

Heat Engines, Entropy, and the Second Law of Thermodynamics

CHAPTER

22



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The first law of thermodynamics, which we studied in Chapter 20, is a statement of conservation of energy and is a special-case reduction of Equation 8.2. This law states that a change in internal energy in a system can occur as a result of energy transfer by heat, by work, or by both. Although the first law of thermodynamics is very important, it makes no distinction between processes that occur spontaneously and those that do not. Only certain types of energy transformation and energy transfer processes actually take place in nature, however. The *second law of thermodynamics*, the major topic in this chapter, establishes which processes do and do not occur. The following are examples

A Stirling engine from the early nineteenth century. Air is heated in the lower cylinder using an external source. As this happens, the air expands and pushes against a piston, causing it to move. The air is then cooled, allowing the cycle to begin again. This is one example of a heat engine, which we study in this chapter. (© SSPL/The Image Works)



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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 object to a hotter object.

of processes that do not violate the first law of thermodynamics if they proceed in either direction, but are observed in reality to proceed in only one direction:

- When two objects at different temperatures are placed in thermal contact with each other, the net transfer of energy by heat is always from the warmer object to the cooler object, 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 gathers internal energy from the ground and 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

22.1 Heat Engines and the Second Law of Thermodynamics

A **heat engine** is a device that takes in energy by heat² and, operating in a cyclic process, expels a fraction of that energy by means of work. For instance, in a typical process by which a power plant produces electricity, a fuel such as coal 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 device that can be modeled as a heat engine is the internal combustion engine in an automobile. This device uses energy from a burning fuel to perform work on pistons that results in the motion of the automobile.

Let us consider the operation of a heat engine in more detail. A heat engine carries some working substance through a cyclic process during which (1) the working substance absorbs energy by heat from a high-temperature energy reservoir, (2) work is done by the engine, and (3) energy is expelled by heat to a lower-temperature reservoir. As an example, consider the operation of a steam engine (Fig. 22.1), which uses water as the working substance. 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. For the mathematical discussion of heat engines, we use absolute values to make all energy transfers by heat positive, and the direction of transfer is indicated with an explicit positive or negative sign. The engine does work W_{eng} (so that *negative* work $W = -W_{\text{eng}}$ is done *on* the engine) and then gives up a quantity of energy $|Q_c|$ to the cold reservoir.



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Figure 22.1 A steam-driven locomotive obtains its energy by burning wood or coal. The generated energy vaporizes water into steam, which powers the locomotive. Modern locomotives use diesel fuel instead of wood or coal. Whether old-fashioned or modern, such locomotives can be modeled as heat engines, which extract energy from a burning fuel and convert a fraction of it to mechanical energy.

¹Although a process occurring in the time-reversed sense has never been *observed*, it is *possible* for it to occur. As we shall see later in this chapter, however, the probability of such a process occurring is infinitesimally small. From this viewpoint, processes occur with a vastly greater probability in one direction than in the opposite direction.

²We use heat as our model for energy transfer into a heat engine. Other methods of energy transfer are possible in the model of a heat engine, however. For example, the Earth's atmosphere can be modeled as a heat engine in which the input energy transfer is by means of electromagnetic radiation from the Sun. The output of the atmospheric heat engine causes the wind structure in the atmosphere.

Because the working substance goes through a cycle, its initial and final internal energies are equal: $\Delta E_{\text{int}} = 0$. Hence, from the first law of thermodynamics, $\Delta E_{\text{int}} = Q + W = Q - W_{\text{eng}} = 0$, and the net work W_{eng} done by a heat engine is equal to the net energy Q_{net} transferred to it. As you can see from Figure 22.2, $Q_{\text{net}} = |Q_h| - |Q_c|$; therefore,

$$W_{\text{eng}} = |Q_h| - |Q_c| \quad (22.1)$$

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 input at the higher temperature during the cycle:

$$e \equiv \frac{W_{\text{eng}}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|} \quad (22.2)$$

You can think of the efficiency as the ratio of what you gain (work) to what you give (energy transfer at the higher temperature). In practice, all heat engines expel only a fraction of the input energy Q_h by mechanical work; consequently, their efficiency is always 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 the input energy by work. Because efficiencies of real engines are well below 100%, the **Kelvin–Planck form of the second law of thermodynamics** states the following:

It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the input of energy by heat 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_{eng} can never be equal to $|Q_h|$ or, alternatively, that some energy $|Q_c|$ *must* be rejected to the environment. Figure 22.3 is a schematic diagram of the impossible “perfect” heat engine.

- Quick Quiz 22.1** The energy input to an engine is 4.00 times greater than the work it performs. (i) What is its thermal efficiency? (a) 4.00 (b) 1.00 (c) 0.250 (d) impossible to determine (ii) What fraction of the energy input is expelled to the cold reservoir? (a) 0.250 (b) 0.750 (c) 1.00 (d) impossible to determine

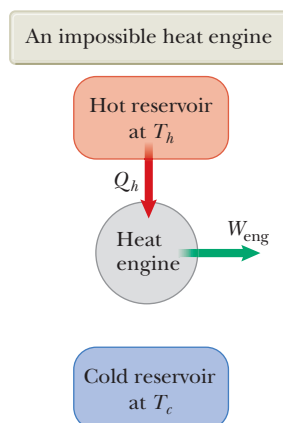


Figure 22.3 Schematic diagram of a heat engine that takes in energy from a hot reservoir and does an equivalent amount of work. It is impossible to construct such a perfect engine.

◀ Thermal efficiency of a heat engine

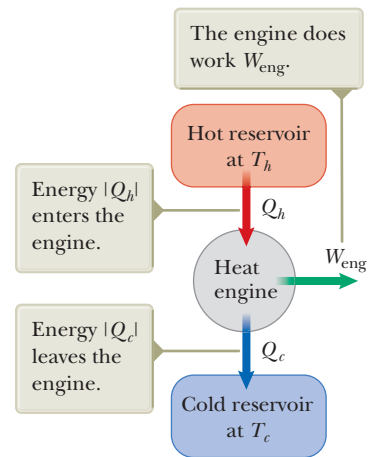


Figure 22.2 Schematic representation of a heat engine.

Pitfall Prevention 22.1

The First and Second Laws Notice the distinction between the first and second laws of thermodynamics. If a gas undergoes a *one-time isothermal process*, then $\Delta E_{\text{int}} = Q + W = 0$ and $W = -Q$. Therefore, the first law allows *all* energy input by heat to be expelled by work. In a heat engine, however, in which a substance undergoes a *cyclic* process, only a *portion* of the energy input by heat can be expelled by work according to the second law.

Example 22.1 The Efficiency of an Engine

An engine transfers $2.00 \times 10^3 \text{ J}$ of energy from a hot reservoir during a cycle and transfers $1.50 \times 10^3 \text{ J}$ as exhaust to a cold reservoir.

(A) Find the efficiency of the engine.

SOLUTION

Conceptualize Review Figure 22.2; think about energy going into the engine from the hot reservoir and splitting, with part coming out by work and part by heat into the cold reservoir.

Categorize This example involves evaluation of quantities from the equations introduced in this section, so we categorize it as a substitution problem.

Find the efficiency of the engine from Equation 22.2:

$$e = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{1.50 \times 10^3 \text{ J}}{2.00 \times 10^3 \text{ J}} = 0.250, \text{ or } 25.0\%$$

(B) How much work does this engine do in one cycle?

SOLUTION

Find the work done by the engine by taking the difference between the input and output energies:

$$W_{\text{eng}} = |Q_h| - |Q_c| = 2.00 \times 10^3 \text{ J} - 1.50 \times 10^3 \text{ J} = 5.0 \times 10^2 \text{ J}$$

WHAT IF? Suppose you were asked for the power output of this engine. Do you have sufficient information to answer this question?

Answer No, you do not have enough information. The power of an engine is the *rate* at which work is done by the engine. You know how much work is done per cycle, but you have no information about the time interval associated with one cycle. If you were told that the engine operates at 2 000 rpm (revolutions per minute), however, you could relate this rate to the period of rotation T of the mechanism of the engine. Assuming there is one thermodynamic cycle per revolution, the power is

$$P = \frac{W_{\text{eng}}}{T} = \frac{5.0 \times 10^2 \text{ J}}{\left(\frac{1}{2000} \text{ min}\right)} \left(\frac{1 \text{ min}}{60 \text{ s}}\right) = 1.7 \times 10^4 \text{ W}$$

22.2 Heat Pumps and Refrigerators

In a heat engine, the direction of energy transfer is from the hot reservoir to the cold reservoir, which is the natural direction. The role of the heat engine is to process the energy from the hot reservoir so as to do useful work. What if we wanted to transfer energy from the cold reservoir to the hot reservoir? Because that is not the natural direction of energy transfer, we must put some energy into a device to be successful. Devices that perform this task are called **heat pumps** and **refrigerators**. For example, homes in summer are cooled using heat pumps called *air conditioners*. The air conditioner transfers energy from the cool room in the home to the warm air outside.

In a refrigerator or a heat pump, the engine takes in energy $|Q_c|$ from a cold reservoir and expels energy $|Q_h|$ to a hot reservoir (Fig. 22.4), which 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 taken in 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

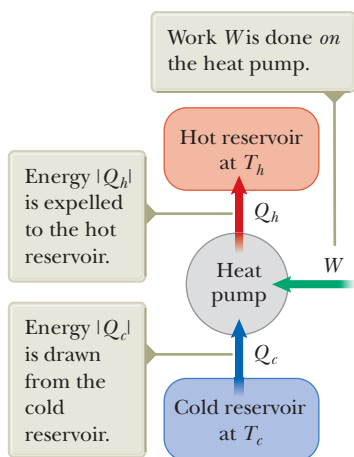


Figure 22.4 Schematic representation of a heat pump.

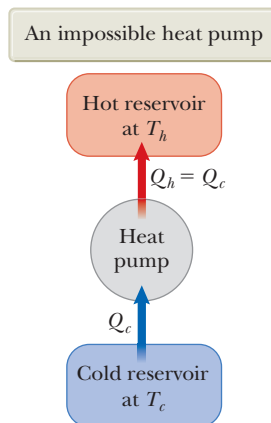


Figure 22.5 Schematic diagram of an impossible heat pump or refrigerator, that is, one that takes in energy from a cold reservoir and expels an equivalent amount of energy to a hot reservoir without the input of energy by work.

a minimum of work. If the process could be accomplished without doing any work, the refrigerator or heat pump would be “perfect” (Fig. 22.5). Again, the existence of such a device would be in violation of the second law of thermodynamics, which in the form of the **Clausius statement**³ states:

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

In simpler terms, energy does not transfer spontaneously by heat from a cold object to a hot object. Work input is required to run a refrigerator.

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, so is the other.⁴

In practice, a heat pump includes a circulating fluid that passes through two sets of metal coils that can exchange energy with the surroundings. The fluid is cold and at low pressure when it is in the coils located in a cool environment, where it absorbs energy by heat. The resulting warm fluid is then compressed and enters the other coils as a hot, high-pressure fluid. There it releases its stored energy to the warm surroundings. In an air conditioner, energy is absorbed into the fluid in coils located in a building’s interior; after the fluid is compressed, energy leaves the fluid through coils located outdoors. In a refrigerator, the external coils are behind the unit (Fig. 22.6) or underneath the unit. The internal coils are in the walls of the refrigerator and absorb energy from the food.

The effectiveness of a heat pump is described in terms of a number called the **coefficient of performance (COP)**. The COP is similar to the thermal efficiency for a heat engine in that it is a ratio of what you gain (energy transferred to or from a reservoir) to what you give (work input). For a heat pump operating in the cooling mode, “what you gain” is energy removed from the cold reservoir. The most effective refrigerator or air conditioner is one that removes the greatest amount of energy



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Figure 22.6 The back of a household refrigerator. The air surrounding the coils is the hot reservoir.

³First expressed by Rudolf Clausius (1822–1888).

⁴See an advanced textbook on thermodynamics for this proof.

from the cold reservoir in exchange for the least amount of work. Therefore, for these devices operating in the cooling mode, we define the COP in terms of $|Q_c|$:

$$\text{COP (cooling mode)} = \frac{\text{energy transferred at low temperature}}{\text{work done on heat pump}} = \frac{|Q_c|}{W} \quad (22.3)$$

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

In addition to cooling applications, heat pumps are becoming increasingly popular for heating purposes. The energy-absorbing coils for a heat pump are located outside a building, in contact with the air or buried in the ground. The other set of coils are in the building's interior. The circulating fluid flowing through the coils absorbs energy from the outside and releases it to the interior of the building from the interior coils.

In the heating mode, the COP of a heat pump is defined as the ratio of the energy transferred to the hot reservoir to the work required to transfer that energy:

$$\text{COP (heating mode)} = \frac{\text{energy transferred at high temperature}}{\text{work done on heat pump}} = \frac{|Q_h|}{W} \quad (22.4)$$

If the outside temperature is 25°F (−4°C) or higher, a typical value of 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. As the outside temperature decreases, however, it becomes more difficult for the heat pump to extract sufficient energy from the air and so the COP decreases. Therefore, the use of heat pumps that extract energy from the air, although 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 that case, the energy is extracted from the ground, which tends to be warmer than the air in the winter.

- Quick Quiz 22.2** The energy entering an electric heater by electrical transmission can be converted to internal energy with an efficiency of 100%. By what factor does the cost of heating your home change when you replace your electric heating system with an electric heat pump that has a COP of 4.00? Assume the motor running the heat pump is 100% efficient. (a) 4.00 (b) 2.00 (c) 0.500 (d) 0.250

Example 22.2 Freezing Water

A certain refrigerator has a COP of 5.00. When the refrigerator is running, its power input is 500 W. A sample of water of mass 500 g and temperature 20.0°C is placed in the freezer compartment. How long does it take to freeze the water to ice at 0°C? Assume all other parts of the refrigerator stay at the same temperature and there is no leakage of energy from the exterior, so the operation of the refrigerator results only in energy being extracted from the water.

SOLUTION

Conceptualize Energy leaves the water, reducing its temperature and then freezing it into ice. The time interval required for this entire process is related to the rate at which energy is withdrawn from the water, which, in turn, is related to the power input of the refrigerator.

Categorize We categorize this example as one that combines our understanding of temperature changes and phase changes from Chapter 20 and our understanding of heat pumps from this chapter.

Analyze Use the power rating of the refrigerator to find the time interval Δt required for the freezing process to occur:

$$P = \frac{W}{\Delta t} \rightarrow \Delta t = \frac{W}{P}$$

22.2 continued

Use Equation 22.3 to relate the work W done on the heat pump to the energy $|Q_c|$ extracted from the water:

$$\Delta t = \frac{|Q_c|}{P(\text{COP})}$$

Use Equations 20.4 and 20.7 to substitute the amount of energy $|Q_c|$ that must be extracted from the water of mass m :

$$\Delta t = \frac{|mc\Delta T + L_f\Delta m|}{P(\text{COP})}$$

Recognize that the amount of water that freezes is $\Delta m = -m$ because all the water freezes:

$$\Delta t = \frac{|m(c\Delta T - L_f)|}{P(\text{COP})}$$

Substitute numerical values:

$$\begin{aligned}\Delta t &= \frac{|(0.500 \text{ kg})[(4 \text{ 186 J/kg}\cdot\text{ }^\circ\text{C})(-20.0^\circ\text{C}) - 3.33 \times 10^5 \text{ J/kg}]|}{(500 \text{ W})(5.00)} \\ &= 83.3 \text{ s}\end{aligned}$$

Finalize In reality, the time interval for the water to freeze in a refrigerator is much longer than 83.3 s, which suggests that the assumptions of our model are not valid. Only a small part of the energy extracted from the refrigerator interior in a given time interval comes from the water. Energy must also be extracted from the container in which the water is placed, and energy that continuously leaks into the interior from the exterior must be extracted.

22.3 Reversible and Irreversible Processes

In the next section, we will 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 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. Let's examine the adiabatic free expansion of a gas, which was already discussed in Section 20.6, and show that it cannot be reversible. Consider 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 displacement, 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. Therefore, in this adiabatic process, the system has changed but the surroundings have not.

For this process to be reversible, we must return the gas to its original volume and temperature without changing the surroundings. Imagine trying 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. The temperature of the gas can be lowered 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 again affected because energy is being added to the surroundings from the gas. If this

Pitfall Prevention 22.2

All Real Processes Are Irreversible
The reversible process is an idealization; all real processes on the Earth are irreversible.

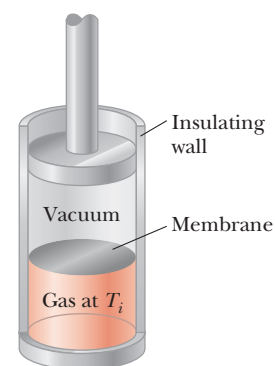


Figure 22.7 Adiabatic free expansion of a gas.

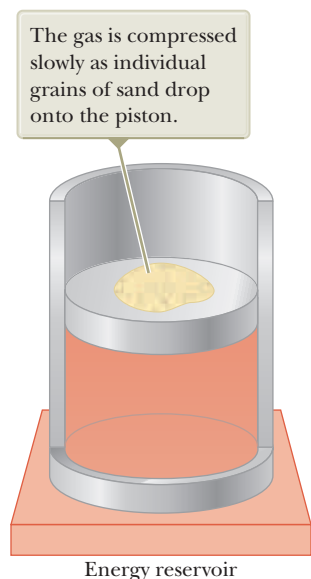


Figure 22.8 A method for compressing a gas in an almost reversible isothermal process.

energy could be used to drive the engine that compressed the gas, 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. The Kelvin–Planck statement of the second law, however, specifies that the energy removed from the gas to return the temperature to its original value cannot be completely converted to mechanical energy by the process of work done by the engine in compressing the gas. Therefore, 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 sudden expansion, significant variations in pressure occur throughout the gas. Therefore, 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. Therefore, because the intermediate conditions between the initial and final states are not equilibrium states, the process is irreversible.

Although all real processes are irreversible, some are almost reversible. If a real process occurs very slowly such that the system is always very nearly in an equilibrium state, the process can be approximated as being reversible. Suppose a gas is compressed isothermally in a piston–cylinder arrangement in which the gas is in thermal contact with an energy reservoir and we continuously transfer just enough energy from the gas to the reservoir to keep the temperature constant. For example, imagine that the gas is compressed very slowly by dropping grains of sand onto a frictionless piston as shown in Figure 22.8. As each grain lands on the piston and compresses the gas a small amount, the system deviates from an equilibrium state, but it is so close to one that it achieves a new equilibrium state in a relatively short time interval. Each grain added represents a change to a new equilibrium state, but the differences between states are so small that the entire process can be approximated as occurring through continuous equilibrium states. The process can be reversed by slowly removing grains from the piston.

A general characteristic of a reversible process is that no nonconservative effects (such as turbulence or friction) that transform 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.

Pitfall Prevention 22.3

Don't Shop for a Carnot Engine

The Carnot engine is an idealization; do not expect a Carnot engine to be developed for commercial use. We explore the Carnot engine only for theoretical considerations.

22.4 The Carnot Engine

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 higher 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.

In this section, we will show that the efficiency of a Carnot engine depends only on the temperatures of the reservoirs. In turn, that efficiency represents the

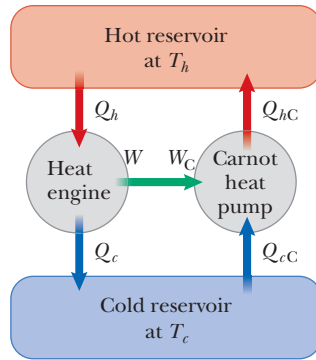


Figure 22.9 A Carnot engine operated as a heat pump and another engine with a proposed higher efficiency operate between two energy reservoirs. The work output and input are matched.

maximum possible efficiency for real engines. Let us confirm that the Carnot engine is the most efficient. We imagine a hypothetical engine with an efficiency greater than that of the Carnot engine. Consider Figure 22.9, which shows the hypothetical engine with $e > e_C$ on the left connected between hot and cold reservoirs. In addition, let us attach a Carnot engine between the same reservoirs. Because the Carnot cycle is reversible, the Carnot engine can be run in reverse as a Carnot heat pump as shown on the right in Figure 22.9. We match the output work of the engine to the input work of the heat pump, $W = W_C$, so there is no exchange of energy by work between the surroundings and the engine–heat pump combination.

Because of the proposed relation between the efficiencies, we must have

$$e > e_C \rightarrow \frac{|W|}{|Q_h|} > \frac{|W_C|}{|Q_{hc}|}$$

The numerators of these two fractions cancel because the works have been matched. This expression requires that

$$|Q_{hc}| > |Q_h| \quad (22.5)$$

From Equation 22.1, the equality of the works gives us

$$|W| = |W_C| \rightarrow |Q_h| - |Q_c| = |Q_{hc}| - |Q_{cC}|$$

which can be rewritten to put the energies exchanged with the cold reservoir on the left and those with the hot reservoir on the right:

$$|Q_{hc}| - |Q_h| = |Q_{cC}| - |Q_c| \quad (22.6)$$

Note that the left side of Equation 22.6 is positive, so the right side must be positive also. We see that the net energy exchange with the hot reservoir is equal to the net energy exchange with the cold reservoir. As a result, for the combination of the heat engine and the heat pump, energy is transferring from the cold reservoir to the hot reservoir by heat with no input of energy by work.

This result is in violation of the Clausius statement of the second law. Therefore, our original assumption that $e > e_C$ must be incorrect, and we must conclude that the Carnot engine represents the highest possible efficiency for an engine. The key feature of the Carnot engine that makes it the most efficient is its *reversibility*; it can be run in reverse as a heat pump. 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 , let's assume 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 non-conducting. Four stages of the Carnot cycle are shown in Figure 22.10(page 662),



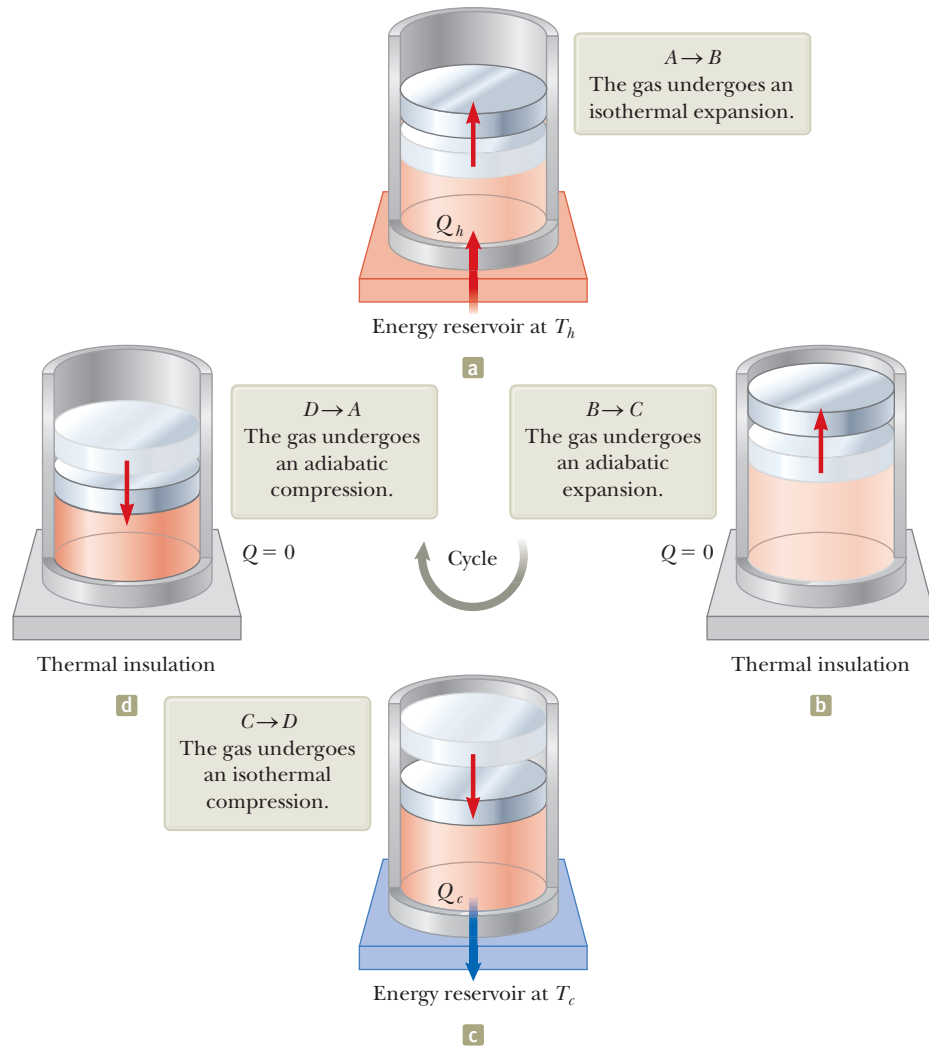
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Sadi Carnot

French engineer (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."

Figure 22.10 The Carnot cycle. The letters A , B , C , and D refer to the states of the gas shown in Figure 22.11. The arrows on the piston indicate the direction of its motion during each process.



and the PV diagram for the cycle is shown in Figure 22.11. The Carnot cycle consists of two adiabatic processes and two isothermal processes, all reversible:

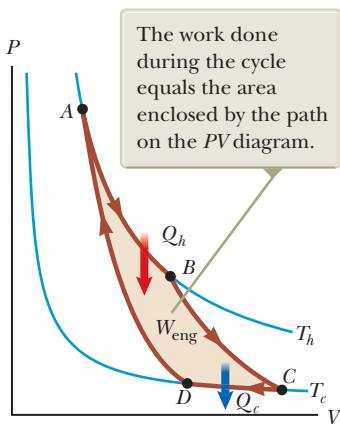


Figure 22.11 PV diagram for the Carnot cycle. The net work done W_{eng} equals the net energy transferred into the Carnot engine in one cycle, $|Q_h| - |Q_c|$.

1. Process $A \rightarrow B$ (Fig. 22.10a) 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. 22.10b), 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 by heat. 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. 22.10c), 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. 22.10d), 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} .

The thermal efficiency of the engine is given by Equation 22.2:

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

In Example 22.3, we show that for a Carnot cycle,

$$\frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h} \quad (22.7)$$

Hence, the thermal efficiency of a Carnot engine is

$$e_C = 1 - \frac{T_c}{T_h} \quad (22.8)$$

◀ Efficiency of a Carnot engine

This result indicates that all Carnot engines operating between the same two temperatures have the same efficiency.⁵

Equation 22.8 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 T_h is raised. The efficiency can be unity (100%), however, only if $T_c = 0$ K. Such reservoirs are not available; therefore, 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 .

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 22.4, we see that the maximum COP for a heat pump in its heating mode is

$$\begin{aligned} \text{COP}_C (\text{heating mode}) &= \frac{|Q_h|}{W} \\ &= \frac{|Q_h|}{|Q_h| - |Q_c|} = \frac{1}{1 - \frac{|Q_c|}{|Q_h|}} = \frac{1}{1 - \frac{T_c}{T_h}} = \frac{T_h}{T_h - T_c} \end{aligned}$$

The Carnot COP for a heat pump in the cooling mode is

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

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.

- Quick Quiz 22.3** Three engines operate between reservoirs separated in temperature by 300 K. The reservoir temperatures are as follows: Engine A: $T_h = 1\,000$ K, $T_c = 700$ K; Engine B: $T_h = 800$ K, $T_c = 500$ K; Engine C: $T_h = 600$ K, $T_c = 300$ K. Rank the engines in order of theoretically possible efficiency from highest to lowest.

⁵For the processes in the Carnot cycle to be reversible, they must be carried out infinitesimally slowly. Therefore, although the Carnot engine is the most efficient engine possible, it has zero power output because it takes an infinite time interval to complete one cycle! For a real engine, the short time interval for each cycle results in the working substance reaching a high temperature lower than that of the hot reservoir and a low temperature higher than that of the cold reservoir. An engine undergoing a Carnot cycle between this narrower temperature range was analyzed by F. L. Curzon and B. Ahlborn ("Efficiency of a Carnot engine at maximum power output," *Am. J. Phys.* **43**(1), 22, 1975), who found that the efficiency at maximum power output depends only on the reservoir temperatures T_c and T_h and is given by $e_{C-A} = 1 - (T_c/T_h)^{1/2}$. The Curzon–Ahlborn efficiency e_{C-A} provides a closer approximation to the efficiencies of real engines than does the Carnot efficiency.

Example 22.3 Efficiency of the Carnot Engine

Show that the ratio of energy transfers by heat in a Carnot engine is equal to the ratio of reservoir temperatures, as given by Equation 22.7.

SOLUTION

Conceptualize Make use of Figures 22.10 and 22.11 to help you visualize the processes in the Carnot cycle.

Categorize Because of our understanding of the Carnot cycle, we can categorize the processes in the cycle as isothermal and adiabatic.

Analyze For the isothermal expansion (process $A \rightarrow B$ in Fig. 22.10), find the energy transfer by heat from the hot reservoir using Equation 20.14 and the first law of thermodynamics:

$$|Q_h| = |\Delta E_{\text{int}} - W_{AB}| = |0 - W_{AB}| = nRT_h \ln \frac{V_B}{V_A}$$

In a similar manner, find the energy transfer to the cold reservoir during the isothermal compression $C \rightarrow D$:

$$|Q_c| = |\Delta E_{\text{int}} - W_{CD}| = |0 - W_{CD}| = nRT_c \ln \frac{V_C}{V_D}$$

Divide the second expression by the first:

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

Apply Equation 21.39 to the adiabatic processes $B \rightarrow C$ and $D \rightarrow A$:

$$\begin{aligned} T_h V_B^{\gamma-1} &= T_c V_C^{\gamma-1} \\ T_h V_A^{\gamma-1} &= T_c V_D^{\gamma-1} \end{aligned}$$

Divide the first equation by the second:

$$\begin{aligned} \left(\frac{V_B}{V_A}\right)^{\gamma-1} &= \left(\frac{V_C}{V_D}\right)^{\gamma-1} \\ (2) \quad \frac{V_B}{V_A} &= \frac{V_C}{V_D} \end{aligned}$$

Substitute Equation (2) into Equation (1):

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

Finalize This last equation is Equation 22.7, the one we set out to prove.

Example 22.4 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

Conceptualize In a steam engine, the gas pushing on the piston in Figure 22.10 is steam. A real steam engine does not operate in a Carnot cycle, but, to find the maximum possible efficiency, imagine a Carnot steam engine.

Categorize We calculate an efficiency using Equation 22.8, so we categorize this example as a substitution problem.

Substitute the reservoir temperatures into Equation 22.8:

$$e_c = 1 - \frac{T_c}{T_h} = 1 - \frac{300 \text{ K}}{500 \text{ K}} = 0.400 \quad \text{or} \quad 40.0\%$$

This result is the highest *theoretical* efficiency of the engine. In practice, the efficiency is considerably lower.

22.4 continued

WHAT IF? Suppose we wished to increase the theoretical efficiency of this engine. This increase can be achieved by raising T_h by ΔT or by decreasing T_c by the same ΔT . Which would be more effective?

Answer A given ΔT would have a larger fractional effect on a smaller temperature, so you would expect a larger change in efficiency if you alter T_c by ΔT . Let's test that numerically. Raising T_h by 50 K, corresponding to $T_h = 550$ K, would give a maximum efficiency of

$$e_C = 1 - \frac{T_c}{T_h} = 1 - \frac{300 \text{ K}}{550 \text{ K}} = 0.455$$

Decreasing T_c by 50 K, corresponding to $T_c = 250$ K, would give a maximum efficiency of

$$e_C = 1 - \frac{T_c}{T_h} = 1 - \frac{250 \text{ K}}{500 \text{ K}} = 0.500$$

Although changing T_c is *mathematically* more effective, often changing T_h is *practically* more feasible.

22.5 Gasoline and Diesel Engines

In a gasoline engine, six processes occur in each cycle; they are illustrated in Figure 22.12. In this discussion, let's consider the interior of the cylinder above the piston to be the system that is taken through repeated cycles in the engine's operation. For a given cycle, the piston moves up and down twice, which represents a four-stroke cycle consisting of two upstrokes and two downstrokes. The processes in the cycle can be approximated by the **Otto cycle** shown in the PV diagram in Figure 22.13 (page 666). In the following discussion, refer to Figure 22.12 for the pictorial representation of the strokes and Figure 22.13 for the significance on the PV diagram of the letter designations below:

1. During the *intake stroke* (Fig. 22.12a and $O \rightarrow A$ in Figure 22.13), the piston moves downward and a gaseous mixture of air and fuel is drawn into the

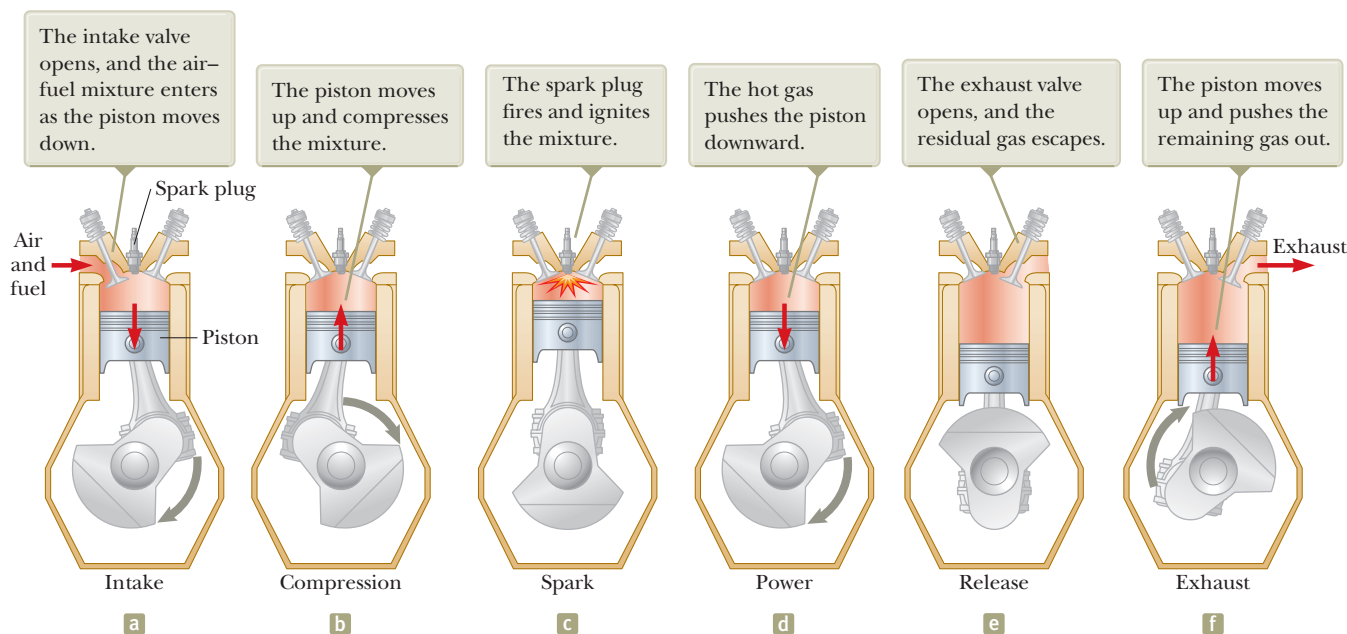


Figure 22.12 The four-stroke cycle of a conventional gasoline engine. The arrows on the piston indicate the direction of its motion during each process.

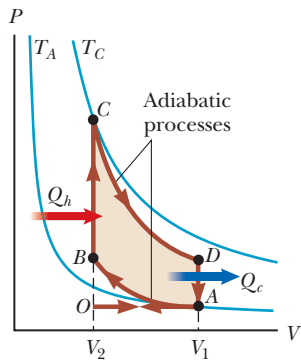


Figure 22.13 PV diagram for the Otto cycle, which approximately represents the processes occurring in an internal combustion engine.

cylinder at atmospheric pressure. That is the energy input part of the cycle: energy enters the system (the interior of the cylinder) by matter transfer as potential energy stored in the fuel. In this process, the volume increases from V_2 to V_1 . This apparent backward numbering is based on the compression stroke (process 2 below), in which the air–fuel mixture is compressed from V_1 to V_2 .

2. During the *compression stroke* (Fig. 22.12b and $A \rightarrow B$ in Fig. 22.13), 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 on the gas is positive, and its value is equal to the negative of the area under the curve AB in Figure 22.13.
3. Combustion occurs when the spark plug fires (Fig. 22.12c and $B \rightarrow C$ in Fig. 22.13). That is not one of the strokes of the cycle because it occurs in a very short time interval while the piston is at its highest position. The combustion represents a rapid energy transformation from potential energy stored in chemical bonds in the fuel to internal energy associated with molecular motion, which is related to temperature. During this time interval, the mixture’s pressure and temperature 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 on or by the gas. We can model this process in the PV diagram (Fig. 22.13) as that process in which the energy $|Q_h|$ enters the system. (In reality, however, this process is a *transformation* of energy already in the cylinder from process $O \rightarrow A$.)
4. In the *power stroke* (Fig. 22.12d and $C \rightarrow D$ in Fig. 22.13), the gas expands adiabatically from V_2 to 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. Release of the residual gases occurs when an exhaust valve is opened (Fig. 22.12e and $D \rightarrow A$ in Fig. 22.13). The pressure suddenly drops for a short time interval. During this time 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* (Fig. 22.12e and $A \rightarrow O$ in Fig. 22.13), 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, the efficiency of the Otto cycle is

$$e = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}} \quad (\text{Otto cycle}) \quad (22.9)$$

where V_1/V_2 is the **compression ratio** and γ is the ratio of the molar specific heats C_p/C_v for the air–fuel mixture. Equation 22.9, which is derived in Example 22.5, shows that the efficiency increases as the compression ratio increases. For a typical compression ratio of 8 and with $\gamma = 1.4$, Equation 22.9 predicts 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 they 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 air–fuel 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. 22.12 and 22.13) is given by Equation 22.9. Treat the working substance as an ideal gas.

SOLUTION

Conceptualize Study Figures 22.12 and 22.13 to make sure you understand the working of the Otto cycle.

Categorize As seen in Figure 22.13, we categorize the processes in the Otto cycle as isovolumetric and adiabatic.

Analyze Model the energy input and output as occurring by heat in processes $B \rightarrow C$ and $D \rightarrow A$. (In reality, most of the energy enters and leaves by matter transfer as the air–fuel mixture enters and leaves the cylinder.) Use Equation 21.23 to find the energy transfers by heat for these processes, which take place at constant volume:

$$B \rightarrow C \quad |Q_h| = nC_V(T_C - T_B)$$

$$D \rightarrow A \quad |Q_c| = nC_V(T_D - T_A)$$

Substitute these expressions into Equation 22.2:

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

Apply Equation 21.39 to the adiabatic processes $A \rightarrow B$ and $C \rightarrow D$:

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

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

Solve these equations for the temperatures T_A and T_D , noting that $V_A = V_D = V_1$ and $V_B = V_C = V_2$:

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

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

Subtract Equation (2) from Equation (3) and rearrange:

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

Substitute Equation (4) into Equation (1):

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

Finalize This final expression is Equation 22.9.

22.6 Entropy

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 variables; that is, the value of each depends only on the thermodynamic state of a system, not on the process that brought it to that state. Another state variable—this one related to the second law of thermodynamics—is *entropy*.

Entropy was originally formulated as a useful concept in thermodynamics. Its importance grew, however, as the field of statistical mechanics developed because the analytical techniques of statistical mechanics provide an alternative means of interpreting entropy and a more global significance to the concept. In statistical

Pitfall Prevention 22.4

Entropy Is Abstract Entropy is one of the most abstract notions in physics, so follow the discussion in this and the subsequent sections very carefully. Do not confuse energy with entropy. Even though the names sound similar, they are very different concepts. On the other hand, energy and entropy are intimately related, as we shall see in this discussion.

mechanics, the behavior of a substance is described in terms of the statistical behavior of its atoms and molecules.

We will develop our understanding of entropy by first considering some non-thermodynamic systems, such as a pair of dice and poker hands. We will then expand on these ideas and use them to understand the concept of entropy as applied to thermodynamic systems.

We begin this process by distinguishing between *microstates* and *macrostates* of a system. A **microstate** is a particular configuration of the individual constituents of the system. A **macrostate** is a description of the system's conditions from a macroscopic point of view.

For any given macrostate of the system, a number of microstates are possible. For example, the macrostate of a 4 on a pair of dice can be formed from the possible microstates 1–3, 2–2, and 3–1. The macrostate of 2 has only one microstate, 1–1. It is assumed all microstates are equally probable. We can compare these two macrostates in three ways: (1) *Uncertainty*: If we know that a macrostate of 4 exists, there is some uncertainty as to the microstate that exists, because there are multiple microstates that will result in a 4. In comparison, there is lower uncertainty (in fact, *zero* uncertainty) for a macrostate of 2 because there is only one microstate. (2) *Choice*: There are more choices of microstates for a 4 than for a 2. (3) *Probability*: The macrostate of 4 has a higher probability than a macrostate of 2 because there are more ways (microstates) of achieving a 4. The notions of uncertainty, choice, and probability are central to the concept of entropy, as we discuss below.

Let's look at another example related to a poker hand. There is only one microstate associated with the macrostate of a royal flush of five spades, laid out in order from ten to ace (Fig. 22.14a). Figure 22.14b shows another poker hand. The macrostate here is “worthless hand.” The *particular* hand (the microstate) in Figure 22.14b and the hand in Figure 22.14a are equally probable. There are, however, *many* other hands similar to that in Figure 22.14b; that is, there are many microstates that also qualify as worthless hands. If you, as a poker player, are told your opponent holds a macrostate of a royal flush in spades, there is *zero uncertainty* as to what five cards are in the hand, only *one choice* of what those cards are, and *low probability* that the hand actually occurred. In contrast, if you are told that your opponent has the macrostate of “worthless hand,” there is *high uncertainty* as to what the five cards are, *many choices* of what they could be, and a *high probability* that a worthless hand occurred. Another variable in poker, of course, is the value of the hand, related to the probability: the higher the probability, the lower the value. The important point to take away from this discussion is that uncertainty, choice, and probability are related in these situations: if one is high, the others are high, and vice versa.

Another way of describing macrostates is by means of “missing information.” For high-probability macrostates with many microstates, there is a large amount



Figure 22.14 (a) A royal flush has low probability of occurring. (b) A worthless poker hand, one of many.

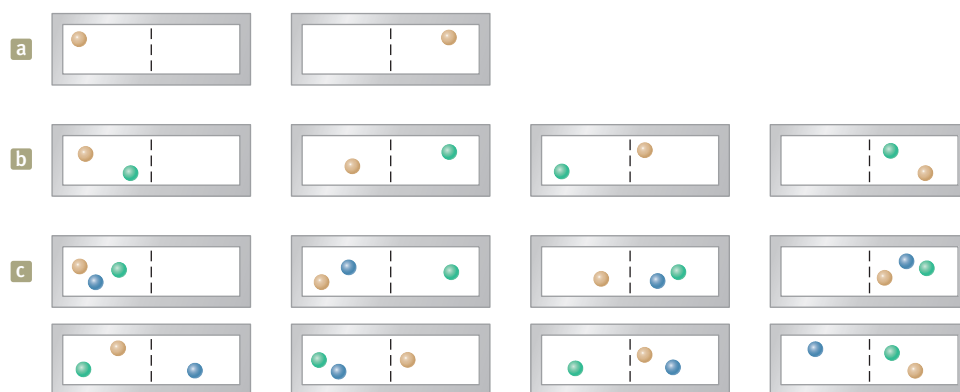
of missing information, meaning we have very little information about what microstate actually exists. For a macrostate of a 2 on a pair of dice, we have no missing information; we *know* the microstate is 1–1. For a macrostate of a worthless poker hand, however, we have lots of missing information, related to the large number of choices we could make as to the actual hand that is held.

Quick Quiz 22.4 (a) Suppose you select four cards at random from a standard deck of playing cards and end up with a macrostate of four deuces. How many microstates are associated with this macrostate? (b) Suppose you pick up two cards and end up with a macrostate of two aces. How many microstates are associated with this macrostate?

For thermodynamic systems, the variable **entropy** S is used to represent the level of uncertainty, choice, probability, or missing information in the system. Consider a configuration (a macrostate) in which all the oxygen molecules in your room are located in the west half of the room and the nitrogen molecules in the east half. Compare that macrostate to the more common configuration of the air molecules distributed uniformly throughout the room. The latter configuration has the higher uncertainty and more missing information as to where the molecules are located because they could be anywhere, not just in one half of the room according to the type of molecule. The configuration with a uniform distribution also represents more choices as to where to locate molecules. It also has a much higher probability of occurring; have you ever noticed your half of the room suddenly being empty of oxygen? Therefore, the latter configuration represents a higher entropy.

For systems of dice and poker hands, the comparisons between probabilities for various macrostates involve relatively small numbers. For example, a macrostate of a 4 on a pair of dice is only three times as probable as a macrostate of 2. The ratio of probabilities of a worthless hand and a royal flush is significantly larger. When we are talking about a macroscopic thermodynamic system containing on the order of Avogadro's number of molecules, however, the ratios of probabilities can be astronomical.

Let's explore this concept by considering 100 molecules in a container. Half of the molecules are oxygen and the other half are nitrogen. At any given moment, the probability of one molecule being in the left part of the container shown in Figure 22.15a as a result of random motion is $\frac{1}{2}$. If there are two molecules as shown in Figure 22.15b, the probability of both being in the left part is $(\frac{1}{2})^2$, or 1 in 4. If there are three molecules (Fig. 22.15c), the probability of them all 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 oxygen molecules will be found in the left part at any moment is $(\frac{1}{2})^{50}$. Likewise, the probability that the remaining 50 nitrogen molecules will be found in the right part at any moment is $(\frac{1}{2})^{50}$. Therefore, the probability of



Pitfall Prevention 22.5

Entropy Is for Thermodynamic Systems We are not applying the word *entropy* to describe systems of dice or cards. We are only discussing dice and cards to set up the notions of microstates, macrostates, uncertainty, choice, probability, and missing information. Entropy can *only* be used to describe thermodynamic systems that contain many particles, allowing the system to store energy as internal energy.

Pitfall Prevention 22.6

Entropy and Disorder Some textbook treatments of entropy relate entropy to the *disorder* of a system. While this approach has some merit, it is not entirely successful. For example, consider two samples of the same solid material at the same temperature. One sample has volume V and the other volume $2V$. The larger sample has higher entropy than the smaller one simply because there are more molecules in it. But there is no sense in which it is more disordered than the smaller sample. We will not use the disorder approach in this text, but watch for it in other sources.

Figure 22.15 Possible distributions of identical molecules in a container. The colors used here exist only to allow us to distinguish among the molecules. (a) One molecule in a 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.

finding this oxygen–nitrogen 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 separated arrangement is found to be *extremely* improbable!

Conceptual Example 22.6 Let's Play Marbles!

Suppose you have a bag of 100 marbles of which 50 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. Shake the bag and 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 and the bag is then shaken, 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

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

to draw a macrostate of four red marbles, so there is only one microstate for that macrostate. There are, however, 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 largest number of choices of microstates, and, therefore, the most uncertainty as to what the exact microstate is. The least likely macrostates—four red marbles or four green marbles—correspond to only one choice of microstate and, therefore, zero uncertainty. There is no missing information for the least likely states: we know the colors of all four marbles.

We have investigated the notions of uncertainty, number of choices, probability, and missing information for some non-thermodynamic systems and have argued that the concept of entropy can be related to these notions for thermodynamic systems. We have not yet indicated how to evaluate entropy numerically for a thermodynamic system. This evaluation was done through statistical means by Boltzmann in the 1870s and appears in its currently accepted form as

$$S = k_B \ln W \quad (22.10)$$

where k_B is Boltzmann's constant. Boltzmann intended W , standing for *Wahrscheinlichkeit*, the German word for probability, to be proportional to the probability that a given macrostate exists. It is equivalent to let W be the number of microstates associated with the macrostate, so we can interpret W as representing the number of "ways" of achieving the macrostate. Therefore, macrostates with larger numbers of microstates have higher probability and, equivalently, higher entropy.

In the kinetic theory of gases, gas molecules are represented as particles moving randomly. Suppose the gas is confined to a volume V . For a uniform distribution of gas in the volume, there are a large number of equivalent microstates, and the entropy of the gas can be related to the number of microstates corresponding to a given macrostate. Let us count the number of microstates by considering the

variety of molecular locations available to the molecules. Let us assume each molecule occupies some microscopic volume V_m . The total number of possible locations of a single molecule in a macroscopic volume V is the ratio $w = V/V_m$, which is a huge number. We use lowercase w here to represent the number of ways a single molecule can be placed in the volume or the number of microstates for a single molecule, which is equivalent to the number of available locations. We assume the probabilities of a molecule occupying any of these locations are equal. As more molecules are added to the system, the number of possible ways the molecules can be positioned in the volume multiplies, as we saw in Figure 22.15. For example, if you consider two molecules, for every possible placement of the first, all possible placements of the second are available. Therefore, there are w ways of locating the first molecule, and for each way, there are w ways of locating the second molecule. The total number of ways of locating the two molecules is $W = w \times w = w^2 = (V/V_m)^2$. (Uppercase W represents the number of ways of putting multiple molecules into the volume and is not to be confused with work.)

Now consider placing N molecules of gas in the volume V . Neglecting the very small probability of having two molecules occupy the same location, each molecule may go into any of the V/V_m locations, and so the number of ways of locating N molecules in the volume becomes $W = w^N = (V/V_m)^N$. Therefore, the spatial part of the entropy of the gas, from Equation 22.10, is

$$S = k_B \ln W = k_B \ln \left(\frac{V}{V_m} \right)^N = Nk_B \ln \left(\frac{V}{V_m} \right) = nR \ln \left(\frac{V}{V_m} \right) \quad (22.11)$$

We will use this expression in the next section as we investigate changes in entropy for processes occurring in thermodynamic systems.

Notice that we have indicated Equation 22.11 as representing only the *spatial* portion of the entropy of the gas. There is also a temperature-dependent portion of the entropy that the discussion above does not address. For example, imagine an isovolumetric process in which the temperature of the gas increases. Equation 22.11 above shows no change in the spatial portion of the entropy for this situation. There *is* a change in entropy, however, associated with the increase in temperature. We can understand this by appealing again to a bit of quantum physics. Recall from Section 21.3 that the energies of the gas molecules are quantized. When the temperature of a gas changes, the distribution of energies of the gas molecules changes according to the Boltzmann distribution law, discussed in Section 21.5. Therefore, as the temperature of the gas increases, there is more uncertainty about the particular microstate that exists as gas molecules distribute themselves into higher available quantum states. We will see the entropy change associated with an isovolumetric process in Example 22.8.

22.7 Changes in Entropy for Thermodynamic Systems

Thermodynamic systems are constantly in flux, changing continuously from one microstate to another. If the system is in equilibrium, a given macrostate exists, and the system fluctuates from one microstate associated with that macrostate to another. This change is unobservable because we are only able to detect the macrostate. Equilibrium states have tremendously higher probability than nonequilibrium states, so it is highly unlikely that an equilibrium state will spontaneously change to a nonequilibrium state. For example, we do not observe a spontaneous split into the oxygen–nitrogen separation discussed in Section 22.6.

What if the system begins in a low-probability macrostate, however? What if the room *begins* with an oxygen–nitrogen separation? In this case, the system will progress from this low-probability macrostate to the much-higher probability

state: the gases will disperse and mix throughout the room. Because entropy is related to probability, a spontaneous increase in entropy, such as in the latter situation, is natural. If the oxygen and nitrogen molecules were initially spread evenly throughout the room, a decrease in entropy would occur if the spontaneous splitting of molecules occurred.

One way of conceptualizing a change in entropy is to relate it to *energy spreading*. A natural tendency is for energy to undergo spatial spreading in time, representing an increase in entropy. If a basketball is dropped onto a floor, it bounces several times and eventually comes to rest. The initial gravitational potential energy in the basketball–Earth system has been transformed to internal energy in the ball and the floor. That energy is spreading outward by heat into the air and into regions of the floor farther from the drop point. In addition, some of the energy has spread throughout the room by sound. It would be unnatural for energy in the room and floor to reverse this motion and concentrate into the stationary ball so that it spontaneously begins to bounce again.

In the adiabatic free expansion of Section 22.3, the spreading of energy accompanies the spreading of the molecules as the gas rushes into the evacuated half of the container. If a warm object is placed in thermal contact with a cool object, energy transfers from the warm object to the cool one by heat, representing a spread of energy until it is distributed more evenly between the two objects.

Now consider a mathematical representation of this spreading of energy or, equivalently, the change in entropy. The original formulation of entropy in thermodynamics involves the transfer of energy by heat during a reversible process. 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, the change in entropy dS is equal to this amount of energy divided by the absolute temperature of the system:

$$dS = \frac{dQ_r}{T} \quad (22.12)$$

Change in entropy for
an infinitesimal process

We have assumed the temperature is constant because the process is infinitesimal. Because entropy is a state variable, the change in entropy during a process depends only on the endpoints and therefore is independent of the actual path followed. Consequently, the entropy change for an irreversible process can be determined by calculating the entropy change for a *reversible* process that connects the same initial and final states.

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. Notice that Equation 22.12 does not define entropy but rather the *change* in entropy. Hence, the meaningful quantity in describing a process is the *change* in entropy.

To calculate the change in entropy for a *finite* process, first recognize that T is generally not constant during the process. Therefore, we must integrate Equation 22.12:

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T} \quad (22.13)$$

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. Therefore, we are free to choose any convenient 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. This point is explored further on in this section.

From Equation 22.10, we see that a change in entropy is represented in the Boltzmann formulation as

$$\Delta S = k_B \ln \left(\frac{W_f}{W_i} \right) \quad (22.14)$$

where W_i and W_f represent the initial and final numbers of microstates, respectively, for the initial and final configurations of the system. If $W_f > W_i$, the final state is more probable than the initial state (there are more choices of microstates), and the entropy increases.

Quick Quiz 22.5 An ideal gas is taken from an initial temperature T_i to a higher final temperature T_f along two different reversible paths. Path A is at constant pressure, and path B is at constant volume. What is the relation between the entropy changes of the gas for these paths? (a) $\Delta S_A > \Delta S_B$ (b) $\Delta S_A = \Delta S_B$ (c) $\Delta S_A < \Delta S_B$

Quick Quiz 22.6 True or False: The entropy change in an adiabatic process must be zero because $Q = 0$.

Example 22.7 Change in Entropy: Melting

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

SOLUTION

Conceptualize We can choose any convenient reversible path to follow that connects the initial and final states. It is not necessary to identify the process or the path because, whatever it is, the effect is the same: energy enters the substance by heat and the substance melts. The mass m of the substance that melts is equal to Δm , the change in mass of the higher-phase (liquid) substance.

Categorize Because the melting takes place at a fixed temperature, we categorize the process as isothermal.

Analyze Use Equation 20.7 in Equation 22.13, noting that the temperature remains fixed:

$$\Delta S = \int \frac{dQ_r}{T} = \frac{1}{T_m} \int dQ_r = \frac{Q_r}{T_m} = \frac{L_f \Delta m}{T_m} = \frac{L_f m}{T_m}$$

Finalize Notice that Δm is positive so that ΔS is positive, representing that energy is added to the substance.

Entropy Change in a Carnot Cycle

Let's consider the changes in entropy that occur in a Carnot heat engine that operates between the temperatures T_c and T_h . In one cycle, the engine takes in 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; therefore, the constant temperature can be brought out in front of the integral sign in Equation 22.13. The integral then simply has the value of the total amount of energy transferred by heat. Therefore, the total change in entropy for one cycle is

$$\Delta S = \frac{|Q_h|}{T_h} - \frac{|Q_c|}{T_c} \quad (22.15)$$

where the minus sign represents that energy is leaving the engine at temperature T_c . In Example 22.3, we showed that for a Carnot engine,

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

Using this result in Equation 22.15, we find that the total change in entropy for a Carnot engine operating in a cycle is *zero*:

$$\Delta S = 0$$

Now consider a system taken through an arbitrary (non-Carnot) reversible cycle. Because entropy is a state variable—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 as

$$\oint \frac{dQ_r}{T} = 0 \quad (\text{reversible cycle}) \quad (22.16)$$

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

Entropy Change in a Free Expansion

Let's again consider the adiabatic free expansion of a gas occupying an initial volume V_i (Fig. 22.16). In this situation, a membrane separating the gas from an evacuated region is broken and the gas expands to a volume V_f . This process is irreversible; the gas would not spontaneously crowd into half the volume after filling the entire volume. What is the change in entropy of the gas during this process? The process is neither reversible nor quasi-static. As shown in Section 20.6, the initial and final temperatures of the gas are the same.

To apply Equation 22.13, we cannot take $Q = 0$, 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 22.13 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 negative of the work done on the gas during the expansion from V_i to V_f , which is given by Equation 20.14. Using this result, we find that the entropy change for the gas is

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) \quad (22.17)$$

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

It is easy to see that the energy has spread after the expansion. Instead of being concentrated in a relatively small space, the molecules and the energy associated with them are scattered over a larger region.

Entropy Change in Thermal Conduction

Let us now consider a system consisting of a hot reservoir and a cold reservoir that are 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 . The process as described is irreversible (energy would not spontaneously flow from cold to hot), so we must find an equivalent reversible process. The overall process is a combination of two processes: energy leaving the hot reservoir and energy entering the cold reservoir. We will calculate the entropy change for the reservoir in each process and add to obtain the overall entropy change.

When the membrane is ruptured, the gas will expand freely and irreversibly into the full volume.

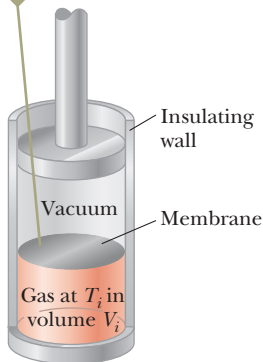


Figure 22.16 Adiabatic free expansion of a gas. The container is thermally insulated from its surroundings; therefore, $Q = 0$.

Consider first the process of energy entering the cold reservoir. Although the reservoir has absorbed some energy, the temperature of the reservoir has not changed. The energy that has entered the reservoir is the same as that which would enter by means of a reversible, isothermal process. The same is true for energy leaving the hot reservoir.

Because the cold reservoir absorbs energy Q , its entropy increases by Q/T_c . At the same time, the hot reservoir loses energy Q , so its entropy change is $-Q/T_h$. Therefore, the change in entropy of the system is

$$\Delta S = \frac{Q}{T_c} + \frac{-Q}{T_h} = Q \left(\frac{1}{T_c} - \frac{1}{T_h} \right) > 0 \quad (22.18)$$

This increase is consistent with our interpretation of entropy changes as representing the spreading of energy. In the initial configuration, the hot reservoir has excess internal energy relative to the cold reservoir. The process that occurs spreads the energy into a more equitable distribution between the two reservoirs.

Example 22.8 Adiabatic Free Expansion: Revisited

Let's 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 the ideal gas in Figure 22.16 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.

SOLUTION

Conceptualize Look back at Figure 22.16, which is a diagram of the system before the adiabatic free expansion. Imagine breaking the membrane so that the gas moves into the evacuated area. The expansion is irreversible.

Categorize We can replace the irreversible process with a reversible isothermal process between the same initial and final states. This approach is macroscopic, so we use a thermodynamic variable, in particular, the volume V .

Analyze Use Equation 22.17 to evaluate the entropy change:

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

(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

Categorize This approach is microscopic, so we use variables related to the individual molecules.

Analyze As in the discussion leading to Equation 22.11, the number of microstates available to a single molecule in the initial volume V_i is $w_i = V_i/V_m$, where V_i is the initial volume of the gas and V_m is the microscopic volume occupied by the molecule. Use this number to find the number of available microstates for N molecules:

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

Find the number of available microstates for N molecules in the final volume $V_f = 4V_i$:

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

continued

22.8 continued

Use Equation 22.14 to find the entropy change:

$$\begin{aligned}\Delta S &= k_B \ln \left(\frac{W_f}{W_i} \right) \\ &= k_B \ln \left(\frac{4V_i}{V_i} \right)^N = k_B \ln (4^N) = Nk_B \ln 4 = nR \ln 4\end{aligned}$$

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

WHAT IF? In part (A), we used Equation 22.17, which was based on a reversible isothermal process connecting the initial and final states. Would you arrive at the same result if you chose a different reversible process?

Answer You *must* arrive at the same result because entropy is a state variable. For example, consider the two-step process in Figure 22.17: a reversible adiabatic expansion from V_i to $4V_i$ ($A \rightarrow B$) during which the temperature drops from T_1 to T_2 and a reversible isovolumetric process ($B \rightarrow C$) that takes the gas back to the initial temperature T_1 . During the reversible adiabatic process, $\Delta S = 0$ because $Q_r = 0$.

For the reversible isovolumetric process ($B \rightarrow C$), use Equation 22.13:

Find the ratio of temperature T_1 to T_2 from Equation 21.39 for the adiabatic process:

Substitute to find ΔS :

We do indeed obtain the exact same result for the entropy change.

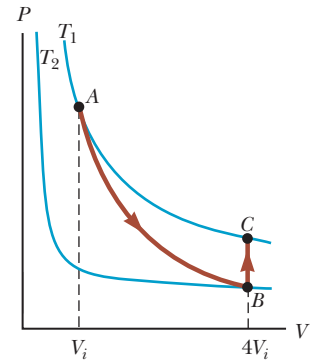


Figure 22.17 (Example 22.8) A gas expands to four times its initial volume and back to the initial temperature by means of a two-step process.

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \int_{T_2}^{T_1} \frac{nC_V dT}{T} = nC_V \ln \left(\frac{T_1}{T_2} \right)$$

$$\frac{T_1}{T_2} = \left(\frac{4V_i}{V_i} \right)^{\gamma-1} = (4)^{\gamma-1}$$

$$\Delta S = nC_V \ln (4)^{\gamma-1} = nC_V (\gamma - 1) \ln 4$$

$$= nC_V \left(\frac{C_P}{C_V} - 1 \right) \ln 4 = n(C_P - C_V) \ln 4 = nR \ln 4$$

22.8 Entropy and the Second Law

If we consider a system and its surroundings to include the entire Universe, the Universe is always moving toward a higher-probability macrostate, corresponding to the continuous spreading of energy. An alternative way of stating this behavior is as follows:

Entropy statement of the second law of thermodynamics

The entropy of the Universe increases in all real processes.

This statement is yet another wording of the second law of thermodynamics that can be shown to be equivalent to the Kelvin-Planck and Clausius statements.

Let us show this equivalence first for the Clausius statement. Looking at Figure 22.5, we see that, if the heat pump operates in this manner, energy is spontaneously flowing from the cold reservoir to the hot reservoir without an input of energy by work. As a result, the energy in the system is not spreading evenly between the two reservoirs, but is *concentrating* in the hot reservoir. Consequently, if the Clausius statement of the second law is not true, then the entropy statement is also not true, demonstrating their equivalence.

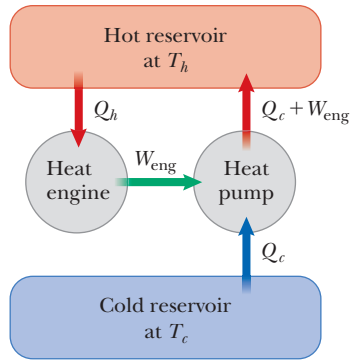


Figure 22.18 The impossible engine of Figure 22.3 transfers energy by work to a heat pump operating between two energy reservoirs. This situation is forbidden by the Clausius statement of the second law of thermodynamics.

For the equivalence of the Kelvin–Planck statement, consider Figure 22.18, which shows the impossible engine of Figure 22.3 connected to a heat pump operating between the same reservoirs. The output work of the engine is used to drive the heat pump. The net effect of this combination is that energy leaves the cold reservoir and is delivered to the hot reservoir without the input of work. (The work done by the engine on the heat pump is *internal* to the system of both devices.) This is forbidden by the Clausius statement of the second law, which we have shown to be equivalent to the entropy statement. Therefore, the Kelvin–Planck statement of the second law is also equivalent to the entropy statement.

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, the change in entropy of the Universe must be greater than zero for an irreversible process and equal to zero for a reversible process.

We can check this statement of the second law for the calculations of entropy change that we made in Section 22.7. Consider first the entropy change in a free expansion, described by Equation 22.17. Because the free expansion takes place in an insulated container, no energy is transferred by heat from the surroundings. Therefore, Equation 22.17 represents the entropy change of the entire Universe. Because $V_f > V_i$, the entropy change of the Universe is positive, consistent with the second law.

Now consider the entropy change in thermal conduction, described by Equation 22.18. Let each reservoir be half the Universe. (The larger the reservoir, the better is the assumption that its temperature remains constant!) Then the entropy change of the Universe is represented by Equation 22.18. Because $T_h > T_c$, this entropy change is positive, again consistent with the second law. The positive entropy change is also consistent with the notion of energy spreading. The warm portion of the Universe has excess internal energy relative to the cool portion. Thermal conduction represents a spreading of the energy more equitably throughout the Universe.

Finally, let us look at the entropy change in a Carnot cycle, given by Equation 22.15. The entropy change of the engine itself is zero. The entropy change of the reservoirs is

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

In light of Equation 22.7, this entropy change is also zero. Therefore, the entropy change of the Universe is only that associated with the work done by the engine. A portion of that work will be used to change the mechanical energy of a system external to the engine: speed up the shaft of a machine, raise a weight, and so on. There is no change in internal energy of the external system due to this portion

of the work, or, equivalently, no energy spreading, so the entropy change is again zero. The other portion of the work will be used to overcome various friction forces or other nonconservative forces in the external system. This process will cause an increase in internal energy of that system. That same increase in internal energy could have happened via a reversible thermodynamic process in which energy Q_r is transferred by heat, so the entropy change associated with that part of the work is positive. As a result, the overall entropy change of the Universe for the operation of the Carnot engine is positive, again consistent with the second law.

Ultimately, because real processes are irreversible, the entropy of the Universe should increase steadily and eventually reach a maximum value. At this value, assuming that the second law of thermodynamics, as formulated here on Earth, applies to the entire expanding Universe, the Universe will be in a state of uniform temperature and density. The total energy of the Universe will have spread more evenly throughout the Universe. All physical, chemical, and biological processes will have ceased at this time. This gloomy state of affairs is sometimes referred to as the *heat death* of the Universe.

Summary

Definitions

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

$$e \equiv \frac{W_{\text{eng}}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|} \quad (22.2)$$

The **microstate** of a system is the description of its individual components. The **macrostate** is a description of the system from a macroscopic point of view. A given macrostate can have many microstates.

From a microscopic viewpoint, the **entropy** of a given macrostate is defined as

$$S \equiv k_B \ln W \quad (22.10)$$

where k_B is Boltzmann's constant and W is the number of microstates of the system corresponding to the macrostate.

In a **reversible** process, the system can be returned to its initial conditions along the same path on a PV diagram, and every point along this path is an equilibrium state. A process that does not satisfy these requirements is **irreversible**.

Concepts and Principles

A **heat engine** is a device that takes in energy by heat and, operating in a cyclic process, expels a fraction of that energy by means of work. The net work done by a heat engine in carrying a working substance through a cyclic process ($\Delta E_{\text{int}} = 0$) is

$$W_{\text{eng}} = |Q_h| - |Q_c| \quad (22.1)$$

where $|Q_h|$ is the energy taken in from a hot reservoir and $|Q_c|$ is the energy expelled to a cold reservoir.

Two ways the **second law of thermodynamics** can be stated are as follows:

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

■ **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

$$e_c = 1 - \frac{T_c}{T_h} \quad (22.8)$$

■ The macroscopic state of a system that has a large number of microstates has four qualities that are all related: (1) *uncertainty*: because of the large number of microstates, there is a large uncertainty as to which one actually exists; (2) *choice*: again because of the large number of microstates, there is a large number of choices from which to select as to which one exists; (3) *probability*: a macrostate with a large number of microstates is more likely to exist than one with a small number of microstates; (4) *missing information*: because of the large number of microstates, there is a high amount of missing information as to which one exists. For a thermodynamic system, all four of these can be related to the state variable of **entropy**.

■ The second law of thermodynamics states that when real (irreversible) processes occur, there is a spatial spreading of energy. This spreading of energy is related to a thermodynamic state variable called **entropy** S . Therefore, yet another way the second law can be stated is as follows:

- 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

$$dS = \frac{dQ_r}{T} \quad (22.12)$$

where dQ_r is the energy transfer by heat for the system for a reversible process that connects the initial and final states.

■ The change in entropy of a system during an arbitrary finite process between an initial state and a final state is

$$\Delta S = \int_i^f \frac{dQ_r}{T} \quad (22.13)$$

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.

Objective Questions

1. denotes answer available in *Student Solutions Manual/Study Guide*

- The second law of thermodynamics implies that the coefficient of performance of a refrigerator must be what? (a) less than 1 (b) less than or equal to 1 (c) greater than or equal to 1 (d) finite (e) greater than 0
- Assume a sample of an ideal gas is at room temperature. What action will *necessarily* make the entropy of the sample increase? (a) Transfer energy into it by heat. (b) Transfer energy into it irreversibly by heat. (c) Do work on it. (d) Increase either its temperature or its volume, without letting the other variable decrease. (e) None of those choices is correct.
- A refrigerator has 18.0 kJ of work done on it while 115 kJ of energy is transferred from inside its interior. What is its coefficient of performance? (a) 3.40 (b) 2.80 (c) 8.90 (d) 6.40 (e) 5.20
- Of the following, which is *not* a statement of the second law of thermodynamics? (a) No heat engine operating in a cycle can absorb energy from a reservoir and use it entirely to do work. (b) No real engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs. (c) When a system undergoes a change in state, the change in the internal energy of the system is the sum of the energy transferred to the system by heat and the work done on the system. (d) The entropy of the Universe increases in all natural processes. (e) Energy will not spontaneously transfer by heat from a cold object to a hot object.
5. Consider cyclic processes completely characterized by each of the following net energy inputs and outputs. In each case, the energy transfers listed are the *only* ones occurring. Classify each process as (a) possible, (b) impossible according to the first law of thermodynamics, (c) impossible according to the second law of thermodynamics, or (d) impossible according to both the first and second laws. (i) Input is 5 J of work, and output is 4 J of work. (ii) Input is 5 J of work, and output is 5 J of energy transferred by heat. (iii) Input is 5 J of energy transferred by electrical transmission, and output is 6 J of work. (iv) Input is 5 J of energy transferred by heat, and output is 5 J of energy transferred

by heat. (v) Input is 5 J of energy transferred by heat, and output is 5 J of work. (vi) Input is 5 J of energy transferred by heat, and output is 3 J of work plus 2 J of energy transferred by heat.

- A compact air-conditioning unit is placed on a table inside a well-insulated apartment and is plugged in and turned on. What happens to the average temperature of the apartment? (a) It increases. (b) It decreases. (c) It remains constant. (d) It increases until the unit warms up and then decreases. (e) The answer depends on the initial temperature of the apartment.
- A steam turbine operates at a boiler temperature of 450 K and an exhaust temperature of 300 K. What is the maximum theoretical efficiency of this system? (a) 0.240 (b) 0.500 (c) 0.333 (d) 0.667 (e) 0.150
- A thermodynamic process occurs in which the entropy of a system changes by -8 J/K . According to the second law of thermodynamics, what can you conclude about the entropy change of the environment? (a) It must be $+8 \text{ J/K}$ or less. (b) It must be between $+8 \text{ J/K}$ and 0. (c) It must be equal to $+8 \text{ J/K}$. (d) It must be $+8 \text{ J/K}$ or more. (e) It must be zero.
- A sample of a monatomic ideal gas is contained in a cylinder with a piston. Its state is represented by the dot in the PV diagram shown in Figure OQ22.9. Arrows A through E represent isobaric, isothermal, adiabatic, and isovolumetric processes that the sample can undergo. In each process except D , the volume changes by a factor of 2. All five processes are reversible. Rank the processes according to the change in entropy of the gas from the largest positive value to the

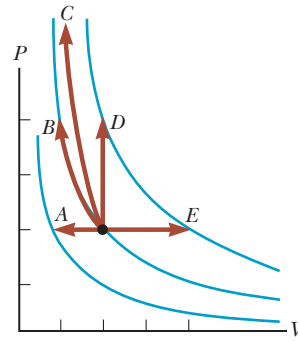


Figure OQ22.9

largest-magnitude negative value. In your rankings, display any cases of equality.

- An engine does 15.0 kJ of work while exhausting 37.0 kJ to a cold reservoir. What is the efficiency of the engine? (a) 0.150 (b) 0.288 (c) 0.333 (d) 0.450 (e) 1.20
- The arrow OA in the PV diagram shown in Figure OQ22.11 represents a reversible adiabatic expansion of an ideal gas. The same sample of gas, starting from the same state O , now undergoes an adiabatic free expansion to the same final volume. What point on the diagram could represent the final state of the gas? (a) the same point A as for the reversible expansion (b) point B (c) point C (d) any of those choices (e) none of those choices

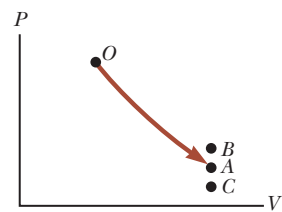


Figure OQ22.11

Conceptual Questions

1. denotes answer available in *Student Solutions Manual/Study Guide*

- The energy exhaust from a certain coal-fired electric generating station is carried by “cooling water” into Lake Ontario. The water is warm from the viewpoint of living things in the lake. Some of them congregate around the outlet port and can impede the water flow. (a) Use the theory of heat engines to explain why this action can reduce the electric power output of the station. (b) An engineer says that the electric output is reduced because of “higher back pressure on the turbine blades.” Comment on the accuracy of this statement.
- Discuss three different common examples of natural processes that involve an increase in entropy. Be sure to account for all parts of each system under consideration.
- Does the second law of thermodynamics contradict or correct the first law? Argue for your answer.
- “The first law of thermodynamics says you can’t really win, and the second law says you can’t even break even.” Explain how this statement applies to a particular device or process; alternatively, argue against the statement.
- “Energy is the mistress of the Universe, and entropy is her shadow.” Writing for an audience of general readers, argue for this statement with at least two examples. Alternatively, argue for the view that entropy is like an executive who instantly determines what will happen, whereas energy is like a bookkeeper telling us how little we can afford. (Arnold Sommerfeld suggested the idea for this question.)
- (a) Give an example of an irreversible process that occurs in nature. (b) Give an example of a process in nature that is nearly reversible.
- The device shown in Figure CQ22.7, called a thermoelectric converter, uses a series of semiconductor cells to transform internal energy to electric potential energy, which we will study in Chapter 25. In the photograph on the left, both legs of the device are at the same temperature and no electric potential energy is produced. When one leg is at a higher temperature than the other as shown in the photograph on the right, however, electric potential energy is produced as

the device extracts energy from the hot reservoir and drives a small electric motor. (a) Why is the difference in temperature necessary to produce electric potential energy in this demonstration? (b) In what sense does this intriguing experiment demonstrate the second law of thermodynamics?

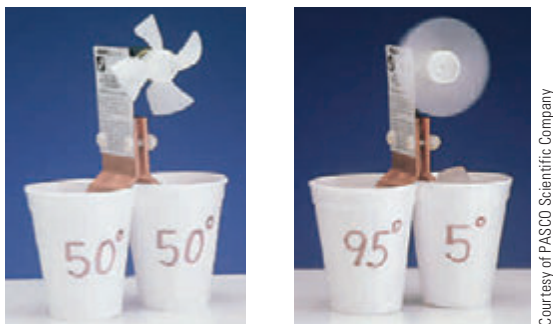


Figure CQ22.7

8. 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?
9. Discuss the change in entropy of a gas that expands (a) at constant temperature and (b) adiabatically.
10. Suppose your roommate cleans and tidies up your messy room after a big party. Because she is creating more order, does this process represent a violation of the second law of thermodynamics?
11. Is it possible to construct a heat engine that creates no thermal pollution? Explain.
12. (a) If you shake a jar full of jelly beans of different sizes, the larger beans tend to appear near the top and the smaller ones tend to fall to the bottom. Why? (b) Does this process violate the second law of thermodynamics?
13. What are some factors that affect the efficiency of automobile engines?

Problems

ENHANCED
WebAssign The problems found in this chapter may be assigned online in Enhanced WebAssign

1. straightforward; 2. intermediate; 3. challenging

1. full solution available in the *Student Solutions Manual/Study Guide*

AMT Analysis Model tutorial available in Enhanced WebAssign

GP Guided Problem

M Master It tutorial available in Enhanced WebAssign

W Watch It video solution available in Enhanced WebAssign

Section 22.1 Heat Engines and the Second Law of Thermodynamics

1. A particular heat engine has a mechanical power output of 5.00 kW and an efficiency of 25.0%. The engine expels 8.00×10^3 J of exhaust energy in each cycle. Find (a) the energy taken in during each cycle and (b) the time interval for each cycle.
2. The work done by an engine equals one-fourth the energy it absorbs from a reservoir. (a) What is its thermal efficiency? (b) What fraction of the energy absorbed is expelled to the cold reservoir?
3. A heat engine takes in 360 J of energy from a hot reservoir 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.
4. A gun is a heat engine. In particular, it is an internal combustion piston engine that does not operate in a cycle, but comes apart during its adiabatic expansion process. A certain gun consists of 1.80 kg of iron. It fires one 2.40-g bullet at 320 m/s with an energy efficiency of 1.10%. Assume the body of the gun absorbs all the energy exhaust—the other 98.9%—and increases uniformly in temperature for a short time interval before

it loses any energy by heat into the environment. Find its temperature increase.

5. An engine absorbs 1.70 kJ from a hot reservoir at 277°C and expels 1.20 kJ to a cold reservoir at 27°C in each cycle. (a) What is the engine's efficiency? (b) How much work is done by the engine in each cycle? (c) What is the power output of the engine if each cycle lasts 0.300 s?
6. A multicylinder gasoline engine in an airplane, operating at 2.50×10^3 rev/min, takes in energy 7.89×10^3 J and exhausts 4.58×10^3 J for each revolution of the crankshaft. (a) How many liters of fuel does it consume in 1.00 h of operation if the heat of combustion of the fuel is equal to 4.03×10^7 J/L? (b) What is the mechanical power output of the engine? Ignore friction and express the answer in horsepower. (c) What is the torque exerted by the crankshaft on the load? (d) What power must the exhaust and cooling system transfer out of the engine?
7. Suppose 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 22.2 Heat Pumps and Refrigerators

- W** 8. A refrigerator has a coefficient of performance equal to 5.00. The refrigerator takes in 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.
9. During each cycle, a refrigerator ejects 625 kJ of energy to a high-temperature reservoir and takes in 550 kJ of energy from a low-temperature reservoir. Determine (a) the work done on the refrigerant in each cycle and (b) the coefficient of performance of the refrigerator.
10. A heat pump has a coefficient of performance of 3.80 and operates with a power consumption of 7.03×10^3 W. (a) How much energy does it deliver into a home during 8.00 h of continuous operation? (b) How much energy does it extract from the outside air?
11. A refrigerator has a coefficient of performance 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.
12. A heat pump has a coefficient of performance equal to 4.20 and requires a power of 1.75 kW to operate. (a) How much energy does the heat pump add to a home in one hour? (b) If the heat pump is reversed so that it acts as an air conditioner in the summer, what would be its coefficient of performance?
13. A freezer has a coefficient of performance of 6.30. It is advertised as using electricity at a rate of 457 kWh/yr. (a) On average, how much energy does it use in a single day? (b) On average, how much energy does it remove from the refrigerator in a single day? (c) What maximum mass of water at 20.0°C could the freezer freeze in a single day? *Note:* One kilowatt-hour (kWh) is an amount of energy equal to running a 1-kW appliance for one hour.

Section 22.3 Reversible and Irreversible Processes

Section 22.4 The Carnot Engine

14. A heat engine operates between a reservoir at 25.0°C and one at 375°C . What is the maximum efficiency possible for this engine?
- M** 15. One of the most efficient heat engines ever built is a coal-fired steam turbine in the Ohio River valley, operating between 1870°C and 430°C . (a) What is its maximum theoretical efficiency? (b) The actual efficiency of the engine is 42.0%. How much mechanical power does the engine deliver if it absorbs 1.40×10^5 J of energy each second from its hot reservoir?
16. *Why is the following situation impossible?* An inventor comes to a patent office with the claim that her heat engine, which employs water as a working substance,

has a thermodynamic efficiency of 0.110. Although this efficiency is low compared with typical automobile engines, she explains that her engine operates between an energy reservoir at room temperature and a water-ice mixture at atmospheric pressure and therefore requires no fuel other than that to make the ice. The patent is approved, and working prototypes of the engine prove the inventor's efficiency claim.

- W** 17. 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 enters the engine by heat per hour? (b) How much energy is exhausted by heat per hour?
18. A Carnot engine has a power output P . The engine operates between two reservoirs at temperature T_c and T_h . (a) How much energy enters the engine by heat in a time interval Δt ? (b) How much energy is exhausted by heat in the time interval Δt ?
19. What is the coefficient of performance of a refrigerator that operates with Carnot efficiency between temperatures -3.00°C and $+27.0^\circ\text{C}$?
- M** 20. An ideal refrigerator or ideal heat pump is equivalent to a Carnot engine running in reverse. That is, energy $|Q_c|$ is taken in 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

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

21. 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? *Note:* The work done to run the heat pump is also available to warm the house.
- M** 22. How much work does an ideal Carnot refrigerator require to remove 1.00 J of energy from liquid helium at 4.00 K and expel this energy to a room-temperature (293-K) environment?
23. If a 35.0%-efficient Carnot heat engine (Fig. 22.2) is run in reverse so as to form a refrigerator (Fig. 22.4), what would be this refrigerator's coefficient of performance?
24. A power plant operates at a 32.0% efficiency during the summer when the seawater used for cooling is at 20.0°C . The plant uses 350°C steam to drive turbines. If 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 seawater is at 10.0°C ?
25. A heat engine is being designed to have a Carnot efficiency of 65.0% when operating between two energy reservoirs. (a) If the temperature of the cold reservoir is 20.0°C , what must be the temperature of the hot res-

ervoir? (b) Can the actual efficiency of the engine be equal to 65.0%? Explain.

26. A Carnot heat engine operates between temperatures T_h and T_c . (a) If $T_h = 500$ K and $T_c = 350$ K, what is the efficiency of the engine? (b) What is the change in its efficiency for each degree of increase in T_h above 500 K? (c) What is the change in its efficiency for each degree of change in T_c ? (d) Does the answer to part (c) depend on T_c ? Explain.

27. 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 . The gas takes in 1.20×10^3 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.

28. An electric power plant that would make use of the temperature gradient in the ocean has been proposed. The system is to operate between 20.0°C (surface-water temperature) and 5.00°C (water temperature at a depth of about 1 km). (a) What is the maximum efficiency of such a system? (b) If the electric power output of the plant is 75.0 MW, how much energy is taken in from the warm reservoir per hour? (c) In view of your answer to part (a), explain whether you think such a system is worthwhile. Note that the “fuel” is free.

29. A heat engine operates in a Carnot cycle between 80.0°C and 350°C . It absorbs 21 000 J of energy per cycle from the hot reservoir. The duration of each cycle is 1.00 s. (a) What is the mechanical power output of this engine? (b) How much energy does it expel in each cycle by heat?

30. Suppose you build a two-engine device with the exhaust energy output from one heat engine supplying the input energy for a second heat engine. We say that the two engines are running *in series*. Let e_1 and e_2 represent the efficiencies of the two engines. (a) The overall efficiency of the two-engine device is defined as the total work output divided by the energy put into the first engine by heat. Show that the overall efficiency e is given by

$$e = e_1 + e_2 - e_1e_2$$

What If? For parts (b) through (e) that follow, assume the two engines are Carnot engines. Engine 1 operates between temperatures T_h and T_i . The gas in engine 2 varies in temperature between T_i and T_c . In terms of the temperatures, (b) what is the efficiency of the combination engine? (c) Does an improvement in net efficiency result from the use of two engines instead of one? (d) What value of the intermediate temperature T_i results in equal work being done by each of the two engines in series? (e) What value of T_i results in each of the two engines in series having the same efficiency?

31. 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 pressure 300 kPa. (a) Calculate its tem-

perature at 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.

32. 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. The gas 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 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 by the engine, and the change in internal energy for each of the steps $A \rightarrow B$, $B \rightarrow C$, $C \rightarrow D$, and $D \rightarrow A$. (c) Calculate the efficiency $W_{\text{net}}/|Q_h|$. (d) Show that the efficiency is equal to $1 - T_c/T_A$, the Carnot efficiency.

33. An electric generating station is designed to have an electric output power of 1.40 MW using a turbine with two-thirds the efficiency of a Carnot engine. The exhaust energy is transferred by heat into a cooling tower at 110°C . (a) Find the rate at which the station exhausts energy by heat as a function of the fuel combustion temperature T_h . (b) If the firebox is modified to run hotter by using more advanced combustion technology, how does the amount of energy exhaust change? (c) Find the exhaust power for $T_h = 800^\circ\text{C}$. (d) Find the value of T_h for which the exhaust power would be only half as large as in part (c). (e) Find the value of T_h for which the exhaust power would be one-fourth as large as in part (c).
34. An ideal (Carnot) freezer in a kitchen has a constant temperature of 260 K, whereas the air in the kitchen has a constant temperature of 300 K. Suppose the insulation for the freezer is not perfect but rather conducts energy into the freezer at a rate of 0.150 W. Determine the average power required for the freezer’s motor to maintain the constant temperature in the freezer.
35. A heat pump used for heating shown in Figure P22.35 is essentially an air conditioner installed backward. It

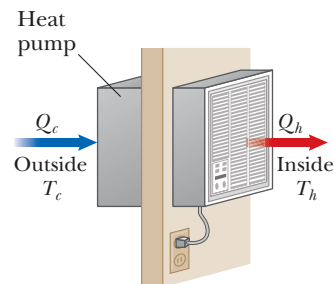


Figure P22.35

extracts energy from colder air outside and deposits it in a warmer room. Suppose 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 given that the inside temperature is 20.0°C and the outside temperature is -5.00°C .

Section 22.5 Gasoline and Diesel Engines

Note: For problems in this section, assume the gas in the engine is diatomic with $\gamma = 1.40$.

36. A gasoline engine has a compression ratio of 6.00. (a) What is the efficiency of the engine if it operates in an idealized Otto cycle? (b) **What If?** If the actual efficiency is 15.0%, what fraction of the fuel is wasted as a result of friction and energy transfers by heat that could be avoided in a reversible engine? Assume complete combustion of the air–fuel mixture.
37. In a cylinder of an automobile engine, immediately after combustion the gas is confined to a volume of 50.0 cm^3 and has an initial pressure of $3.00 \times 10^6\text{ Pa}$. The piston moves outward to a final volume of 300 cm^3 , and the gas expands without energy transfer by heat. (a) What is the final pressure of the gas? (b) How much work is done by the gas in expanding?
38. An idealized diesel engine operates in a cycle known as the *air-standard diesel cycle* shown in Figure P22.38. Fuel is sprayed into the cylinder at the point of maximum compression, B . Combustion occurs during the expansion $B \rightarrow C$, which is modeled as an isobaric process. Show that the efficiency of an engine operating in this idealized diesel cycle is

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

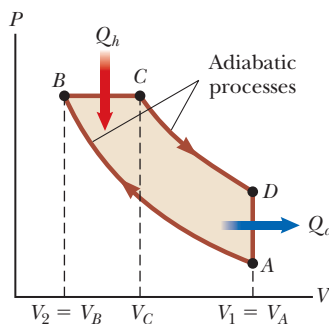


Figure P22.38

Section 22.6 Entropy

39. Prepare a table like Table 22.1 by using the same procedure (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 marbles rather than four.
40. (a) Prepare a table like Table 22.1 for the following occurrence. You toss four coins into the air simulta-

neously and then record the results of your tosses in terms of the numbers of heads (H) and tails (T) that result. For example, HHTH and HTHH are two possible ways in which three heads and one tail can be achieved. (b) On the basis of your table, what is the most probable result recorded for a toss?

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

Section 22.7 Changes in Entropy for Thermodynamic Systems

Section 22.8 Entropy and the Second Law

42. An ice tray contains 500 g of liquid water at 0°C . Calculate the change in entropy of the water as it freezes slowly and completely at 0°C .
43. A Styrofoam cup holding 125 g of hot water at 100°C cools to room temperature, 20.0°C . What is the change in entropy of the room? Neglect the specific heat of the cup and any change in temperature of the room.
44. A 1.00-kg iron horseshoe is taken from a forge 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 horseshoe-plus-water system. (*Suggestion:* Note that $dQ = mc\,dT$.)
45. A 1 500-kg car is moving at 20.0 m/s. The driver brakes **AMT** 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?
46. Two 2.00×10^3 -kg cars both traveling at 20.0 m/s **AMT** undergo a head-on collision and stick together. Find the change in entropy of the surrounding air resulting from the collision if the air temperature is 23.0°C . Ignore the energy carried away from the collision by sound.
47. A 70.0-kg log falls from a height of 25.0 m into a lake. If **AMT** the log, the lake, and the air are all at 300 K, find the change in entropy of the air during this process.
48. A 1.00-mol sample of H_2 gas is contained in the left side of the container shown in Figure P22.48, which has equal volumes on the left and right. The right side is evacuated. When the valve is opened, the gas streams into the right side. (a) What is the entropy change of the gas? (b) Does the temperature of the gas change? Assume the container is so large that the hydrogen behaves as an ideal gas.

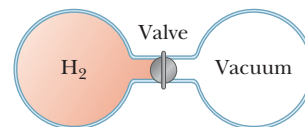


Figure P22.48

49. A 2.00-L container has a center partition that divides it into two equal parts as shown in Figure P22.49. The left side contains 0.044 0 mol of H_2 gas, and the right side contains 0.044 0 mol of 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?

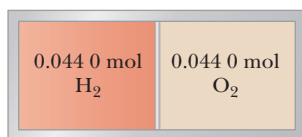


Figure P22.49

50. What change in entropy occurs when a 27.9-g ice cube at -12°C is transformed into steam at 115°C ?
51. Calculate the change in entropy of 250 g of water warmed slowly from 20.0°C to 80.0°C .
52. How fast are you personally making the entropy of the Universe increase right now? Compute an order-of-magnitude estimate, stating what quantities you take as data and the values you measure or estimate for them.
53. When an aluminum bar is connected between a hot reservoir at 725 K and a cold reservoir at 310 K, 2.50 kJ of energy is transferred by heat from the hot reservoir to the cold reservoir. In this irreversible process, calculate the change in entropy of (a) the hot reservoir, (b) the cold reservoir, and (c) the Universe, neglecting any change in entropy of the aluminum rod.
54. When a metal bar is connected between a hot reservoir at T_h and a cold reservoir at T_c , the energy transferred by heat from the hot reservoir to the cold reservoir is Q . In this irreversible process, find expressions for the change in entropy of (a) the hot reservoir, (b) the cold reservoir, and (c) the Universe, neglecting any change in entropy of the metal rod.
55. The temperature at the surface of the Sun is approximately 5 800 K, and the temperature at the surface of the Earth is approximately 290 K. What entropy change of the Universe occurs when 1.00×10^3 J of energy is transferred by radiation from the Sun to the Earth?
- Additional Problems**
56. 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 \cdot $^{\circ}\text{C}$.
57. How much work is required, using an ideal Carnot refrigerator, 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 .
58. 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, instead, superheated steam at 200°C is used, find the maximum possible efficiency.
59. 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?
60. Every second at Niagara Falls, some 5.00×10^3 m³ of water falls a distance of 50.0 m. What is the increase in entropy of the Universe per second due to the falling water? Assume the mass of the surroundings is so great that its temperature and that of the water stay nearly constant at 20.0°C . Also assume a negligible amount of water evaporates.
61. Find the maximum (Carnot) efficiency of an engine that absorbs energy from a hot reservoir at 545°C and exhausts energy to a cold reservoir at 185°C .
62. In 1993, the U.S. 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 British thermal units per hour, or 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. State how the operating costs compare for 10 000-Btu/h air conditioners with EERs of 5.00 and 10.0. Assume each air conditioner operates for 1 500 h during the summer in a city where electricity costs 17.0¢ per kWh.
63. Energy transfers by heat through the exterior walls and roof of a house at a rate of 5.00×10^3 J/s = 5.00 kW when the interior temperature is 22.0°C and the outside temperature is -5.00°C . (a) Calculate the electric power required to maintain the interior temperature at 22.0°C if the power is used in electric resistance heaters that convert all the energy transferred in by electrical transmission into internal energy. (b) **What If?** Calculate the electric power required to maintain the interior temperature at 22.0°C if the power is used to drive an electric motor that operates the compressor of a heat pump that has a coefficient of performance equal to 60.0% of the Carnot-cycle value.
64. One mole of neon gas is heated from 300 K to 420 K at constant pressure. Calculate (a) the energy Q transferred to the gas, (b) the change in the internal energy of the gas, and (c) the work done *on* the gas. Note that neon has a molar specific heat of $C_p = 20.79$ J/mol \cdot K for a constant-pressure process.
65. An airtight freezer holds n moles 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 entropy change be if the pressure were maintained at 1.00 atm during the cooling?
66. Suppose an ideal (Carnot) heat pump could be constructed for use as an air conditioner. (a) Obtain an

expression for the coefficient of performance (COP) for such an air conditioner in terms of T_h and T_c . (b) Would such an air conditioner operate on a smaller energy input if the difference in the operating temperatures were greater or smaller? (c) Compute the COP for such an air conditioner if the indoor temperature is 20.0°C and the outdoor temperature is 40.0°C .

- 67.** In 1816, Robert Stirling, a Scottish clergyman, patented the *Stirling engine*, which has found a wide variety of applications ever since, including current use in solar energy collectors to transform sunlight into electricity. Fuel is burned externally to warm one of the engine's two cylinders. A fixed quantity of inert gas moves cyclically between the cylinders, expanding in the hot one and contracting in the cold one. Figure P22.67 represents a model for its thermodynamic cycle. Consider n moles of an ideal monatomic gas being taken once through the cycle, consisting of two isothermal processes at temperatures $3T_i$ and T_i and two constant-volume processes. Let us find the efficiency of this engine. (a) Find the energy transferred by heat into the gas during the isovolumetric process AB . (b) Find the energy transferred by heat into the gas during the isothermal process BC . (c) Find the energy transferred by heat into the gas during the isovolumetric process CD . (d) Find the energy transferred by heat into the gas during the isothermal process DA . (e) Identify which of the results from parts (a) through (d) are positive and evaluate the energy input to the engine by heat. (f) From the first law of thermodynamics, find the work done by the engine. (g) From the results of parts (e) and (f), evaluate the efficiency of the engine. A Stirling engine is easier to manufacture than an internal combustion engine or a turbine. It can run on burning garbage. It can run on the energy transferred by sunlight and produce no material exhaust. Stirling engines are not currently used in automobiles due to long startup times and poor acceleration response.

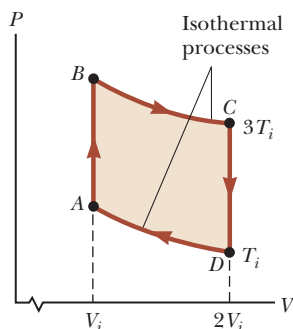


Figure P22.67

- 68.** 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 take in energy $150\text{ J}/0.600 = 250\text{ J}$ from the hot reservoir and must put out 100 J of energy by heat into the

environment. To follow Carnot's reasoning, suppose some other heat engine S could have an efficiency of 70.0% . (a) Find the energy input and exhaust 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 between the same reservoirs. The output work of engine S is the input work for the Carnot refrigerator. Find the total energy transferred to or from the firebox and the total energy transferred to or from the environment as both engines operate together. (c) Explain how the results of parts (a) and (b) show that the Clausius statement of the second law of thermodynamics is violated. (d) Find the energy input and work output of engine S as it puts out exhaust energy of 100 J . Let engine S operate as in part (c) and contribute 150 J of its work output to running the Carnot engine in reverse. Find (e) the total energy the firebox puts out as both engines operate together, (f) the total work output, and (g) the total energy transferred to the environment. (h) Explain how the results show that the Kelvin-Planck statement of the second law is violated. Therefore, our assumption about the efficiency of engine S must be false. (i) Let the engines operate together through one cycle as in part (d). Find the change in entropy of the Universe. (j) Explain how the result of part (i) shows that the entropy statement of the second law is violated.

- 69. Review.** This problem complements Problem 88 in Chapter 10. In the operation of a single-cylinder internal combustion piston engine, one charge of fuel explodes to drive the piston outward in the *power stroke*. Part of its energy output is stored in a turning flywheel. This energy is then used to push the piston inward to compress the next charge of fuel and air. In this compression process, assume an original volume of 0.120 L of a diatomic ideal gas at atmospheric pressure is compressed adiabatically to one-eighth of its original volume. (a) Find the work input required to compress the gas. (b) Assume the flywheel is a solid disk of mass 5.10 kg and radius 8.50 cm , turning freely without friction between the power stroke and the compression stroke. How fast must the flywheel turn immediately after the power stroke? This situation represents the minimum angular speed at which the engine can operate without stalling. (c) When the engine's operation is well above the point of stalling, assume the flywheel puts 5.00% of its maximum energy into compressing the next charge of fuel and air. Find its maximum angular speed in this case.
- 70.** A biology laboratory is maintained at a constant temperature of 7.00°C by an air conditioner, which is vented to the air outside. On a typical hot summer day, the outside temperature is 27.0°C and the air-conditioning unit emits energy to the outside at a rate of 10.0 kW . Model the unit as having a coefficient of performance (COP) equal to 40.0% of the COP of an ideal Carnot device. (a) At what rate does the air conditioner remove energy from the laboratory? (b) Calculate the power required for the work input. (c) Find the change

in entropy of the Universe produced by the air conditioner in 1.00 h. (d) **What If?** The outside temperature increases to 32.0°C . Find the fractional change in the COP of the air conditioner.

71. A power plant, having a Carnot efficiency, produces 1.00 GW of electrical power from turbines that take in steam at 500 K and reject water at 300 K into a flowing river. The water downstream is 6.00 K warmer due to the output of the power plant. Determine the flow rate of the river.
72. A power plant, having a Carnot efficiency, produces electric power 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. The water downstream is warmer by ΔT due to the output of the power plant. Determine the flow rate of the river.
73. A 1.00-mol sample of an ideal monatomic gas is taken through the cycle shown in Figure P22.73. 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 by heat, (c) the energy exhausted from the gas by heat, and (d) the efficiency of the cycle. (e) Explain how the efficiency compares with that of a Carnot engine operating between the same temperature extremes.

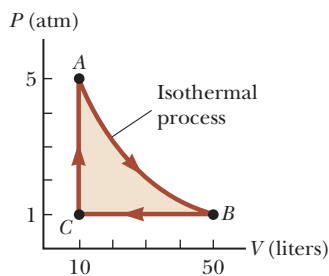


Figure P22.73

74. A system consisting of n moles of an ideal gas with molar specific heat at constant pressure C_p undergoes two reversible processes. It starts with pressure P_i and volume V_i , expands isothermally, and then contracts adiabatically to reach a final state with pressure P_i and volume $3V_i$. (a) Find its change in entropy in the isothermal process. (The entropy does not change in the adiabatic process.) (b) **What If?** Explain why the answer to part (a) must be the same as the answer to Problem 77. (You do not need to solve Problem 77 to answer this question.)
75. A heat engine operates between two reservoirs at $T_2 = 600\text{ K}$ and $T_1 = 350\text{ K}$. It takes in $1.00 \times 10^3\text{ J}$ 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 amounts of work done in parts (a) and (b) is $T_1 \Delta S_U$.

76. A 1.00-mol sample of a monatomic ideal gas is taken through the cycle shown in Figure P22.76. 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, and (c) the efficiency of an engine operating in this cycle. (d) Explain how the efficiency compares with that of an engine operating in a Carnot cycle between the same temperature extremes.

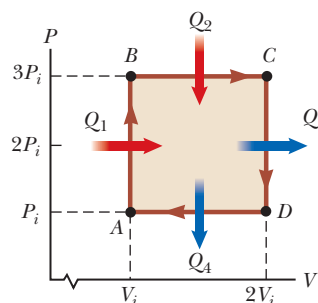


Figure P22.76

77. A sample consisting of n moles of an ideal gas undergoes a reversible isobaric expansion from volume V_i to volume $3V_i$. Find the change in entropy of the gas by calculating $\int_i^f dQ/T$, where $dQ = nC_p dT$.
78. An athlete whose mass is 70.0 kg drinks 16.0 ounces (454 g) of refrigerated water. The water is at a temperature of 35.0°F . (a) Ignoring the temperature change of the body that results from the water intake (so that the body is regarded as a reservoir always at 98.6°F), find the entropy increase of the entire system. (b) **What If?** Assume the entire body is cooled by the drink and the average specific heat of a person is equal to the specific heat of liquid water. Ignoring 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 . (c) Under these assumptions, what is the entropy increase of the entire system? (d) State how this result compares with the one you obtained in part (a).
79. A sample of an ideal gas expands isothermally, doubling in volume. (a) Show that the work done on the gas in expanding is $W = -nRT \ln 2$. (b) Because the internal energy E_{int} of an ideal gas depends solely on its temperature, the change in internal energy is zero during the expansion. It follows from the first law that the energy input to the gas by heat during the expansion is equal to the energy output by work. Does this process have 100% efficiency in converting energy input by heat into work output? (c) Does this conversion violate the second law? Explain.
80. *Why is the following situation impossible?* Two samples of water are mixed at constant pressure inside an insulated container: 1.00 kg of water at 10.0°C and 1.00 kg of water at 30.0°C . Because the container is insulated, there is no exchange of energy by heat between the water and the

environment. Furthermore, the amount of energy that leaves the warm water by heat is equal to the amount that enters the cool water by heat. Therefore, the entropy change of the Universe is zero for this process.

Challenge Problems

81. A 1.00-mol sample of an ideal gas ($\gamma = 1.40$) is carried through the Carnot cycle described in Figure 22.11. 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.

82. The compression ratio of an Otto cycle as shown in Figure 22.13 is $V_A/V_B = 8.00$. At the beginning A of the compression process, 500 cm³ of gas is at 100 kPa and 20.0°C. At the beginning of the adiabatic expansion, the temperature is $T_C = 750^\circ\text{C}$. Model the working fluid as an ideal gas with $\gamma = 1.40$. (a) Fill in this table to follow the states of the gas:

	T (K)	P (kPa)	V (cm ³)
A	293	100	500
B			
C	1 023		
D			

(b) Fill in this table to follow the processes:

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

(c) Identify the energy input $|Q_h|$, (d) the energy exhaust $|Q_c|$, and (e) the net output work W_{eng} . (f) Calculate the thermal efficiency. (g) Find the number of crankshaft revolutions per minute required for a one-cylinder engine to have an output power of 1.00 kW = 1.34 hp. *Note:* The thermodynamic cycle involves four piston strokes.