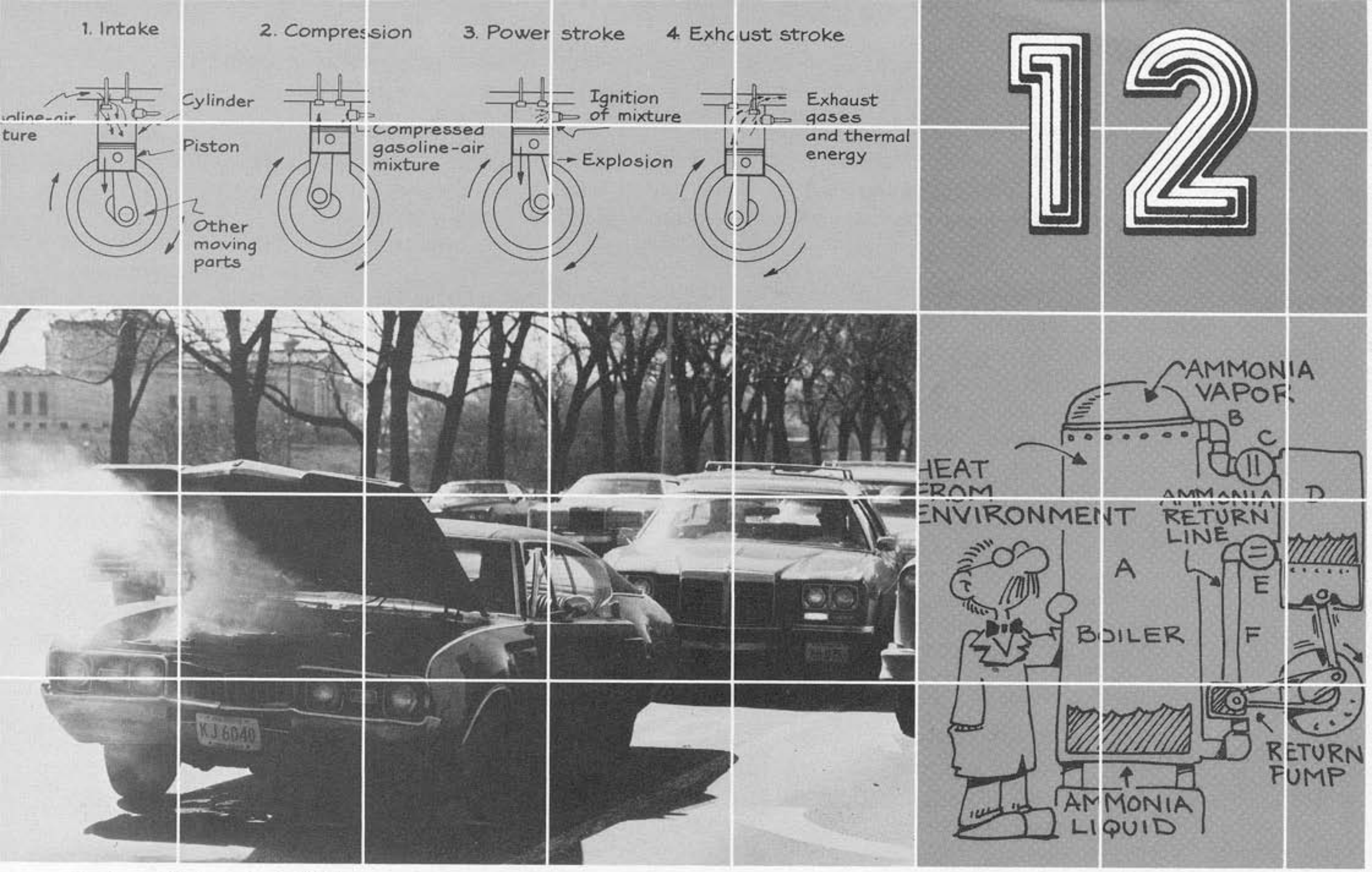


Freelance Photographer's Guild.

Thermodynamics

The energy crisis, the energy problem, the energy situation, decreasing energy reserves—these phrases appear over and over on politicians' lips, during TV newscasts, and in newspaper headlines. Behind these phrases lies the idea that we are somehow running out of energy. Yet energy is conserved. How can we run out of it?

Seen only from the physicist's concept of energy conservation, the notion that we are running out of energy seems absurd. When we drive an automobile, the energy stored in the gasoline does not disappear; it merely changes form. The chemical potential energy in the gasoline is converted into the kinetic energy needed to get us from place to place and the thermal energy that is exhausted to the environment. Nothing is lost—we still have the energy with which we started. All that we have lost is the original source, the gasoline.

If it is the gasoline that is in short supply, why not substitute a different source of energy? Better yet, why not recycle the energy we produced with the gasoline? We could build a "miracle machine" that sucks in the hot automobile exhaust, extracts the thermal energy from it, and exhausts cooler air to the environment. The thermal energy we extract could then be used to generate electricity or produce some other form of energy. If we used electric cars, it could even be used to run the car again. Such a machine would solve everyone's problems—we would have transportation, the environment would be cooler and we would have more electricity. Ah . . . but no such machine exists and, as our name for it implies, physicists are not betting that one will ever be invented. While energy is conserved, something irreplaceable is lost when the automobile converts gasoline into motion and heat. This something is the energy's usefulness, its availability to do work.

Thermodynamics is the study of the conversion of thermal energy into other forms of energy, and vice versa. This branch of physics originated in the practical study of heat engines such as the steam engine, but it has provided some of our most fundamental insights into the concept of energy. Using the *heat engine* as a basic model, this chapter explores the thermodynamic problems involved in building our miracle machine. As applied to heat engines, the law of conservation of energy is called the *first law of thermodynamics* and tells us we can never get more energy from a machine than we put into it. We introduce the concept of *entropy,* a measure of the disorder of a system, to distinguish between the chemical potential energy stored in gasoline and thermal energy found in the environment. The *second law of thermodynamics* limits the kinds of energy transformations that occur, according to the resulting changes in entropy. It also tells us that in every useful energy transformation, some energy must be wasted. This is the law that sounds the death knell of our miracle machine.

THE FIRST LAW OF THERMODYNAMICS: YOU CAN'T GET SOMETHING FOR NOTHING

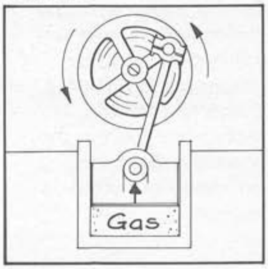
Consider a machine even more fantastic than the miracle machine just described. Suppose someone proposed that you invest in the production of a machine that actually supplies more energy than it consumes. Such a machine could be used to drive two machines, which could be used to drive four machines, and so on. For the fuel used to drive one machine, we could drive hundreds of machines that would do useful work. Of course you would laugh off the would-be inventor. The law of conservation of energy tells us that we cannot end up with more energy than we had at the start.

Machines can never create more energy than we put into them, but they can make existing energy more useful to us. Most modern machines operate on the principle of the heat engine, a device which converts thermal energy into kinetic energy. In this section of the chapter we examine heat engines and use their operation to illustrate the first law of thermodynamics. To understand the operation of the heat engine, however, you must first know something about the behavior of gases.

Gases and Heat Engines

Heat engines convert the thermal energy stored in gases into the kinetic energy of moving pistons or turbines. In its simplest form, this conversion occurs through the two-step process shown in Figure 12-1. During the expansion

Expansion Stroke



Compression Stroke

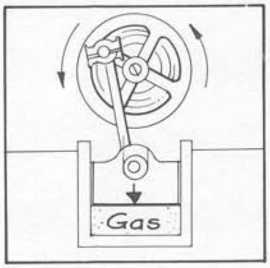


Figure 12-1

A simplified model of a heat engine. During the expansion stroke, the gas expands, doing work on the piston. During the compression stroke, the piston does work in compressing the gas.

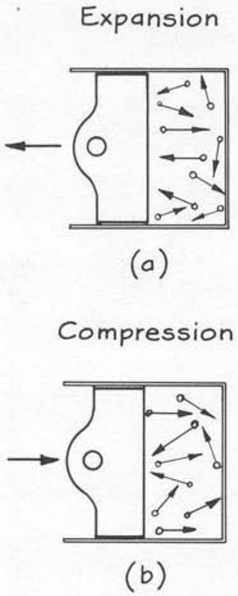


Figure 12-2
During expansion, the molecules push in the same direction the piston moves. During compression, the molecules push in the opposite direction, opposing the piston's motion.

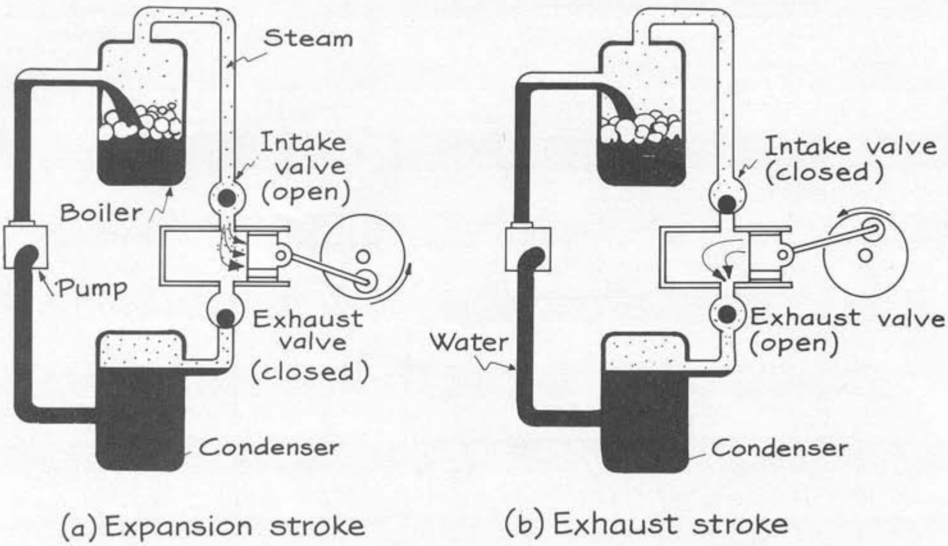
stroke, a gas enters the cylinder and expands, pushing the cylinder to the left. If we connect the piston to a wheel as shown, then its motion can be used to rotate a fan, move a car, or do some other useful work. During the compression stroke, the piston moves back to the right, compressing the gas and eventually exhausting it from the cylinder. The entire process produces useful energy only when the two steps—expansion and compression—occur at different temperatures. To see why, we must look more closely at the interactions between individual gas molecules and the piston.

As we saw in Chapter 10, a gas is a collection of molecules moving about independently of one another. When these molecules strike an object, like the movable piston, they apply a force to it. These forces can either enhance or retard the motion of the piston, depending on the direction in which the piston is moving. During the expansion stroke (Figure 12-2(a)), the molecules exert forces that act in the same direction as the piston moves. The piston speeds up, gaining energy from the gas molecules with which it collides. As the piston moves back to the right during the compression stroke, however, the molecules exert forces that oppose its motion (Figure 12-2(b)). The piston slows down, losing energy to the individual gas molecules. In order for the piston to gain energy during the two-step process, the forces exerted by the molecules during expansion must be greater than those exerted during compression. A sample of gas molecules will exert a greater force when at a higher temperature. Consequently, the piston gains energy only if expansion occurs at a higher temperature than compression. Heat engines are designed with this in mind.

Heat Engines and the First Law

The first successful heat engine was the steam engine, invented by James Watt early in the nineteenth century. As its name implies, the steam engine uses the thermal energy stored in steam to create motion. A simple steam engine consists of three chambers connected to one another, as shown in Figure 12-3. Water is heated to produce steam in the boiler. A controlled quantity of high-pressure steam moves into the cylinder, where it pushes the piston to the right. The compression stroke then occurs at a lower temperature. The cooled steam flows into a condenser, where it is cooled and pumped back up to the boiler to be reheated and used again. The cycle continues as long as thermal energy is available to convert the water into steam in the boiler and the environment can handle the thermal energy released at the condenser.

If we trace energy through the steam engine, the original source of energy is the chemical potential energy of the fuel—wood or coal—used to produce the steam. This energy is converted into thermal energy, which is eventually stored in the steam. In the cylinder, part of the thermal energy stored in the steam is used to move the piston and the remaining thermal energy is exhausted to the environment. We have gone from chemical potential energy



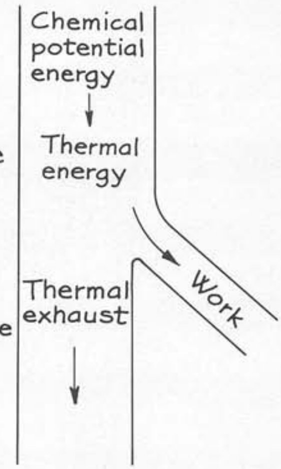
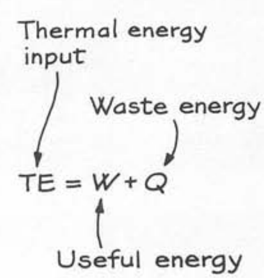


Figure 12-3 Wood or coal is burned to convert water into steam in the boiler. Steam flows into the cylinder, where it forces the piston to move to the right. The piston moves back to the left, forcing the steam into the condenser where it is cooled. The thermal energy in the steam is converted into the kinetic energy of the piston and the thermal exhaust dumped into the environment at the condenser.

to thermal energy to kinetic energy, with some thermal energy exhausted to the environment.

The steam engine provides us with a generalized model of a heat engine. A **heat engine** is any device that converts thermal energy into kinetic energy and thermal exhaust. The kinetic energy can be considered an end product, as in the case of steamships and steam locomotives, or it can be used to produce another useful form of energy, such as electricity in electric generators. Regardless of its use, this energy is called the **useful energy** produced by the process, the energy available to do work. The thermal energy released to the environment is often called the **thermal exhaust,** or waste energy.

Like other processes, heat engines must obey the law of conservation of energy. For each cycle, the thermal energy put into the system must equal the useful energy and waste energy released by the system.



$$\text{Thermal energy input} = \text{useful energy} + \text{waste energy}$$

For Watt's steam engine, the thermal energy stored in the steam must equal the sum of the kinetic energy of the piston and the thermal energy exhausted to the environment. As applied to heat engines, the law of conservation of

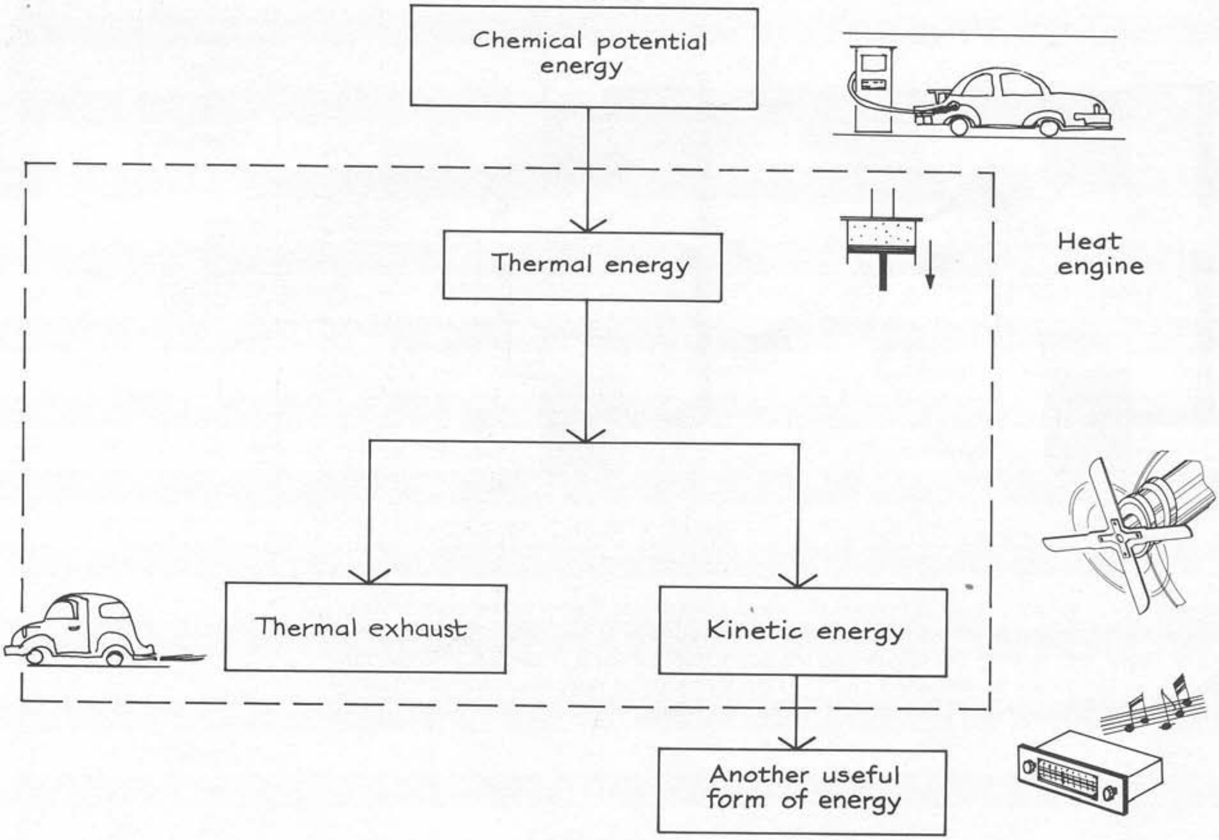


Figure 12-4
A heat engine performs one part of the complete process—converting thermal energy into kinetic energy and thermal exhaust.

energy is called the **first law of thermodynamics.** In this context the law of conservation of energy is often stated as: Energy is neither created nor destroyed, but only changed from one form to another. Or, as wits have long expressed it, you can't get something for nothing.

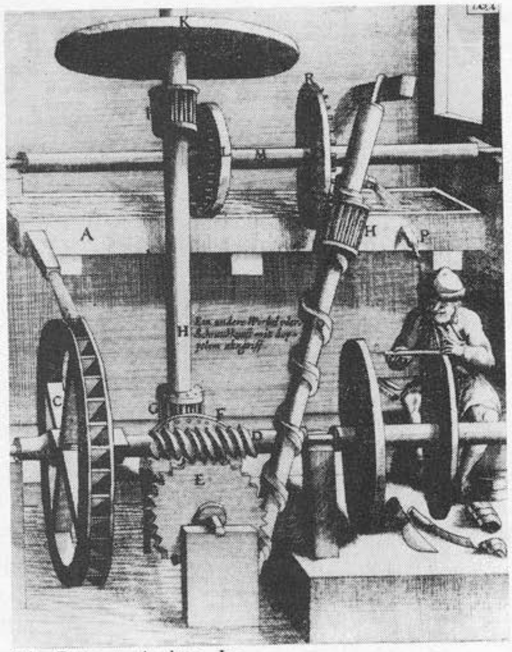
SELF-CHECK 12A

In 1 second (s), a typical power plant uses 3 billion joules (J) of thermal energy to produce 1 billion joules of electrical energy. How many billion joules of waste energy are exhausted to the environment?

Automobiles and Refrigerators

The generalized heat engine accurately describes the energy changes that occur in a variety of everyday devices. In addition to the steam engine, typical examples of heat engines include the moped motor, an electrical generating plant, and automobile engines. To see how some of these real engines can be described in terms of the generalized heat engine, we trace the form that

SOMETHING FOR NOTHING—ALMOST



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What we need is a machine that does work, yet puts back into itself at least as much energy as it takes out. Commonly called perpetual motion machines, these devices have been the dreams of inventors for centuries. One perpetual motion machine was described by Robert Fludd in 1618. Water falling from a reservoir (A) drives a wheel (C) that turns a shaft (D). This motion turns the grinding wheel that enables the local smith to sharpen knives. At the same time a series of gears (E–L and R) turns a coiled pipe (Q) that brings the water back up to the reservoir. The water has regained its initial gravitational potential energy and has done useful work along the way. Energy comes out of the machine, but no net energy goes in. This type of machine violates the first law of thermodynamics (conservation of energy) and is called a *perpetual motion machine of the first kind.* It cannot work, but Robert Fludd had no way of knowing that. He devised it 220 years before the principle of conservation of energy was discovered.

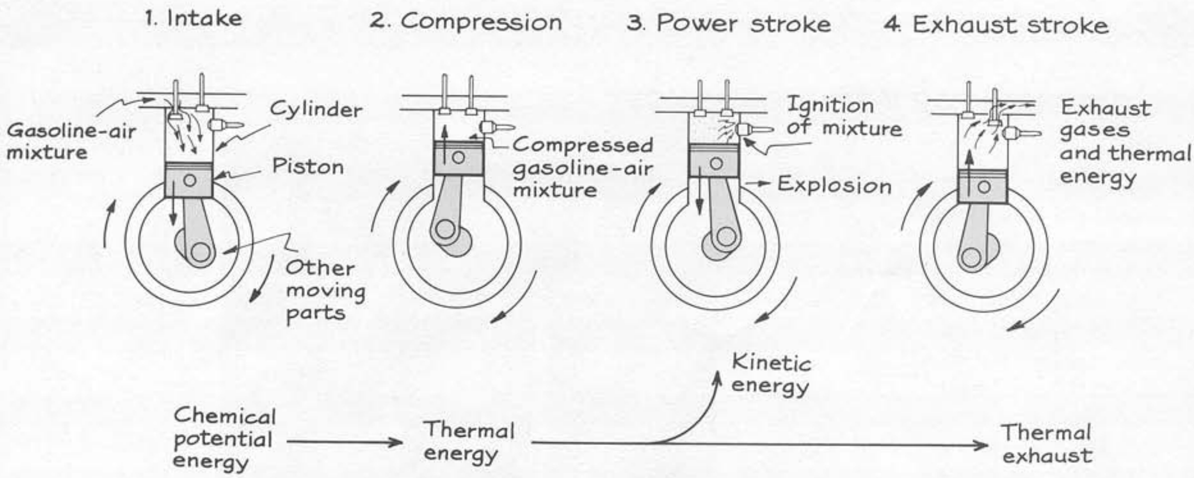

Figure 12-5

The generalized heat engine illustrates the operation of the four-cycle internal combustion engine. Thermal energy released in Step 3 is converted into the motion of the piston and the thermal energy exhausted to the environment.

energy takes throughout each step in the engine's operation. We consider one of the most well-known engines, the automobile engine, and a heat engine that runs backwards, the refrigerator.

Most automobiles use engines called *four-cycle internal combustion engines.* The four-step process, illustrated in Figure 12-5, is a slight variation on the steam engine cycle. In Step 1 the piston drops, drawing a mixture of air and gasoline (in the form of very fine droplets) into the cylinder. A valve closes and the piston moves upward to compress the gasoline-air mixture. In Step 3 the spark plug fires, igniting the gasoline-air mixture. The resulting explosion drives the piston downward. Finally, in Step 4 the piston moves upward, forcing the remaining gases out the exhaust system. Useful energy is derived primarily in Step 3. Energy must be supplied to move the piston in Steps 1, 2, and 4. Typically, an automobile has four to eight of these cylinders.

We can examine this four-step process in terms of the generalized heat engine. Instead of using coal or wood to convert thermal energy into kinetic energy, the automobile engine uses gasoline. The gasoline is burned directly in the cylinder—hence the name **internal combustion engine.** The chemical potential energy of the gasoline is converted into thermal energy, which causes the gases in the cylinder to expand. This expansion pushes the piston downward, converting thermal energy into kinetic energy. Thermal waste is released through engine cooling as well as through the exhaust system.

The refrigerator can also be described in terms of the generalized heat engine. As described in Chapter 10, liquid Freon is pumped through a series of coils inside the refrigerator. It absorbs thermal energy from the air inside the refrigerator and changes into a gas. Gaseous Freon is then pumped back outside the refrigerator by a compresser, where it is liquefied. In many respects a compresser is just a simple piston-cylinder arrangement like those used in steam engines and automobile engines. Gaseous Freon enters the cylinder. As the piston moves upward, it compresses the gaseous Freon, changing it back into a liquid. The thermal energy released by the Freon as it changes state is released to the environment, namely, your kitchen.

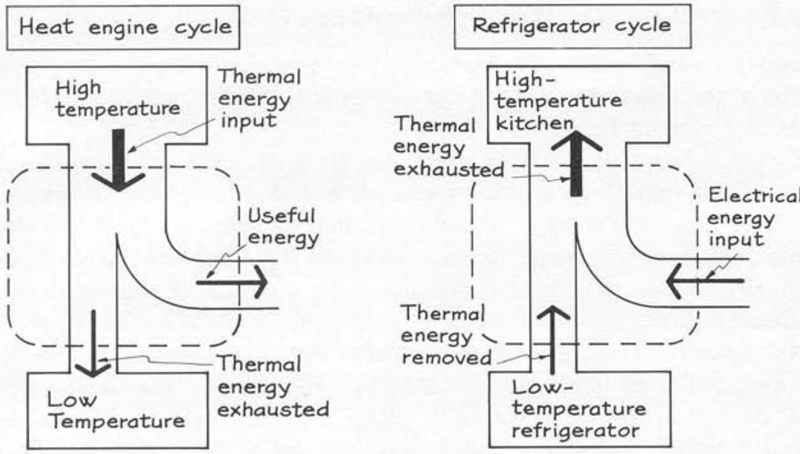

Figure 12-6

A conventional heat engine moves thermal energy from a high temperature reservoir to a low temperature reservoir, diverting some of it for useful work. A refrigerator reverses the process, using electrical energy to move thermal energy from the low temperature (refrigerator) and exhausting it at a higher temperature (the kitchen).

If we trace the various forms energy takes in the refrigerator cycle (Figure 12-6), we see that a refrigerator behaves like a heat engine running backwards. The original energy source is electricity, which is used to drive the compresser. The kinetic energy of the piston in the compresser is converted into thermal energy, which is then exhausted to the environment. Instead of converting thermal energy into kinetic energy, the refrigerator uses kinetic energy to move thermal energy.

THE SECOND LAW OF THERMODYNAMICS: YOU CAN'T EVEN BREAK EVEN

The first law of thermodynamics says we cannot get more energy out of a machine than we put into it. But the miracle machine we proposed at the beginning of the chapter does something more modest—it simply recycles thermal waste energy. Heat engines use thermal energy, and they also dump thermal exhaust into the environment. Why not use this thermal exhaust to run other heat engines?

What we are proposing is a machine that runs on thermal energy extracted from the environment. Actual heat engines, of course, rely upon some external source of energy to produce the thermal energy needed for their operation. Steam engines burn wood or coal, automobile engines burn gasoline, and the human body requires food. It is quite possible to build a heat engine that extracts thermal energy from the air if we use another form of energy to run the extraction process. But that would defeat the whole purpose of our miracle machine. What we need, in light of today's dwindling resources, is a machine that will extract thermal energy from the environment without using another form of energy to do so. Such a machine cannot be built. To see why, we need to investigate spontaneous processes, the concept of entropy, and the second law of thermodynamics.

Some Processes Are Not Spontaneous

Processes by which energy is changed from one form into another or transferred from one place to another can be separated into two categories: spontaneous and nonspontaneous.

Spontaneous processes are those processes that occur without the addition of energy. When a diver steps off a diving board, for example, her gravitational potential energy is converted into kinetic energy. When she hits the water, her kinetic energy is transferred to the water as thermal energy. Both processes are spontaneous because no additional energy is needed to make them occur.

Nonspontaneous processes require external sources of energy. We do not expect the diving-board scene to occur in reverse spontaneously. The thermal energy in the water will not collect itself and spontaneously convert itself into the diver's kinetic energy, lifting her out of the water. Nor does the diver's kinetic energy transform itself into gravitational potential energy, lifting her back up on to the diving board. Conceivably, we could build machines to accomplish both these tasks, but external sources of energy would be needed to run the machines. Nonspontaneous processes require external sources of energy.

The observation that we can separate processes into two categories—spontaneous and nonspontaneous—seems puzzling. The law of conservation of energy makes no distinction between the two. Energy conservation allows the diver to spontaneously rise from the water to the diving board. The thermal energy lost by the water would be gained by the diver as kinetic energy, then as gravitational potential energy. Energy would be conserved. Yet we know this never happens. Observation tells us that nature does make a distinction—energy transformations do have a preferred direction. In searching for an explanation, physicists compared the various forms of energy involved in energy transfer. The concept of entropy emerged to describe the differences they found.

Entropy

Entropy is a measure of the disorder of a system. The greater the disorder, the higher the entropy. To describe what we mean by this, consider the system of poker chips shown in Figure 12-7. We can arrange the poker chips neatly in piles according to color, as shown in (a), or we can scatter them about as shown in (b) and (c). While we cannot assign numerical values to the amount of disorder in each system, we can make qualitative comparisons. The system in (c) is more disordered than that in (b), and (b) is more disordered than (a). Using the concept of entropy, we say that (c) has the most entropy and (a) has the least entropy. As the entropy of a system increases, so does its disorder.

In a sense, entropy describes how easily we can locate something. In the poker-chip example, we might want to locate all the darkest chips. When the chips are scattered about over a large volume, they are distributed so randomly that it would take some time to locate all the darkest ones. When they are stacked neatly according to color, the location of each chip is very well

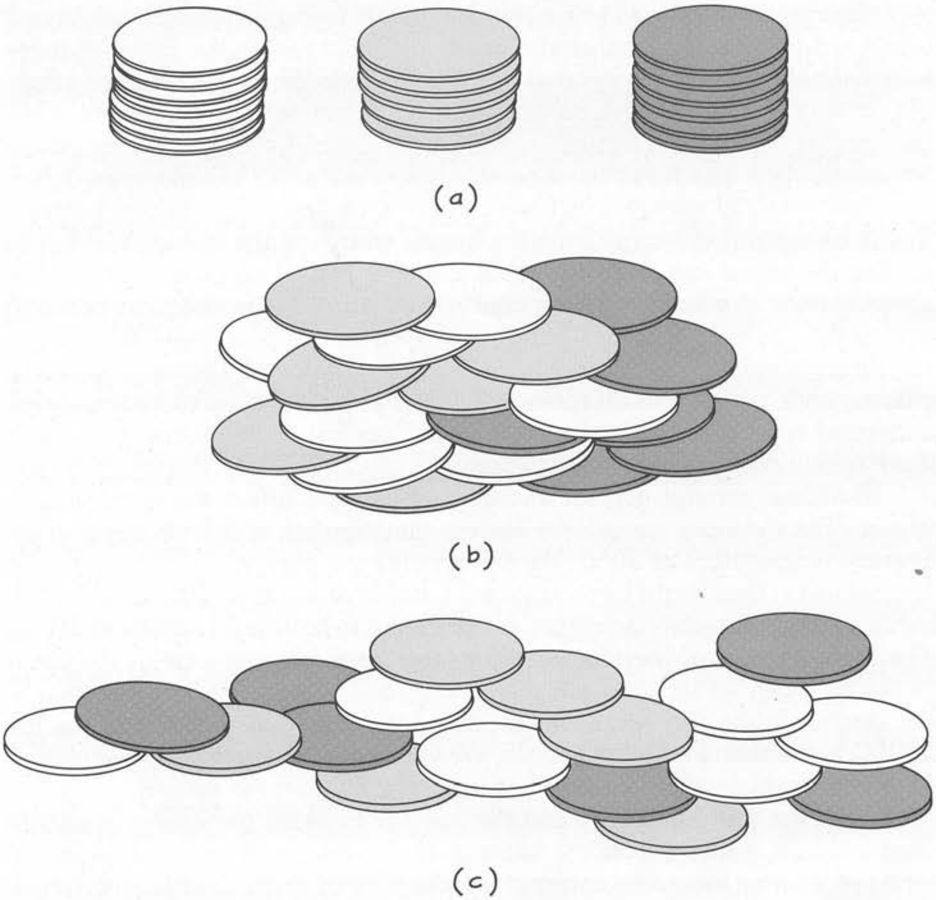

Figure 12-7
Entropy describes the disorder of a system; (a) has the least entropy and (c) has the most entropy.

defined. As the entropy of the system increases, we find it increasingly difficult to locate a specific group of chips.

SELF-CHECK 12B

Which system has the higher entropy: (a) two small glasses of water, one hot and the other cold, or (b) one large glass of lukewarm water?

Entropy and the Energy Stored in Matter

Entropy can be used to describe the manner in which energy is stored in a system—whether it is "stacked up neatly" or "strewn around randomly." In a sense entropy describes how easily we can locate and extract energy from the system. Two characteristics, the form in which energy is stored in the system and the distribution of that energy in the system, help describe differences in entropy. Let's consider examples of each.

Energy can be stored in matter as potential energy involved in molecular bonds and as kinetic energy stored in the motion of molecules. Either of these forms of energy can be converted into thermal energy. In gasoline, for example, energy stored in the electrical bonds among molecules is released when the gasoline burns. We have called this form of stored energy *chemical potential energy*. One liter (L) of gasoline contains roughly 32,000 kilojoules (kJ) of chemical potential energy, which we can extract by burning. We could extract this same amount of energy from the kinetic energy of the molecules—but to do this we would need to cool about 2.4×10^8 L of gasoline 100°C. The same amount of energy can be stored more compactly as chemical potential energy than as kinetic energy. In terms of the poker-chip example, we need to sift through only 1 L of gasoline to find 32,000 kJ of chemical potential energy, while we have to sift through 2.4×10^8 L of gasoline to find the same amount of kinetic energy in the molecules. Chemical potential energy is much more neatly stacked than kinetic energy.

Both the arrangement of energy and its form affect the entropy of a system. For example, consider a system that consists of 2 L of water at an average temperature of 50°C. We can arrange the energy of such a system in several ways. One might be to have a 1 L bottle of water at 100°C and a 1 L bottle at 0°C. A second arrangement would be to have a 2 L bottle at 50°C. The same amount of thermal energy is present in both arrangements, but it would be much easier to locate that energy in the first arrangement than in the second. In the first arrangement, more of the energy is distributed in the 100°C bottle than in the 0°C bottle. We would look in the 100°C bottle first. The first arrangement of energy has less entropy than the second.

Both the form of energy and the manner in which the energy is distributed within a system affect the entropy of the system. In general, potential forms of energy have less entropy associated with them than kinetic forms. And, given two systems with equal amounts of thermal energy stored in their molecules, the system in which the energy is distributed over fewer molecules has less entropy.

SELF-CHECK 12C

Consider a system that consists of the diver and the pool. Before hitting the water, the diver has all the kinetic energy. After entering the water, the diver transfers that kinetic energy to the water molecules. The diver stops moving and the water warms up slightly. Compare the distribution of energy before and after the diver enters the water. Which arrangement has more entropy?

Entropy Must Increase

In any spontaneous process, the entropy of the system increases. When the diver jumps off the diving board, her gravitational potential energy will be

spontaneously converted into kinetic energy. Gravitational potential energy has less entropy associated with it than kinetic energy. When the diver enters the water, her kinetic energy is immediately shared with the surrounding water molecules. Kinetic energy located with the motion of a single object—the diver—has less entropy associated with it than the same amount of kinetic energy shared among thousands of separately moving water molecules. Because it is associated with the random motions of many objects, thermal energy has more entropy associated with it than any other form of energy. Thermal energy is the ultimate product of a series of spontaneous energy transformations.

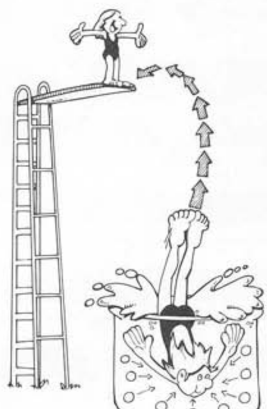

Figure 12-8
Thermal energy stored in the molecules cannot exert a net force upward on the diver, pushing her out of the water and back up to the top of the diving board. This is a nonspontaneous process.

Thermal energy itself flows spontaneously from warmer objects to cooler ones. If we place a glass of hot water in contact with a glass of cold water, both will be lukewarm a short time later. Initially, more thermal energy is distributed among molecules in the glass of hot water than among molecules in the glass of cold water. More of the thermal energy of the system is distributed among fewer molecules. When thermal energy moves from the glass of hot water to the glass of cold water, the thermal energy of the system is shared among more molecules. The entropy of the system increases. Were thermal energy to move from the glass of cold water to the glass of hot water, more thermal energy would be shared among fewer molecules and entropy would decrease. Such a process does not occur spontaneously.

What about nonspontaneous processes, like thermal energy flowing from a cooler object to a warmer object? When a refrigerator cools, thermal energy moves from a cooler environment to a warmer environment—from the inside of the refrigerator to your kitchen. The refrigerator gets colder and the kitchen gets warmer. Like the two glasses of water, this arrangement has less entropy than one in which thermal energy is evenly distributed throughout the refrigerator and the kitchen. At first thought, we might say that the entropy of the system has decreased. However, electrical energy must be supplied in order for the heat extraction process to occur. Before drawing any conclusions about changes in entropy, we have to include electricity in our analysis.

Electrical energy is usually generated in power plants that burn oil, coal, or natural gas. To cool the refrigerator, the chemical potential energy of the fuel must be converted into electrical energy. This electrical energy is then converted into the kinetic energy of the piston, which is converted, in turn, into the thermal energy exhausted from the Freon gas. Entropy increases as low-entropy chemical potential energy is converted into higher-entropy thermal energy. The entropy increase in this conversion process far exceeds the entropy decrease that occurs when thermal energy moves from the cooler refrigerator into the warmer kitchen.

A nonspontaneous process does result in a local decrease in entropy, which is why it is nonspontaneous. Entropy does decrease in the refrigerator-kitchen system if we ignore the electrical generating plant. But we cannot ignore the plant. Without it, our nonspontaneous process would not occur. When we include the energy source required to initiate the nonspontaneous process, the entropy of the entire system increases.

These examples illustrate the way in which entropy can be used to explain our experiences with spontaneous and nonspontaneous processes. All processes result in an increase in entropy. Known as the **second law of thermodynamics,** this principle can be stated in a variety of ways, each specific to a particular application. Thermal energy never flows from a cooler object to a warmer object. Natural processes move toward greater disorder. No matter what the application or how it is worded, the second law of thermodynamics clearly reflects nature's preference in the direction of energy transformations.

SELF-CHECK 12D

The air around us contains lots of water vapor—water in the form of gas. Use the second law of thermodynamics to explain why the water vapor in air at room temperature (20°C) does not condense on our skin, transferring the latent heat of vaporization to our bodies at 37°C.

When applied to the heat engine, the second law of thermodynamics is often stated as: It is impossible to build an engine that transforms thermal energy into kinetic energy without exhausting some thermal energy in the

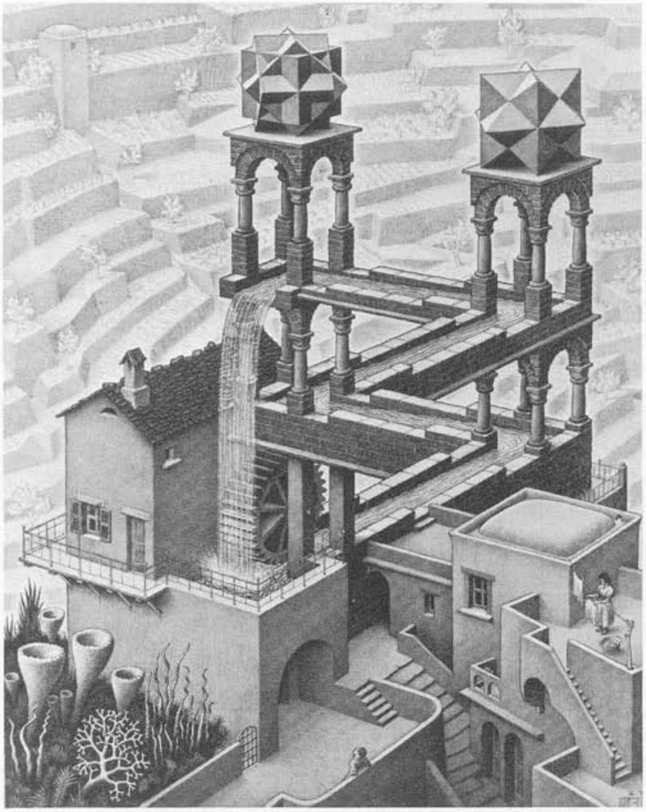

Figure 12-9
While you might not know why, experience tells you that something is wrong with Escher's drawing. What laws of thermodynamics does it violate?

process. A heat engine converts thermal energy into kinetic energy. The thermal energy stored in steam, for example, becomes the kinetic energy of a piston. By itself, such a process involves a decrease in entropy—it will not occur spontaneously. The local decrease in entropy that occurs inside the cylinder is offset by the increase in entropy that occurs at the condenser, where thermal energy once restricted to a certain volume of steam is dispersed among molecules in the environment. The second law of thermodynamics demands that this waste energy be present.

A conventional heat engine, like the steam engine, uses the environment as the condenser. Consequently, the gas must be heated above the temperature of the environment in order for thermal energy to be exhausted at the condenser. Coal or some other form of chemical potential energy is needed to produce the higher-temperature steam. In our miracle machine we wanted to use the thermal energy exhausted to the environment to drive yet another heat engine. In order to do so, we would have to build a condenser that operates at temperatures below environmental temperatures—we would have to build a refrigerator. Electricity or some other form of energy is needed to operate the refrigerator, so we have not gained a thing!

Billions of heat engines are in operation today (Figure 12-10). Each takes some form of potential energy, converts it into kinetic energy, and dumps the thermal exhaust into the environment. We continually diminish the world's

Figure 12-10
Billions of heat engines convert highly organized energy—fossil fuels—into kinetic energy and thermal exhaust.

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supply of chemical potential energy—to the detriment of our pocketbooks—and increase the thermal energy of the environment, to the dismay of the environmentalists. The second law of thermodynamics allows us no way out of this state of affairs—you can't even break even!

HOW WELL CAN WE DO?

In any process, the entropy of the system must increase. The real energy crisis lies in the fact that we have been rapidly consuming known stores of useful energy and increasing the useless thermal energy dumped into the environment. In a sense, our energy crisis is an entropy crisis—entropy is increasing too rapidly. While we cannot change the second law of thermodynamics, we can use our understanding of it to slow this rate of increase.

The analysis of heat engines tells us that the entropy increase occurs at two places: in the conversion of a fuel into thermal energy and in the release of thermal waste into the environment. Let's examine each of these processes with the goal of minimizing the increase in entropy that accompanies all energy conversions.

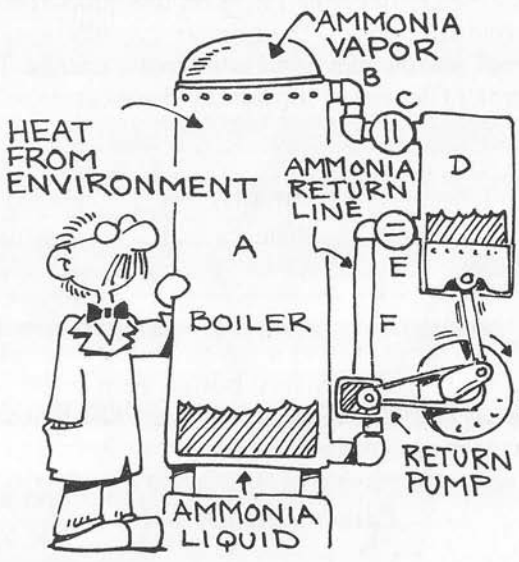
Efficiency

In any heat engine, thermal energy in a hot reservoir is converted into kinetic energy (useful energy) and thermal exhaust (waste energy) which is released to a cold reservoir. We use the concept of efficiency to describe how effectively a heat engine or any other energy conversion device produces useful

THE SECOND LAW GETS IN THE WAY, TOO

In the continual search for energy from nothing John Gamge, in the 1880s, designed the zeromotor. Thermal energy from the environment vaporizes liquid ammonia in a tank (A). The ammonia gas travels to a cylinder (D), where it pushes down a piston (H), driving a wheel (I). Having lost its energy, the ammonia spontaneously becomes a liquid again and is pumped (G) back to the tank. There is only one problem: the second law of thermodynamics. When the gas expands and does work at D, its temperature must drop. It is a gas at a temperature lower than the environment. To become a liquid it must give up even more energy. However, since its temperature is already below the environment's, it cannot give up energy spontaneously. That would cause a spontaneous decrease in the entropy of the system. This device, an example of a *perpetual motion machine of the second kind,* will not solve our problems.

Perhaps the only thing truly perpetual about perpetual motion machines is the stream of inventors who claim to have designed them. An inventor obtained a patent for one as recently as 1979. He said he got the idea while taking a college physics course.



Efficiency

Useful energy

$\text{Eff.} = \frac{W}{TE} \times 100\%$

Thermal energy input

energy. **Efficiency** is defined as the ratio of the useful energy produced to the thermal energy with which we began. Since we often express efficiency as a percentage, this ratio is then multiplied by 100.

$$\text{Efficiency} = \frac{\text{useful energy}}{\text{thermal energy input}} \times 100\%$$

The second law of thermodynamics requires that some waste energy be produced. Consequently, the useful energy produced will never equal the thermal energy input. Heat engines can never be 100% efficient.

While heat engines are always less than 100% efficient, we can reasonably ask just how efficient they can be. An engineer, Sadi Carnot (pronounced Kar′-nō), examined this question; in 1824 he derived an expression for its efficiency.

Real heat engines lose thermal energy in the cylinder as well as in the condenser. Frictional and thermal energy lost to the environment are the usual culprits. While the second law of thermodynamics requires that thermal energy be released at the cold reservoir, losses that occur at other locations in the engine can be minimized. Carnot was able to show that an engine's efficiency ideally depends solely on the temperature difference between the hot and cold reservoirs—the greater the difference, the higher the proportion of thermal energy converted into kinetic energy. This ideal efficiency, called the **Carnot efficiency,** is given by the expression

Carnot efficiency

Temperature of cold reservoir (K)

$\text{C. Eff.} = \left(1 - \frac{T_c}{T_H}\right) \times 100\%$

Temperature of hot reservoir (K)

$$\begin{matrix}\text{Carnot} \\ \text{efficiency}\end{matrix} = \left(1 - \frac{\begin{matrix}\text{absolute temperature} \\ \text{of cold reservoir}\end{matrix}}{\begin{matrix}\text{absolute temperature} \\ \text{of hot reservoir}\end{matrix}}\right) \times 100\%$$

(Absolute temperature (K) = temperature in Celsius (°C) + 273)

For example, an electrical power plant might operate between the temperatures of 700 K (hot reservoir) and 300 K (cold reservoir). The Carnot efficiency for such a plant is

$$\text{Carnot efficiency} = \left(1 - \frac{300\text{ K}}{700\text{ K}}\right) \times 100\% = 57\%$$

No matter how well designed it is, a power plant operating at these temperatures can never exceed 57% efficiency. Such a plant typically only reaches 30%-40% efficiency.

Carnot's ideal heat engine provides a goal toward which designers strive and a way with which to evaluate our consumption of useful forms of energy. The greater the temperature difference between the hot and cold reservoirs, the more efficient the engine. Practically speaking, this difference is limited by our use of the environment as the cold reservoir and by the maximum temperature at which most materials still function. Table 12-1 lists typical hot and cold reservoir temperatures, Carnot efficiencies, and usual operating efficiencies for several common heat engines. In most cases we can still improve.

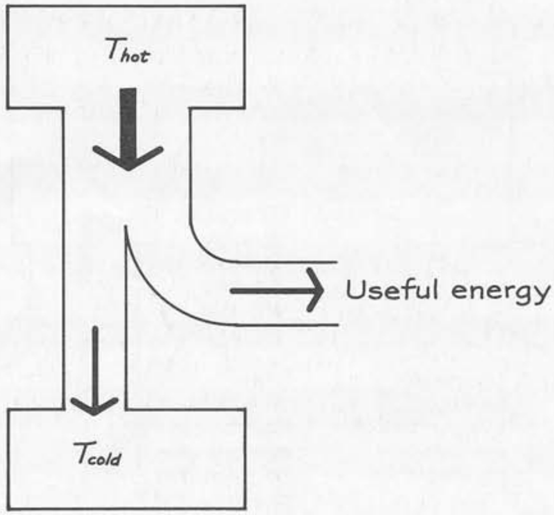


Figure 12-11
Carnot described the ideal efficiency of a heat engine in terms of the temperatures of the hot and cold reservoirs. As the difference in temperature increases, the efficiency of the engine becomes greater.

Table 12-1 Efficiencies of Several Heat Engines

Heat Engine	Temperature of Cold Reservoir (K)	Temperature of Hot Reservoir (K)	Carnot Efficiency (%)	Actual Efficiency (%)
Gasoline engine	300	450	33	25
Diesel engine	300	550	45	35
Piston steam engine	375	475	21	10
Copper-Bessemer engine*	240	700	65	42
Electrical generating plant	300	800	62.5	35

*Most efficient engine constructed so far.

SELF-CHECK 12E

Suppose your moped engine operates between the temperatures of 450 K and 290 K. What is the best efficiency it can reach?

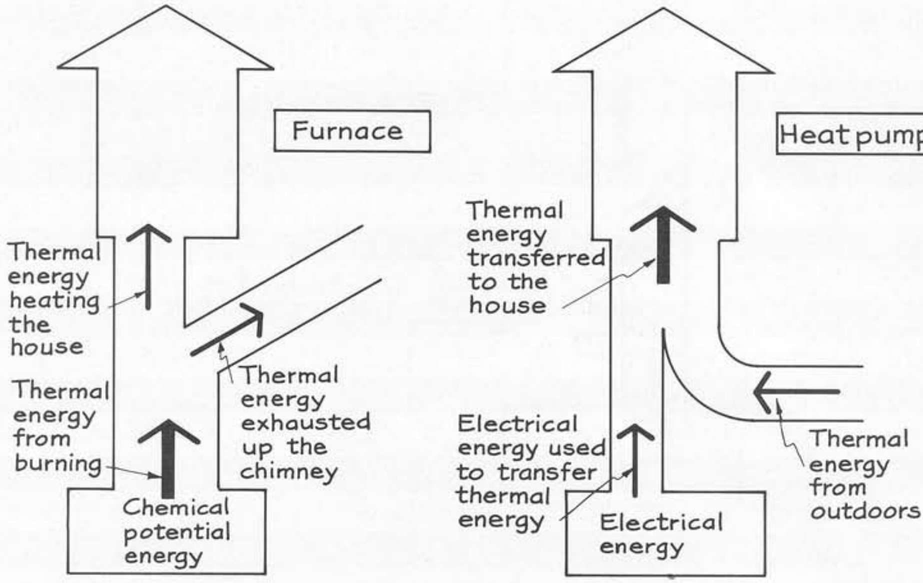


Figure 12-12

A furnace and a heat pump differ in the way in which they produce thermal energy to heat your home. A furnace converts the chemical potential energy stored in a fuel into thermal energy. Some of this thermal energy heats your home, and the rest is exhausted up the chimney. A heat pump uses electrical energy to move thermal energy from outside to inside. The heat pump uses considerably less low-entropy energy to produce the same amount of thermal energy to heat your home.

Selecting the Energy Source

The other way in which heat engines increase the entropy of a system is in the conversion of a fuel into the thermal energy needed to operate the heat engine. Usually, we select a low-entropy form of energy, the chemical potential energy stored in a fuel, and convert it into the highest-entropy form of energy, the thermal energy stored in the motion of gas molecules. We could decrease the rate of entropy increase by replacing the fuel with an energy source that has more entropy.

The heat pump uses this approach to decrease your home-heating costs. A conventional furnace takes a low-entropy form of energy (oil or gas) and converts it into thermal energy to be distributed throughout the house. A heat pump takes a somewhat higher entropy form of energy (electricity) and uses it to "pump" thermal energy from the outside air into the inside air. It works very much like a refrigerator, using electricity to extract thermal energy from a cooler environment and pump it into a warmer environment.

Heat pumps do require lower-entropy forms of energy, namely, electricity. Ultimately, however, they consume less of these lower-entropy forms of energy because they take advantage of the thermal energy already present in the environment. If we contrast a furnace with a heat pump (Figure 12-12), the two processes differ in how the thermal energy added to the air is obtained. In a furnace, all the thermal energy added to the air is provided by the chemical potential energy released when gas or oil is burned. By contrast, some of the thermal energy added to the air by a heat pump was thermal energy already present in the environment. The heat pump simply moves it to a different location.

Table 12-2 lists the amount of low-entropy energy needed to deliver 1,000,000 J of thermal energy to a house by four different devices. For the gas and oil furnace, the low entropy energy needed is measured directly in terms of the oil or gas consumed. Since all the thermal energy delivered by a furnace comes directly from the chemical potential energy of the fuel, a furnace consumes more energy than it produces. Real heat pumps and electrical furnaces use electricity, which ultimately has been produced by an electrical generating plant that burns fuel. Most electrical generating plants are about 33% efficient, so about three times the energy delivered by the electricity has been consumed from lower-entropy fuels. This makes an electrical furnace much less efficient than a gas or oil furnace that burns the fuel directly where the thermal energy is needed. The heat pump, however, delivers 1,000,000 J of thermal energy while consuming only 600,000 J of low-entropy energy. We have not gotten more energy out than we put in. Some of the energy delivered by the heat pump is present in the air that is being moved. This energy does not show up in a comparison of the low-entropy energy consumed. What we have done is move 1,000,000 J of thermal energy for one-third of the lower-entropy energy consumed by a furnace. Ideal heat pumps do even better.

This reasoning can be used to select appropriate methods of energy conversion for a variety of situations. The goal is to decrease, as much as possible, the amount of low-entropy energy consumed. When thermal energy is desired, using some of the thermal energy already present in the environment decreases the overall increase in entropy. The net effect—a warm house—is the same as when low-entropy energy is burned, but the entropy increase is much less. These considerations have led to the definition of a **second law efficiency.** Among those methods possible, the method that uses the least low-entropy energy has the greatest second law efficiency.

Why not use a heat pump as our miracle machine? It extracts thermal energy from the environment, so it could use the waste energy generated by other machines. However, a heat pump cannot do useful work. It merely moves thermal energy from one location to another; it does not transform thermal energy into kinetic energy. The second law of thermodynamics allows

Table 12-2 Comparison of Low Entropy Energy Needed to Produce 1,000,000 J of Thermal Energy

Method	Efficiency (%)	Low-Entropy Energy Needed (J)
Ideal heat pump	100	204,000
Real heat pump	33	600,000
Gas/oil furnace	60	1,667,000
Electric heat	33	3,000,000

us a few miracles, but not this ultimate one. The concept of using the thermal energy strewn throughout the environment is an intriguing one, however. And while physicists are not betting that our miracle machine will ever be invented, they also are not betting that people will stop trying. The idea is much too enticing!

ENTROPY AND THE UNIVERSE

The energy crisis we face is one of running out of lower-entropy forms of energy. Historians report past crises—water power shortages or wood scarcity. Our century seems to be the century of the oil crisis. The development of fusion and fission power plants may bring momentary relief. One day, their fuels, like the firewood, gas, and oil before them, will also be exhausted. We have no choice of endings. Our choice is only how quickly we reach the predictable end. Wise application of the laws of thermodynamics would allow future generations their chance at dealing with the problem.

The laws of thermodynamics apply beyond just our time and our planet. The largest closed system we have is the universe. The second law of thermodynamics tells us that the entropy of this system is continually increasing. Useful sources of energy, like stars, are transforming highly ordered nuclear energy into disordered, or degraded, thermal energy. Our own sun provides an enormous amount of thermal energy to us daily. Energy once localized will eventually be strewn about randomly, unavailable for the most useful task—maintaining life. When all forms of energy degrade to the thermal energy of molecules in space, we have reached what is called the *heat death* of the universe. If our understanding of thermodynamics is correct, the heat death cannot be avoided. Entropy must increase. But, must it increase forever? To answer this question, we will return to our molecular model of matter.

CHAPTER SUMMARY

Thermodynamics, the study of the transformation of thermal energy into other forms, and vice versa, originated largely in the study of heat engines. A *heat engine* is any device that converts thermal energy into kinetic energy and thermal exhaust. The kinetic energy can be an end product or can be used to produce another useful form of energy. Common examples of heat engines include the steam engine and the automobile engine. A refrigerator is a heat engine run in reverse. When applied to the heat engine, the law of conservation of energy states that for one complete cycle,

$$\text{Thermal energy input} = \text{useful energy} + \text{waste energy}$$

This is known as the *first law of thermodynamics.* The first law says that we can never get more energy out of a machine than we put into it.

Processes by which energy is changed from one form into another or transferred from one object to another can be separated into two categories: spontaneous and nonspontaneous. In both cases energy is conserved, but nonspontaneous processes do not occur without the addition of energy from external sources. In searching for a basis for this distinction, physicists have developed the concept of entropy. *Entropy* is a measure of the disorder of a system. The greater the disorder, the higher the entropy. *Spontaneous* processes are those in which entropy increases. *Nonspontaneous* processes are those in which the entropy of the system decreases, when the external energy sources are ignored. When the external energy source is included in the system, the entropy of the system always increases. *The second law of thermodynamics* states that in all processes, the entropy of a closed system increases. Applied to the heat engine, the second law of thermodynamics tells us that thermal energy cannot be used to do useful work without losing some of it to thermal exhaust.

The *efficiency* of an energy conversion device is defined as:

$$\text{Efficiency} = \frac{\text{useful energy}}{\text{thermal energy input}} \times 100\%$$

Since some of the thermal energy input must be exhausted to the environment, a heat engine can never be 100% efficient. The maximum efficiency attainable, called the *Carnot efficiency,* is determined by the temperature of the hot and cold reservoirs used in the heat engine.

$$\text{Carnot efficiency} = \left(1 - \frac{\begin{array}{c}\text{absolute temperature}\\ \text{of cold reservoir}\end{array}}{\begin{array}{c}\text{absolute temperature}\\ \text{of hot reservoir}\end{array}}\right) \times 100\%$$

Heat engines should be selected according to their operating efficiencies and the amounts of low-entropy energy consumed.

ANSWERS TO SELF-CHECKS

12A. Thermal energy input = useful energy + waste energy

$$3 \text{ billion J} = 1 \text{ billion J} + \text{waste energy}$$

$$\text{Waste energy} = 2 \text{ billion J}$$

12B. (b) has the higher entropy because the thermal energy is spread among more water molecules. In (a) more thermal energy is located in the glass of hot water, so we would know to look there first.

12C. Before the diver enters the pool, the kinetic energy is located with her. After she enters the pool, the kinetic energy is shared between all the water molecules and herself. The arrangement in which the energy is shared with the water molecules has more entropy.

12D. In order for water to condense on our skin, thermal energy equal to the latent heat of vaporization of water would have to be transferred from the air to our skin. Our bodies are at a higher temperature (37°C) than the surrounding air (20°C). Thermal energy will not spontaneously move from a colder environment to a warmer environment, since the entropy of the system would have to decrease.

12E. $$\text{Carnot efficiency} = 1 - \left(\frac{290\ \text{K}}{450\ \text{K}}\right) \times 100\% = 36\%$$

PROBLEMS AND QUESTIONS

A. Review of Chapter Material

A1. Define the following terms:
Heat engine
First law of thermodynamics
Spontaneous processes
Nonspontaneous processes
Entropy
Second law of thermodynamics
Efficiency
Carnot efficiency
Second law efficiency

A2. Describe the heat engine cycle and explain why it is useful.

A3. Describe what happens when a heat engine runs backwards.

A4. How is the first law of thermodynamics related to the law of conservation of energy?

A5. How is entropy related to disorder?

A6. How does the second law of thermodynamics distinguish between processes that occur spontaneously and those that do not?

A7. How do we calculate the efficiency of a device?

A8. What does the Carnot efficiency tell us about a heat engine?

A9. How is the second law of thermodynamics useful in selecting an energy conservation device?

A10. Why does a heat pump have a greater second law efficiency than a furnace?

B. Using the Chapter Material

B1. The Stanley Steamer was an automobile (circa 1900) that was propelled by a steam engine. Can the Stanley Steamer be described as a heat engine? If yes, identify the processes and forms of energy. If no, why not?

B2. An old tale is: On a hot summer day you can cool the kitchen by leaving the refrigerator door open. Why will this process make the kitchen warmer instead of cooler?

B3. Your friend decides that it is easier to operate his air conditioner under his bed rather than in a window. Use the concept of the heat engine to explain why his room gets warmer instead of cooler.

B4. An air conditioner uses 100 J of electrical energy to move 400 J of thermal energy from inside to outside. What is the total energy exhausted by the air conditioner?

B5. Hot water in a kitchen sink is allowed to cool. Why does entropy increase during this process?

B6. When a pan of water is heated on a stove, thermal energy is concentrated in the water. Why does entropy increase even though we can identify more energy as being in the water?

B7. A common practice is throwing empty beverage cans along roads rather than placing them in trash containers. Why do beverage cans strewn along the road represent a higher "beverage-can entropy" state than cans placed in a trash container?

B8. What is the Carnot efficiency of the following engines:

Hot Reservoir	*Cold Reservoir*
300 K	300 K
600 K	300 K
900 K	300 K
900 K	150 K
900 K	0 K

B9. A diesel engine operates at a hot temperature of 550 K, while a gasoline engine operates at 450 K. If everything else is equal, why is the diesel engine more efficient?

B10. What is the actual efficiency of a lawn mower that exhausts 70 J for every 100 J of chemical potential energy used?

C. Extensions to New Situations

C1. Bert and Ernie buy identical air conditioners and install them in identical houses. Both keep their homes at 25°C. Bert lives in a large city, where the temperature is higher than at Ernie's country home.
   a. Whose air conditioner will run more efficiently?
   b. Who will use more electrical energy?

C2. A freezer uses 100 kJ of electrical energy to move 330 kJ of thermal energy from inside the freezer to outside. We can determine how much the room temperature increases when 1 kg of ice freezes.
   a. How much thermal energy must be removed from 1 kg of 0°C water to turn it into 0°C ice? (The latent heat of fusion of water is 320 kJ/kg.)
   b. How much electrical energy is used to freeze the ice?
   c. What is the total energy, including waste heat, exhausted by the freezer into the kitchen?
   d. A kitchen contains 43 kg of air (specific heat capacity = 1.0 kJ/°C · kg). Before the ice freezes, the air temperature is 20°C. After the ice freezes, at which temperature will the air be—22°C, 25°C, or 30°C?

C3. An automobile engine uses 500 J of chemical potential energy to produce 100 J of kinetic energy. The operating temperature of the engine is 500 K and the exhaust goes to a 300 K environment.
   a. What is the highest efficiency this engine can reach?
   b. What is its actual efficiency?
   c. Could this engine be made three times as efficient as it is? Explain your answer.

C4. An inventor is looking for people to invest money in her great new engine. She claims that the engine has a hot reservoir temperature of 800 K and a cold reservoir temperature of 400 K. Further, the engine delivers 700 J of useful energy when the thermal energy input is 1000 J.
   a. What is the actual efficiency of the inventor's engine?
   b. What is the best possible efficiency of the engine?
   c. Does this engine violate the first law of thermodynamics? The second law of thermodynamics?
   d. Do you recommend investing in this engine?

C5. Dacia, whose father is a physicist, describes the concept of entropy as: If you clean up your room, the rest of the house gets messier. Is this a correct statement? Why or why not?

C6. You carefully hang up the clothes your friend has left scattered throughout the house.
   a. Has the entropy of the clothes increased or decreased?
   b. What is the entire system involved?
   c. Has the entropy of the system increased or decreased?

C7. A swamp cooler is a home-cooling device used in dry climates, like those found in the southwest part of the United States. Air is blown across water, causing the water to evaporate and the air to cool.
   a. Why is the air cooler after passing over the water?
   b. Will the swamp cooler have a greater second law efficiency than a conventional air conditioner? Why?

C8. Joe Engineer says he has solved an efficiency problem for his company. The factory has several engines operating in it. Joe argues that if they air-condition the factory, the cold reservoir to which the engines dump their exhaust will be cooler. Thus, Joe reasons, the engines will operate more efficiently.
   a. Will an engine's efficiency increase if the cold reservoir is cooled?
   b. Will the factory's overall energy consumption decrease if it is air-conditioned? Explain your answer.
   c. How will the rate of entropy increase change if air conditioning is installed?

C9. A refrigerator's efficiency is generally described by its coefficient of performance, which is defined as:

$$\frac{\text{energy removed from inside}}{\text{electrical energy used}}$$

The Carnot coefficient of performance is

$$\frac{T(\text{K})\text{inside}}{T(\text{K})\text{outside}} - T(\text{K})\text{inside}$$

These numbers are usually greater than 1.

a. A refrigerator uses 400 J to remove 800 J of thermal energy that is inside. What is its actual coefficient of performance?
b. For the refrigerator in (a), how much energy is exhausted to the room?
c. If the inside temperature of this refrigerator is 275 K and the outside temperature is 300 K, what is the Carnot coefficient of performance?

C10. The Carnot coefficient of performance (See Problem C9) can be used to see how real performance changes with temperature. If the Carnot value decreases, so does the actual operating efficiency, and vice versa.

a. How does the Carnot coefficient change as the outside temperature increases? As the inside temperature increases?
b. On a hot night in the city, lots of air conditioners are operating. What happens to the outside air temperature of the city? Explain your answer.
c. How will the change described in (b) affect the performance of the air conditioner?

D. Activities

D1. Heat pumps and swamp coolers (see Problem C7) are two devices that slow down entropy increases. However, they do not work equally well in all climates. Investigate their usefulness to your area.

D2. Some science fiction stories are based on changes in entropy. You might enjoy *The Last Question* by Isaac Asimov.