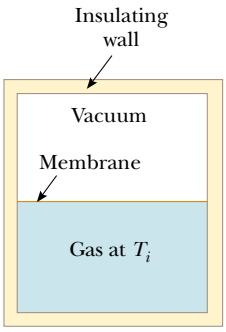


Figure 22.16 Adiabatic free expansion of a gas. When the membrane separating the gas from the evacuated region is ruptured, the gas expands freely and irreversibly. As a result, it occupies a greater final volume. The container is thermally insulated from its surroundings; thus, $Q = 0$.

EXAMPLE 22.8 Free Expansion of a Gas

Calculate the change in entropy for a process in which 2.00 mol of an ideal gas undergoes a free expansion to three times its initial volume.

Solution Using Equation 22.13 with $n = 2.00$ mol and $V_f = 3V_i$, we find that

$$\Delta S = nR \ln \frac{V_f}{V_i} = (2.00 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(\ln 3)$$

$$= 18.3 \text{ J/K}$$

It is easy to see that the gas is more disordered after the expansion. Instead of being concentrated in a relatively small space, the molecules are scattered over a larger region.

Entropy Change in Calorimetric Processes

A substance of mass m_1, specific heat c_1, and initial temperature T_1 is placed in thermal contact with a second substance of mass m_2, specific heat c_2, and initial

temperature $T_2 > T_1$. The two substances are contained in a calorimeter so that no energy is lost to the surroundings. The system of the two substances is allowed to reach thermal equilibrium. What is the total entropy change for the system?

First, let us calculate the final equilibrium temperature T_f. Using the techniques of Section 20.2—namely, Equation 20.5, $Q_{\text{cold}} = -Q_{\text{hot}}$, and Equation 20.4, $Q = mc\,\Delta T$, we obtain

$$m_1 c_1\,\Delta T_1 = -m_2 c_2\,\Delta T_2$$

$$m_1 c_1 (T_f - T_1) = -m_2 c_2 (T_f - T_2)$$

Solving for T_f, we have

$$T_f = \frac{m_1 c_1 T_1 + m_2 c_2 T_2}{m_1 c_1 + m_2 c_2} \tag{22.14}$$

The process is irreversible because the system goes through a series of nonequilibrium states. During such a transformation, the temperature of the system at any time is not well defined because different parts of the system have different temperatures. However, we can imagine that the hot substance at the initial temperature T_2 is slowly cooled to the temperature T_f as it comes into contact with a series of reservoirs differing infinitesimally in temperature, the first reservoir being at T_2 and the last being at T_f. Such a series of very small changes in temperature would approximate a reversible process. We imagine doing the same thing for the cold substance. Applying Equation 22.9 and noting that $dQ = mc\,dT$ for an infinitesimal change, we have

$$\Delta S = \int_1 \frac{dQ_{\text{cold}}}{T} + \int_2 \frac{dQ_{\text{hot}}}{T} = m_1 c_1 \int_{T_1}^{T_f} \frac{dT}{T} + m_2 c_2 \int_{T_2}^{T_f} \frac{dT}{T}$$

where we have assumed that the specific heats remain constant. Integrating, we find that

Change in entropy for a calorimetric process

$$\Delta S = m_1 c_1 \ln \frac{T_f}{T_1} + m_2 c_2 \ln \frac{T_f}{T_2} \tag{22.15}$$

where T_f is given by Equation 22.14. If Equation 22.14 is substituted into Equation 22.15, we can show that one of the terms in Equation 22.15 is always positive and the other is always negative. (You may want to verify this for yourself.) The positive term is always greater than the negative term, and this results in a positive value for ΔS. Thus, we conclude that the entropy of the Universe increases in this irreversible process.

Finally, you should note that Equation 22.15 is valid only when no mixing of different substances occurs, because a further entropy increase is associated with the increase in disorder during the mixing. If the substances are liquids or gases and mixing occurs, the result applies only if the two fluids are identical, as in the following example.

EXAMPLE 22.9 Calculating ΔS for a Calorimetric Process

Suppose that 1.00 kg of water at 0.00°C is mixed with an equal mass of water at 100°C. After equilibrium is reached, the mixture has a uniform temperature of 50.0°C. What is the change in entropy of the system?

Solution We can calculate the change in entropy from Equation 22.15 using the values $m_1 = m_2 = 1.00$ kg, $c_1 = c_2 = 4\,186$ J/kg·K, $T_1 = 273$ K, $T_2 = 373$ K, and $T_f = 323$ K:

$$\Delta S = m_1 c_1 \ln \frac{T_f}{T_1} + m_2 c_2 \ln \frac{T_f}{T_2}$$

$$= (1.00\ \text{kg})(4\,186\ \text{J/kg}\cdot\text{K}) \ln\left(\frac{323\ \text{K}}{273\ \text{K}}\right) + (1.00\ \text{kg})(4\,186\ \text{J/kg}\cdot\text{K}) \ln\left(\frac{323\ \text{K}}{373\ \text{K}}\right)$$

$$= 704\ \text{J/K} - 602\ \text{J/K} = \boxed{102\ \text{J/K}}$$

That is, as a result of this irreversible process, the increase in entropy of the cold water is greater than the decrease in entropy of the warm water. Consequently, the increase in entropy of the system is 102 J/K.

Optional Section

22.8 ENTROPY ON A MICROSCOPIC SCALE[4]

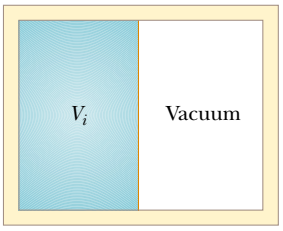
As we have seen, we can approach entropy by relying on macroscopic concepts and using parameters such as pressure and temperature. We can also treat entropy from a microscopic viewpoint through statistical analysis of molecular motions. We now use a microscopic model to investigate once again the free expansion of an ideal gas, which was discussed from a macroscopic point of view in the preceding section.

In the kinetic theory of gases, gas molecules are represented as particles moving randomly. Let us suppose that the gas is initially confined to a volume V_i, as shown in Figure 22.17a. When the partition separating V_i from a larger container is removed, the molecules eventually are distributed throughout the greater volume V_f (Fig. 22.17b). For a given uniform distribution of gas in the volume, there are a large number of equivalent microstates, and we can relate the entropy of the gas to the number of microstates corresponding to a given macrostate.

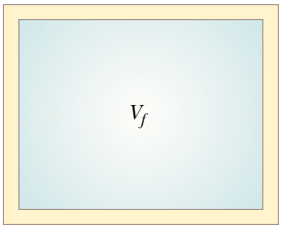
We count the number of microstates by considering the variety of molecular locations involved in the free expansion. The instant after the partition is removed (and before the molecules have had a chance to rush into the other half of the container), all the molecules are in the initial volume. We assume that each molecule occupies some microscopic volume V_m. The total number of possible locations of a single molecule in a macroscopic initial volume V_i is the ratio $w_i = V_i/V_m$, which is a huge number. We use w_i here to represent the number of *ways* that the molecule can be placed in the volume, or the number of microstates, which is equivalent to the number of available locations. We assume that the molecule's occupying each of these locations is equally probable.

As more molecules are added to the system, the number of possible ways that the molecules can be positioned in the volume multiplies. For example, in considering two molecules, for every possible placement of the first, all possible placements of the second are available. Thus, there are w_1 ways of locating the first molecule, and for each of these, there are w_2 ways of locating the second molecule. The total number of ways of locating the two molecules is $w_1 w_2$.

Neglecting the very small probability of having two molecules occupy the same location, each molecule may go into any of the V_i/V_m locations, and so the number of ways of locating N molecules in the volume becomes $W_i = w_i^N = (V_i/V_m)^N$. ($W_i$ is not to be confused with work.) Similarly, when the volume is increased to V_f, the number of ways of locating N molecules increases to $W_f = w_f^N = (V_f/V_m)^N$. The ratio of the number of ways of placing the molecules in the volume for the



(a)



(b)

Figure 22.17 In a free expansion, the gas is allowed to expand into a region that was previously a vacuum.

[4] This section was adapted from A. Hudson and R. Nelson, *University Physics,* Philadelphia, Saunders College Publishing, 1990.

initial and final configurations is

$$\frac{W_f}{W_i} = \frac{(V_f/V_m)^N}{(V_i/V_m)^N} = \left(\frac{V_f}{V_i}\right)^N$$

If we now take the natural logarithm of this equation and multiply by Boltzmann's constant, we find that

$$k_B \ln\left(\frac{W_f}{W_i}\right) = nN_A k_B \ln\left(\frac{V_f}{V_i}\right)$$

where we have used the equality $N = nN_A$. We know from Equation 19.11 that $N_A k_B$ is the universal gas constant R; thus, we can write this equation as

$$k_B \ln W_f - k_B \ln W_i = nR \ln\left(\frac{V_f}{V_i}\right) \quad \textbf{(22.16)}$$

From Equation 22.13 we know that when n mol of a gas undergoes a free expansion from V_i to V_f, the change in entropy is

$$S_f - S_i = nR \ln\left(\frac{V_f}{V_i}\right) \quad \textbf{(22.17)}$$

Note that the right-hand sides of Equations 22.16 and 22.17 are identical. Thus, we make the following important connection between entropy and the number of microstates for a given macrostate:

Entropy (microscopic definition)

$$S \equiv k_B \ln W \quad \textbf{(22.18)}$$

The more microstates there are that correspond to a given macrostate, the greater is the entropy of that macrostate. As we have discussed previously, there are many more disordered microstates than ordered microstates. Thus, Equation 22.18 indicates mathematically that **entropy is a measure of microscopic disorder.** Although in our discussion we used the specific example of the free expansion of an ideal gas, a more rigorous development of the statistical interpretation of entropy would lead us to the same conclusion.

Imagine the container of gas depicted in Figure 22.18a as having all of its molecules traveling at speeds greater than the mean value on the left side and all of its molecules traveling at speeds less than the mean value on the right side (an ordered microstate). Compare this with the uniform mixture of fast- and slow-mov-

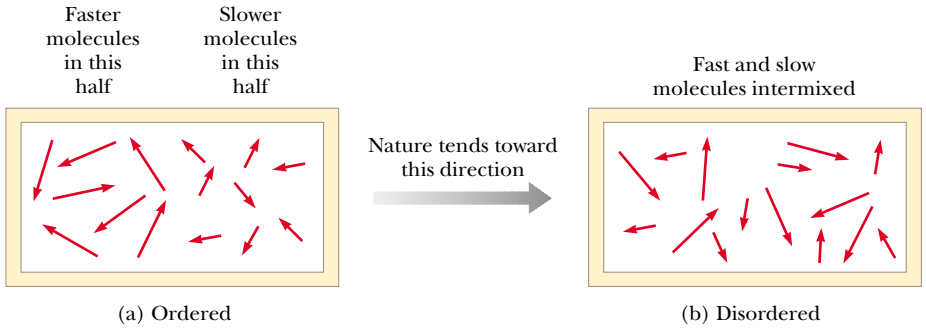


Figure 22.18 A container of gas in two equally probable states of molecular motion. (a) An ordered arrangement, which is one of a few and therefore a collectively unlikely set. (b) A disordered arrangement, which is one of many and therefore a collectively likely set.

Figure 22.19 By tossing a coin into a jar, the carnival-goer can win the fish in the jar. It is more likely that the coin will land in a jar containing a goldfish than in the one containing the black fish.

ing molecules in Figure 22.18b (a disordered microstate). You might expect the ordered microstate to be very unlikely because random motions tend to mix the slow- and fast-moving molecules uniformly. Yet *individually* each of these microstates is equally probable. However, there are far more disordered microstates than ordered microstates, and so a macrostate corresponding to a large number of equivalent disordered microstates is much more probable than a macrostate corresponding to a small number of equivalent ordered microstates.

Figure 22.19 shows a real-world example of this concept. There are two possible macrostates for the carnival game—winning a goldfish and winning a black fish. Because only one jar in the array of jars contains a black fish, only one possible microstate corresponds to the macrostate of winning a black fish. A large number of microstates are described by the coin's falling into a jar containing a goldfish. Thus, for the macrostate of winning a goldfish, there are many equivalent microstates. As a result, the probability of winning a goldfish is much greater than the probability of winning a black fish. If there are 24 goldfish and 1 black fish, the probability of winning the black fish is 1 in 25. This assumes that all microstates have the same probability, a situation that may not be quite true for the situation shown in Figure 22.19. If you are an accurate coin tosser and you are aiming for the edge of the array of jars, then the probability of the coin's landing in a jar near the edge is likely to be greater than the probability of its landing in a jar near the center.

Let us consider a similar type of probability problem for 100 molecules in a container. At any given moment, the probability of one molecule's being in the left part of the container shown in Figure 22.20a as a result of random motion is $\frac{1}{2}$. If there are two molecules, as shown in Figure 22.20b, the probability of both being in the left part is $(\frac{1}{2})^2$ or 1 in 4. If there are three molecules (Fig. 22.20c), the probability of all of them being in the left portion at the same moment is $(\frac{1}{2})^3$, or 1 in 8. For 100 independently moving molecules, the probability that the 50 fastest ones will be found in the left part at any moment is $(\frac{1}{2})^{50}$. Likewise, the probability that the remaining 50 slower molecules will be found in the right part at any moment is $(\frac{1}{2})^{50}$. Therefore, the probability of finding this fast-slow separation as a result of random motion is the product $(\frac{1}{2})^{50}(\frac{1}{2})^{50} = (\frac{1}{2})^{100}$, which corresponds to about 1 in 10^{30}. When this calculation is extrapolated from 100 molecules to the number in 1 mol of gas (6.02×10^{23}), the ordered arrangement is found to be *extremely* improbable!

QuickLab

Roll a pair of dice 100 times and record the total number of spots appearing on the dice for each throw. Which total comes up most frequently? Is this expected?

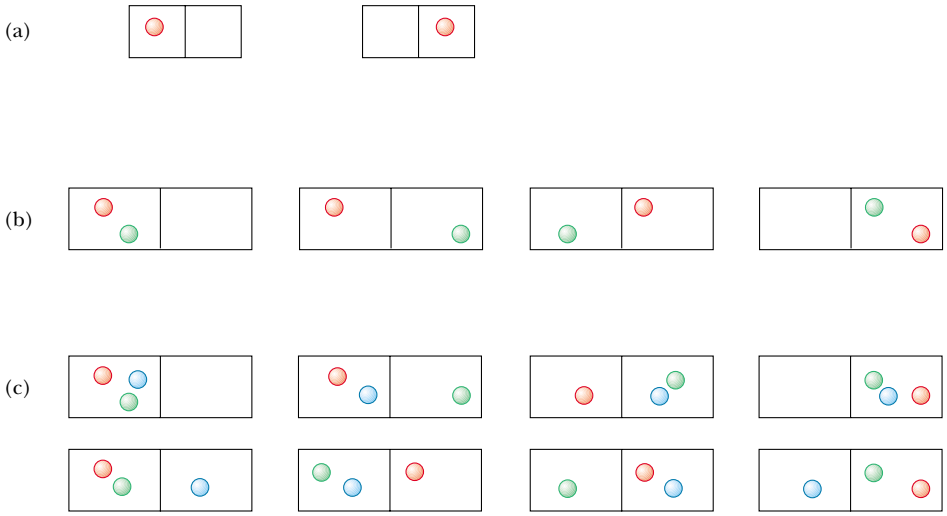


Figure 22.20 (a) One molecule in a two-sided container has a 1-in-2 chance of being on the left side. (b) Two molecules have a 1-in-4 chance of being on the left side at the same time. (c) Three molecules have a 1-in-8 chance of being on the left side at the same time.

EXAMPLE 22.10 Adiabatic Free Expansion — One Last Time

Let us verify that the macroscopic and microscopic approaches to the calculation of entropy lead to the same conclusion for the adiabatic free expansion of an ideal gas. Suppose that 1 mol of gas expands to four times its initial volume. As we have seen for this process, the initial and final temperatures are the same. (a) Using a macroscopic approach, calculate the entropy change for the gas. (b) Using statistical considerations, calculate the change in entropy for the gas and show that it agrees with the answer you obtained in part (a).

Solution (a) Using Equation 22.13, we have

$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right) = (1)R\ln\left(\frac{4V_i}{V_i}\right) = R\ln 4$$

(b) The number of microstates available to a single molecule in the initial volume V_i is $w_i = V_i/V_m$. For 1 mol (N_A molecules), the number of available microstates is

$$W_i = w_i^{N_A} = \left(\frac{V_i}{V_m}\right)^{N_A}$$

The number of microstates for all N_A molecules in the final volume $V_f = 4V_i$ is

$$W_f = \left(\frac{V_f}{V_m}\right)^{N_A} = \left(\frac{4V_i}{V_m}\right)^{N_A}$$

Thus, the ratio of the number of final microstates to initial microstates is

$$\frac{W_f}{W_i} = 4^{N_A}$$

Using Equation 22.18, we obtain

$$\Delta S = k_B \ln W_f - k_B \ln W_i = k_B \ln\left(\frac{W_f}{W_i}\right)$$

$$= k_B \ln(4^{N_A}) = N_A k_B \ln 4 = R\ln 4$$

The answer is the same as that for part (a), which dealt with macroscopic parameters.

CONCEPTUAL EXAMPLE 22.11 Let's Play Marbles!

Suppose you have a bag of 100 marbles. Fifty of the marbles are red, and 50 are green. You are allowed to draw four marbles from the bag according to the following rules: Draw one marble, record its color, and return it to the bag. Then draw another marble. Continue this process until you have drawn and returned four marbles. What are the possible macrostates for this set of events? What is the most likely macrostate? What is the least likely macrostate?

Solution Because each marble is returned to the bag before the next one is drawn, the probability of drawing a red marble is always the same as the probability of drawing a

green one. All the possible microstates and macrostates are shown in Table 22.1. As this table indicates, there is only one way to draw four red marbles, and so there is only one microstate. However, there are four possible microstates that correspond to the macrostate of one green marble and three red marbles; six microstates that correspond to two green marbles and two red marbles; four microstates that correspond to three green marbles and one red marble; and one microstate that corresponds to four green marbles. The most likely macrostate—two red marbles and two green marbles—corresponds to the most disordered microstates. The least likely macrostates—four red marbles or four green marbles—correspond to the most ordered microstates.

TABLE 22.1 Possible Results of Drawing Four Marbles from a Bag

Macrostate	Possible Microstates	Total Number of Microstates
All R	RRRR	1
1G, 3R	RRRG, RRGR, RGRR, GRRR	4
2G, 2R	RRGG, RGRG, GRRG, RGGR, GRGR, GGRR	6
3G, 1R	GGGR, GGRG, GRGG, RGGG	4
All G	GGGG	1

SUMMARY

A **heat engine** is a device that converts internal energy to other useful forms of energy. The net work done by a heat engine in carrying a working substance through a cyclic process ($\Delta E_{\text{int}} = 0$) is

$$W = Q_h - Q_c \tag{22.1}$$

where Q_h is the energy absorbed from a hot reservoir and Q_c is the energy expelled to a cold reservoir.

The **thermal efficiency** e of a heat engine is

$$e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} \tag{22.2}$$

The **second law of thermodynamics** can be stated in the following two ways:

- It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the absorption of energy from a reservoir and the performance of an equal amount of work (the Kelvin–Planck statement).
- It is impossible to construct a cyclic machine whose sole effect is the continuous transfer of energy from one object to another object at a higher temperature without the input of energy by work (the Clausius statement).

In a **reversible** process, the system can be returned to its initial conditions along the same path shown on a PV diagram, and every point along this path is an equilibrium state. A process that does not satisfy these requirements is **irreversible. Carnot's theorem** states that no real heat engine operating (irreversibly) between the temperatures T_c and T_h can be more efficient than an engine operating reversibly in a Carnot cycle between the same two temperatures.

The **thermal efficiency** of a heat engine operating in the Carnot cycle is

$$e_C = 1 - \frac{T_c}{T_h} \tag{22.4}$$

You should be able to use this equation (or an equivalent form involving a ratio of heats) to determine the maximum possible efficiency of any heat engine.

The second law of thermodynamics states that when real (irreversible) processes occur, the degree of disorder in the system plus the surroundings increases. When a process occurs in an isolated system, the state of the system becomes more disordered. The measure of disorder in a system is called **entropy** S. Thus, another way in which the second law can be stated is

- The entropy of the Universe increases in all real processes.

The **change in entropy** dS of a system during a process between two infinitesimally separated equilibrium states is

$$dS = \frac{dQ_r}{T} \tag{22.8}$$

where dQ_r is the energy transfer by heat for a reversible process that connects the initial and final states. The change in entropy of a system during an arbitrary process between an initial state and a final state is

$$\Delta S = \int_i^f \frac{dQ_r}{T} \tag{22.9}$$

The value of ΔS for the system is the same for all paths connecting the initial and final states. The change in entropy for a system undergoing any reversible, cyclic process is zero, and when such a process occurs, the entropy of the Universe remains constant.

From a microscopic viewpoint, entropy is defined as

$$S \equiv k_B \ln W \tag{22.18}$$

where k_B is Boltzmann's constant and W is the number of microstates available to the system for the existing macrostate. Because of the statistical tendency of systems to proceed toward states of greater probability and greater disorder, all natural processes are irreversible, and entropy increases. Thus, entropy is a measure of microscopic disorder.

QUESTIONS

1. Is it possible to convert internal energy to mechanical energy? Describe a process in which such a conversion occurs.
2. What are some factors that affect the efficiency of automobile engines?
3. In practical heat engines, which are we able to control more: the temperature of the hot reservoir, or the temperature of the cold reservoir? Explain.
4. A steam-driven turbine is one major component of an electric power plant. Why is it advantageous to have the temperature of the steam as high as possible?
5. Is it possible to construct a heat engine that creates no thermal pollution? What does this tell us about environmental considerations for an industrialized society?
6. Discuss three common examples of natural processes that involve an increase in entropy. Be sure to account for all parts of each system under consideration.
7. Discuss the change in entropy of a gas that expands (a) at constant temperature and (b) adiabatically.
8. In solar ponds constructed in Israel, the Sun's energy is concentrated near the bottom of a salty pond. With the proper layering of salt in the water, convection is prevented, and temperatures of 100°C may be reached. Can you estimate the maximum efficiency with which useful energy can be extracted from the pond?
9. The vortex tube (Fig. Q22.9) is a T-shaped device that takes in compressed air at 20 atm and 20°C and gives off air at −20°C from one flared end and air at 60°C from the other flared end. Does the operation of this device vi-

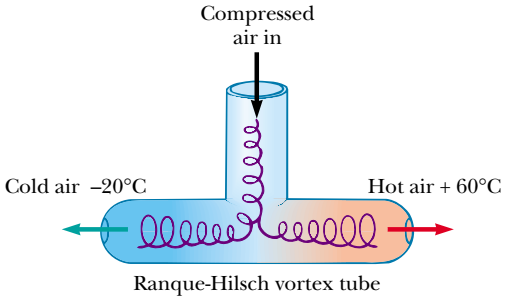


Figure Q22.9

olate the second law of thermodynamics? If not, explain why not.

10. Why does your automobile burn more gas in winter than in summer?

11. Can a heat pump have a coefficient of performance (COP) less than unity? Explain.

12. Give some examples of irreversible processes that occur in nature.

13. Give an example of a process in nature that is nearly reversible.

14. A thermodynamic process occurs in which the entropy of a system changes by -8.0 J/K. According to the second law of thermodynamics, what can you conclude about the entropy change of the environment?

15. If a supersaturated sugar solution is allowed to evaporate slowly, sugar crystals form in the container. Hence, sugar molecules go from a disordered form (in solution) to a highly ordered crystalline form. Does this process violate the second law of thermodynamics? Explain.

16. How could you increase the entropy of 1 mol of a metal that is at room temperature? How could you decrease its entropy?

17. A heat pump is to be installed in a region where the average outdoor temperature in the winter months is $-20°$C. In view of this, why would it be advisable to place the outdoor compressor unit deep in the ground? Why are heat pumps not commonly used for heating in cold climates?

18. Suppose your roommate is "Mr. Clean" and tidies up your messy room after a big party. That is, your roommate is increasing order in the room. Does this represent a violation of the second law of thermodynamics?

19. Discuss the entropy changes that occur when you (a) bake a loaf of bread and (b) consume the bread.

20. The device shown in Figure Q22.20, which is called a thermoelectric converter, uses a series of semiconductor cells to convert internal energy to electrical energy. In the photograph on the left, both legs of the device are at the same temperature and no electrical energy is produced. However, when one leg is at a higher temperature than the other, as shown in the photograph on the right, electrical energy is produced as the device extracts energy from the hot reservoir and drives a small electric motor. (a) Why does the temperature differential produce electrical energy in this demonstration? (b) In what sense does this intriguing experiment demonstrate the second law of thermodynamics?

21. A classmate tells you that it is just as likely for all the air molecules in the room you are both in to be concentrated in one corner (with the rest of the room being a vacuum) as it is for the air molecules to be distributed uniformly about the room in their current state. Is this true? Why doesn't the situation he describes actually happen?

Figure Q22.20 *(Courtesy of PASCO Scientific Company)*

PROBLEMS

1, 2, 3 = straightforward, intermediate, challenging ☐ = full solution available in the *Student Solutions Manual and Study Guide*
WEB = solution posted at **http://www.saunderscollege.com/physics/** = Computer useful in solving problem = Interactive Physics
= paired numerical/symbolic problems

Section 22.1 Heat Engines and the Second Law of Thermodynamics

Section 22.2 Reversible and Irreversible Processes

1. A heat engine absorbs 360 J of energy and performs 25.0 J of work in each cycle. Find (a) the efficiency of the engine and (b) the energy expelled to the cold reservoir in each cycle.
2. The energy absorbed by an engine is three times greater than the work it performs. (a) What is its thermal efficiency? (b) What fraction of the energy absorbed is expelled to the cold reservoir?
3. A particular engine has a power output of 5.00 kW and an efficiency of 25.0%. Assuming that the engine expels 8 000 J of energy in each cycle, find (a) the energy absorbed in each cycle and (b) the time for each cycle.
4. A heat engine performs 200 J of work in each cycle and has an efficiency of 30.0%. For each cycle, how much energy is (a) absorbed and (b) expelled?
5. An ideal gas is compressed to half its original volume while its temperature is held constant. (a) If 1 000 J of energy is removed from the gas during the compression, how much work is done on the gas? (b) What is the change in the internal energy of the gas during the compression?
6. Suppose that a heat engine is connected to two energy reservoirs, one a pool of molten aluminum (660°C) and the other a block of solid mercury (− 38.9°C). The engine runs by freezing 1.00 g of aluminum and melting 15.0 g of mercury during each cycle. The heat of fusion of aluminum is 3.97×10^5 J/kg; the heat of fusion of mercury is 1.18×10^4 J/kg. What is the efficiency of this engine?

Section 22.3 The Carnot Engine

7. One of the most efficient engines ever built (actual efficiency 42.0%) operates between 430°C and 1 870°C. (a) What is its maximum theoretical efficiency? (b) How much power does the engine deliver if it absorbs 1.40×10^5 J of energy each second from the hot reservoir?
8. A heat engine operating between 80.0°C and 200°C achieves 20.0% of the maximum possible efficiency. What energy input will enable the engine to perform 10.0 kJ of work?
9. A Carnot engine has a power output of 150 kW. The engine operates between two reservoirs at 20.0°C and 500°C. (a) How much energy does it absorb per hour? (b) How much energy is lost per hour in its exhaust?
10. A steam engine is operated in a cold climate where the exhaust temperature is 0°C. (a) Calculate the theoretical maximum efficiency of the engine, using an intake steam temperature of 100°C. (b) If superheated steam at 200°C were used instead, what would be the maximum possible efficiency?

WEB 11. An ideal gas is taken through a Carnot cycle. The isothermal expansion occurs at 250°C, and the isothermal compression takes place at 50.0°C. Assuming that the gas absorbs 1 200 J of energy from the hot reservoir during the isothermal expansion, find (a) the energy expelled to the cold reservoir in each cycle and (b) the net work done by the gas in each cycle.

12. The exhaust temperature of a Carnot heat engine is 300°C. What is the intake temperature if the efficiency of the engine is 30.0%?
13. A power plant operates at 32.0% efficiency during the summer when the sea water for cooling is at 20.0°C. The plant uses 350°C steam to drive turbines. Assuming that the plant's efficiency changes in the same proportion as the ideal efficiency, what would be the plant's efficiency in the winter, when the sea water is at 10.0°C?
14. Argon enters a turbine at a rate of 80.0 kg/min, a temperature of 800°C, and a pressure of 1.50 MPa. It expands adiabatically as it pushes on the turbine blades and exits at a pressure of 300 kPa. (a) Calculate its temperature at the time of exit. (b) Calculate the (maximum) power output of the turning turbine. (c) The turbine is one component of a model closed-cycle gas turbine engine. Calculate the maximum efficiency of the engine.
15. A power plant that would make use of the temperature gradient in the ocean has been proposed. The system is to operate between 5.00°C (water temperature at a depth of about 1 km) and 20.0°C (surface water temperature). (a) What is the maximum efficiency of such a system? (b) If the power output of the plant is 75.0 MW, how much energy is absorbed per hour? (c) In view of your answer to part (a), do you think such a system is worthwhile (considering that there is no charge for fuel)?
16. A 20.0%-efficient real engine is used to speed up a train from rest to 5.00 m/s. It is known that an ideal (Carnot) engine having the same cold and hot reservoirs would accelerate the same train from rest to a speed of 6.50 m/s using the same amount of fuel. Assuming that the engines use air at 300 K as a cold reservoir, find the temperature of the steam serving as the hot reservoir.
17. A firebox is at 750 K, and the ambient temperature is 300 K. The efficiency of a Carnot engine doing 150 J of work as it transports energy between these constant-temperature baths is 60.0%. The Carnot engine must absorb energy 150 J/0.600 = 250 J from the hot reser-

voir and release 100 J of energy into the environment. To follow Carnot's reasoning, suppose that some other heat engine S could have an efficiency of 70.0%. (a) Find the energy input and energy output of engine S as it does 150 J of work. (b) Let engine S operate as in part (a) and run the Carnot engine in reverse. Find the total energy the firebox puts out as both engines operate together and the total energy absorbed by the environment. Show that the Clausius statement of the second law of thermodynamics is violated. (c) Find the energy input and work output of engine S as it exhausts 100 J of energy. (d) Let engine S operate as in (c) and contribute 150 J of its work output to running the Carnot engine in reverse. Find the total energy that the firebox puts out as both engines operate together, the total work output, and the total energy absorbed by the environment. Show that the Kelvin–Planck statement of the second law is violated. Thus, our assumption about the efficiency of engine S must be false. (e) Let the engines operate together through one cycle as in part (d). Find the change in entropy of the Universe. Show that the entropy statement of the second law is violated.

18. At point A in a Carnot cycle, 2.34 mol of a monatomic ideal gas has a pressure of 1 400 kPa, a volume of 10.0 L, and a temperature of 720 K. It expands isothermally to point B, and then expands adiabatically to point C, where its volume is 24.0 L. An isothermal compression brings it to point D, where its new volume is 15.0 L. An adiabatic process returns the gas to point A. (a) Determine all the unknown pressures, volumes, and temperatures as you fill in the following table:

	P	V	T
A	1 400 kPa	10.0 L	720 K
B			
C		24.0 L	
D		15.0 L	

(b) Find the energy added by heat, the work done, and the change in internal energy for each of the following steps: $A \rightarrow B$, $B \rightarrow C$, $C \rightarrow D$, and $D \rightarrow A$. (c) Show that $W_{\text{net}}/Q_{\text{in}} = 1 - T_C/T_A$, the Carnot efficiency.

Section 22.4 Gasoline and Diesel Engines

19. In a cylinder of an automobile engine just after combustion, the gas is confined to a volume of 50.0 cm^3 and has an initial pressure of 3.00×10^6 Pa. The piston moves outward to a final volume of 300 cm^3, and the gas expands without energy loss by heat. (a) If $\gamma = 1.40$ for the gas, what is the final pressure? (b) How much work is done by the gas in expanding?

20. A gasoline engine has a compression ratio of 6.00 and uses a gas for which $\gamma = 1.40$. (a) What is the efficiency of the engine if it operates in an idealized Otto cycle? (b) If the actual efficiency is 15.0%, what fraction of the fuel is wasted as a result of friction and energy losses by heat that could by avoided in a reversible engine? (Assume complete combustion of the air–fuel mixture.)

21. A 1.60-L gasoline engine with a compression ratio of 6.20 has a power output of 102 hp. Assuming that the engine operates in an idealized Otto cycle, find the energy absorbed and exhausted each second. Assume that the fuel–air mixture behaves like an ideal gas, with $\gamma = 1.40$.

22. The compression ratio of an Otto cycle, as shown in Figure 22.12, is $V_A/V_B = 8.00$. At the beginning A of the compression process, 500 cm^3 of gas is at 100 kPa and 20.0°C. At the beginning of the adiabatic expansion, the temperature is $T_C = 750$°C. Model the working fluid as an ideal gas, with $E_{\text{int}} = nC_VT = 2.50nRT$ and $\gamma = 1.40$. (a) Fill in the following table to track the states of the gas:

	T (K)	P (kPa)	V (cm^3)	E_{int}
A	293	100	500	
B				
C	1 023			
D				
A				

(b) Fill in the following table to track the processes:

	Q	W	ΔE_{int}
$A \rightarrow B$			
$B \rightarrow C$			
$C \rightarrow D$			
$D \rightarrow A$			
$ABCDA$			

(c) Identify the energy input Q_h, the energy exhaust Q_c, and the net output work W. (d) Calculate the thermal efficiency. (e) Find the number of revolutions per minute that the crankshaft must complete for a one-cylinder engine to have an output power of 1.00 kW = 1.34 hp. (*Hint:* The thermodynamic cycle involves four piston strokes.)

Section 22.5 Heat Pumps and Refrigerators

23. What is the coefficient of performance of a refrigerator that operates with Carnot efficiency between the temperatures − 3.00°C and + 27.0°C?

24. What is the maximum possible coefficient of performance of a heat pump that brings energy from outdoors at − 3.00°C into a 22.0°C house? (*Hint:* The heat pump does work W, which is also available to warm up the house.)

25. An ideal refrigerator or ideal heat pump is equivalent to a Carnot engine running in reverse. That is, energy Q_c is absorbed from a cold reservoir, and energy Q_h is rejected to a hot reservoir. (a) Show that the work that must be supplied to run the refrigerator or heat pump is

$$W = \frac{T_h - T_c}{T_c} Q_c$$

(b) Show that the coefficient of performance (COP) of the ideal refrigerator is

$$\text{COP} = \frac{T_c}{T_h - T_c}$$

26. A heat pump (Fig. P22.26) is essentially a heat engine run backward. It extracts energy from colder air outside and deposits it in a warmer room. Suppose that the ratio of the actual energy entering the room to the work done by the device's motor is 10.0% of the theoretical maximum ratio. Determine the energy entering the room per joule of work done by the motor when the inside temperature is 20.0°C and the outside temperature is −5.00°C.

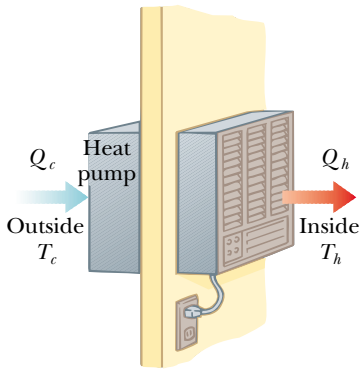


Figure P22.26

WEB **27.** How much work does an ideal Carnot refrigerator require to remove 1.00 J of energy from helium at 4.00 K and reject this energy to a room-temperature (293-K) environment?

28. How much work does an ideal Carnot refrigerator require to remove energy Q from helium at T_c and reject this energy to a room-temperature environment at T_h?

29. A refrigerator has a coefficient of performance equal to 5.00. Assuming that the refrigerator absorbs 120 J of energy from a cold reservoir in each cycle, find (a) the work required in each cycle and (b) the energy expelled to the hot reservoir.

30. A refrigerator maintains a temperature of 0°C in the cold compartment with a room temperature of 25.0°C. It removes energy from the cold compartment at the rate 8 000 kJ/h. (a) What minimum power is required to operate the refrigerator? (b) At what rate does the refrigerator exhaust energy into the room?

Section 22.6 Entropy

31. An ice tray contains 500 g of water at 0°C. Calculate the change in entropy of the water as it freezes slowly and completely at 0°C.

32. At a pressure of 1 atm, liquid helium boils at 4.20 K. The latent heat of vaporization is 20.5 kJ/kg. Determine the entropy change (per kilogram) of the helium resulting from vaporization.

33. Calculate the change in entropy of 250 g of water heated slowly from 20.0°C to 80.0°C. (*Hint:* Note that $dQ = mc\,dT$.)

34. An airtight freezer holds 2.50 mol of air at 25.0°C and 1.00 atm. The air is then cooled to −18.0°C. (a) What is the change in entropy of the air if the volume is held constant? (b) What would the change be if the pressure were maintained at 1 atm during the cooling?

Section 22.7 Entropy Changes in Irreversible Processes

35. The temperature at the surface of the Sun is approximately 5 700 K, and the temperature at the surface of the Earth is approximately 290 K. What entropy change occurs when 1 000 J of energy is transferred by radiation from the Sun to the Earth?

36. A 1.00-kg iron horseshoe is taken from a furnace at 900°C and dropped into 4.00 kg of water at 10.0°C. Assuming that no energy is lost by heat to the surroundings, determine the total entropy change of the system (horseshoe and water).

WEB **37.** A 1 500-kg car is moving at 20.0 m/s. The driver brakes to a stop. The brakes cool off to the temperature of the surrounding air, which is nearly constant at 20.0°C. What is the total entropy change?

38. How fast are you personally making the entropy of the Universe increase right now? Make an order-of-magnitude estimate, stating what quantities you take as data and the values you measure or estimate for them.

39. One mole of H_2 gas is contained in the left-hand side of the container shown in Figure P22.39, which has equal volumes left and right. The right-hand side is evacuated. When the valve is opened, the gas streams into the right-hand side. What is the final entropy change of the gas? Does the temperature of the gas change?

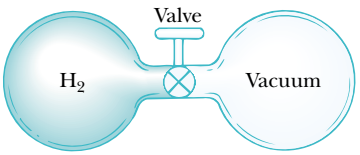


Figure P22.39

40. A rigid tank of small mass contains 40.0 g of argon, initially at 200°C and 100 kPa. The tank is placed into a reservoir at 0°C and is allowed to cool to thermal equi-

librium. Calculate (a) the volume of the tank, (b) the change in internal energy of the argon, (c) the energy transferred by heat, (d) the change in entropy of the argon, and (e) the change in entropy of the constant-temperature bath.

41. A 2.00-L container has a center partition that divides it into two equal parts, as shown in Figure P22.41. The left-hand side contains H_2 gas, and the right-hand side contains O_2 gas. Both gases are at room temperature and at atmospheric pressure. The partition is removed, and the gases are allowed to mix. What is the entropy increase of the system?

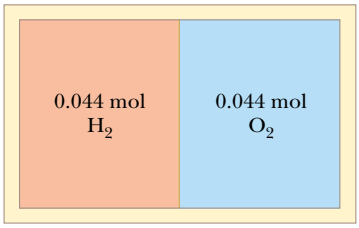


Figure P22.41

42. A 100 000-kg iceberg at $-5.00°C$ breaks away from the polar ice shelf and floats away into the ocean, at 5.00°C. What is the final change in the entropy of the system after the iceberg has completely melted? (The specific heat of ice is 2010 J/kg · °C.)

43. One mole of an ideal monatomic gas, initially at a pressure of 1.00 atm and a volume of 0.025 0 m^3, is heated to a final state with a pressure of 2.00 atm and a volume of 0.040 0 m^3. Determine the change in entropy of the gas for this process.

44. One mole of a diatomic ideal gas, initially having pressure P and volume V, expands so as to have pressure $2P$ and volume $2V$. Determine the entropy change of the gas in the process.

(Optional)

Section 22.8 Entropy on a Microscopic Scale

45. If you toss two dice, what is the total number of ways in which you can obtain (a) a 12 and (b) a 7?

46. Prepare a table like Table 22.1 for the following occurrence. You toss four coins into the air simultaneously and then record the results of your tosses in terms of the numbers of heads and tails that result. For example, HHTH and HTHH are two possible ways in which three heads and one tail can be achieved. (a) On the basis of your table, what is the most probable result of a toss? In terms of entropy, (b) what is the most ordered state, and (c) what is the most disordered?

47. Repeat the procedure used to construct Table 22.1 (a) for the case in which you draw three marbles from your bag rather than four and (b) for the case in which you draw five rather than four.

ADDITIONAL PROBLEMS

48. Every second at Niagara Falls, some 5 000 m^3 of water falls a distance of 50.0 m (Fig. P22.48). What is the increase in entropy per second due to the falling water? (Assume that the mass of the surroundings is so great that its temperature and that of the water stay nearly constant at 20.0°C. Suppose that a negligible amount of water evaporates.)

Figure P22.48 Niagara Falls. *(Jan Kopec/Tony Stone Images)*

49. If a 35.0%-efficient Carnot heat engine is run in reverse so that it functions as a refrigerator, what would be the engine's (that is, the refrigerator's) coefficient of performance (COP)?

50. How much work does an ideal Carnot refrigerator use to change 0.500 kg of tap water at 10.0°C into ice at $-20.0°C$? Assume that the freezer compartment is held at $-20.0°C$ and that the refrigerator exhausts energy into a room at 20.0°C.

WEB **51.** A house loses energy through the exterior walls and roof at a rate of 5 000 J/s = 5.00 kW when the interior temperature is 22.0°C and the outside temperature is $-5.00°C$. Calculate the electric power required to maintain the interior temperature at 22.0°C for the following two cases: (a) The electric power is used in electric resistance heaters (which convert all of the electricity supplied into internal energy). (b) The electric power is used to drive an electric motor that operates the compressor of a heat pump (which has a coefficient of performance [COP] equal to 60.0% of the Carnot-cycle value).

52. A heat engine operates between two reservoirs at T_2 = 600 K and T_1 = 350 K. It absorbs 1 000 J of energy from the higher-temperature reservoir and performs 250 J of work. Find (a) the entropy change of the Universe ΔS_U for this process and (b) the work W that could have been done by an ideal Carnot engine operating between these two reservoirs. (c) Show that the difference between the work done in parts (a) and (b) is $T_1 \Delta S_U$.

WEB **53.** Figure P22.53 represents n mol of an ideal monatomic gas being taken through a cycle that consists of two isothermal processes at temperatures $3T_i$ and T_i and two constant-volume processes. For each cycle, determine,

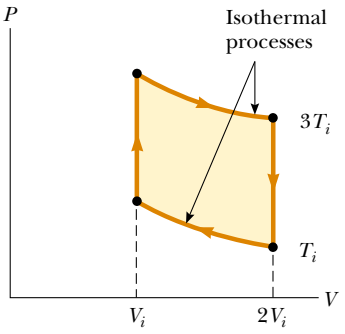


Figure P22.53

in terms of n, R, and T_i, (a) the net energy transferred by heat to the gas and (b) the efficiency of an engine operating in this cycle.

54. A refrigerator has a coefficient of performance (COP) of 3.00. The ice tray compartment is at $-20.0°C$, and the room temperature is 22.0°C. The refrigerator can convert 30.0 g of water at 22.0°C to 30.0 g of ice at $-20.0°C$ each minute. What input power is required? Give your answer in watts.

55. An ideal (Carnot) freezer in a kitchen has a constant temperature of 260 K, while the air in the kitchen has a constant temperature of 300 K. Suppose that the insulation for the freezer is not perfect, such that some energy flows into the freezer at a rate of 0.150 W. Determine the average power that the freezer's motor needs to maintain the constant temperature in the freezer.

56. An electric power plant has an overall efficiency of 15.0%. The plant is to deliver 150 MW of power to a city, and its turbines use coal as the fuel. The burning coal produces steam, which drives the turbines. The steam is then condensed to water at 25.0°C as it passes through cooling coils in contact with river water. (a) How many metric tons of coal does the plant consume each day (1 metric ton $= 10^3$ kg)? (b) What is the total cost of the fuel per year if the delivered price is \$8.00/metric ton? (c) If the river water is delivered at 20.0°C, at what minimum rate must it flow over the cooling coils in order that its temperature not exceed 25.0°C? (*Note:* The heat of combustion of coal is 33.0 kJ/g.)

57. A power plant, having a Carnot efficiency, produces 1 000 MW of electrical power from turbines that take in steam at 500 K and reject water at 300 K into a flowing river. Assuming that the water downstream is 6.00 K warmer due to the output of the power plant, determine the flow rate of the river.

58. A power plant, having a Carnot efficiency, produces electric power $\mathcal{P}$ from turbines that take in energy from steam at temperature T_h and discharge energy at temperature T_c through a heat exchanger into a flowing river. Assuming that the water downstream is warmer by ΔT due to the output of the power plant, determine the flow rate of the river.

59. An athlete whose mass is 70.0 kg drinks 16 oz (453.6 g) of refrigerated water. The water is at a temperature of 35.0°F. (a) Neglecting the temperature change of her body that results from the water intake (that is, the body is regarded as a reservoir that is always at 98.6°F), find the entropy increase of the entire system. (b) Assume that the entire body is cooled by the drink and that the average specific heat of a human is equal to the specific heat of liquid water. Neglecting any other energy transfers by heat and any metabolic energy release, find the athlete's temperature after she drinks the cold water, given an initial body temperature of 98.6°F. Under *these* assumptions, what is the entropy increase of the entire system? Compare this result with the one you obtained in part (a).

60. One mole of an ideal monatomic gas is taken through the cycle shown in Figure P22.60. The process $A \rightarrow B$ is a reversible isothermal expansion. Calculate (a) the net work done by the gas, (b) the energy added to the gas, (c) the energy expelled by the gas, and (d) the efficiency of the cycle.

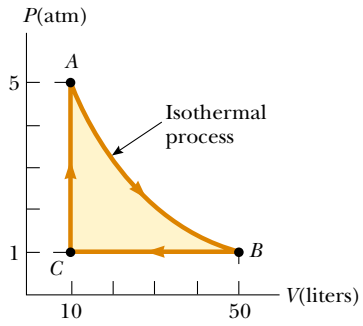


Figure P22.60

61. Calculate the increase in entropy of the Universe when you add 20.0 g of 5.00°C cream to 200 g of 60.0°C coffee. Assume that the specific heats of cream and coffee are both 4.20 J/g · °C.

62. In 1993 the federal government instituted a requirement that all room air conditioners sold in the United States must have an energy efficiency ratio (EER) of 10 or higher. The EER is defined as the ratio of the cooling capacity of the air conditioner, measured in Btu/h, to its electrical power requirement in watts. (a) Convert the EER of 10.0 to dimensionless form, using the conversion 1 Btu = 1 055 J. (b) What is the appropriate name for this dimensionless quantity? (c) In the 1970s it was common to find room air conditioners with EERs of 5 or lower. Compare the operating costs for 10 000-Btu/h air conditioners with EERs of 5.00 and 10.0 if each air conditioner were to operate for 1 500 h during the summer in a city where electricity costs 10.0¢ per kilowatt-hour.

63. One mole of a monatomic ideal gas is taken through the cycle shown in Figure P22.63. At point *A*, the pressure, volume, and temperature are P_i, V_i, and T_i, respectively. In terms of R and T_i, find (a) the total energy entering the system by heat per cycle, (b) the total energy leaving the system by heat per cycle, (c) the efficiency of an engine operating in this cycle, and (d) the efficiency of an engine operating in a Carnot cycle between the same temperature extremes.

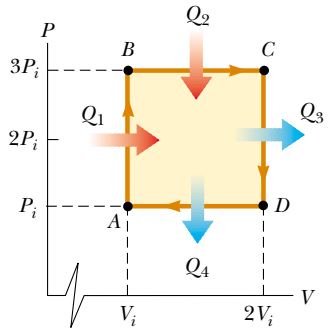


Figure P22.63

64. One mole of an ideal gas expands isothermally. (a) If the gas doubles its volume, show that the work of expansion is $W = RT \ln 2$. (b) Because the internal energy E_{int} of an ideal gas depends solely on its temperature, no change in E_{int} occurs during the expansion. It follows from the first law that the heat input to the gas during the expansion is equal to the energy output by work. Why does this conversion *not* violate the second law?

65. A system consisting of n mol of an ideal gas undergoes a reversible, *isobaric* process from a volume V_i to a volume $3V_i$. Calculate the change in entropy of the gas. (*Hint:* Imagine that the system goes from the initial state to the final state first along an isotherm and then along an adiabatic path—no change in entropy occurs along the adiabatic path.)

66. Suppose you are working in a patent office, and an inventor comes to you with the claim that her heat engine, which employs water as a working substance, has a thermodynamic efficiency of 0.61. She explains that it operates between energy reservoirs at 4°C and 0°C. It is a very complicated device, with many pistons, gears, and pulleys, and the cycle involves freezing and melting. Does her claim that $e = 0.61$ warrant serious consideration? Explain.

67. An idealized diesel engine operates in a cycle known as the *air-standard diesel cycle,* as shown in Figure 22.13. Fuel is sprayed into the cylinder at the point of maximum compression *B*. Combustion occurs during the expansion $B \rightarrow C$, which is approximated as an isobaric process. Show that the efficiency of an engine operating in this idealized diesel cycle is

$$e = 1 - \frac{1}{\gamma}\left(\frac{T_D - T_A}{T_C - T_B}\right)$$

68. One mole of an ideal gas ($\gamma = 1.40$) is carried through the Carnot cycle described in Figure 22.10. At point *A*, the pressure is 25.0 atm and the temperature is 600 K. At point *C*, the pressure is 1.00 atm and the temperature is 400 K. (a) Determine the pressures and volumes at points *A*, *B*, *C*, and *D*. (b) Calculate the net work done per cycle. (c) Determine the efficiency of an engine operating in this cycle.

69. A typical human has a mass of 70.0 kg and produces about 2 000 kcal (2.00×10^6 cal) of metabolic energy per day. (a) Find the rate of metabolic energy production in watts and in calories per hour. (b) If none of the metabolic energy were transferred out of the body, and the specific heat of the human body is 1.00 cal/g · °C, what is the rate at which body temperature would rise? Give your answer in degrees Celsius per hour and in degrees Fahrenheit per hour.

70. Suppose that 1.00 kg of water at 10.0°C is mixed with 1.00 kg of water at 30.0°C at constant pressure. When the mixture has reached equilibrium, (a) what is the final temperature? (b) Take $c_P = 4.19$ kJ/kg · K for water. Show that the entropy of the system increases by

$$\Delta S = 4.19 \ln\left[\left(\frac{293}{283}\right)\left(\frac{293}{303}\right)\right] \text{kJ/K}$$

(c) Verify numerically that $\Delta S > 0$. (d) Is the mixing an irreversible process?

Answers to Quick Quizzes

22.1 The cost of heating your home decreases to 25% of the original cost. With electric heating, you receive the same amount of energy for heating your home as enters it by electricity. The COP of 4 for the heat pump means that you are receiving four times as much energy as the energy entering by electricity. With four times as much energy per unit of energy from electricity, you need only one-fourth as much electricity.

22.2 (b) Because the process is reversible and adiabatic, $Q_r = 0$; therefore, $\Delta S = 0$.

22.3 False. The second law states that the entropy of the *Universe* increases in real processes. Although the organization of molecules into ordered leaves and branches represents a decrease in entropy *of the tree,* this organization takes place because of a number of processes in which the tree interacts with its surroundings. If we include the entropy changes associated with all these processes, the entropy change of the Universe during the growth of a tree is still positive.