13 Entropy and the Second Law of Thermodynamics

KEY IDEA

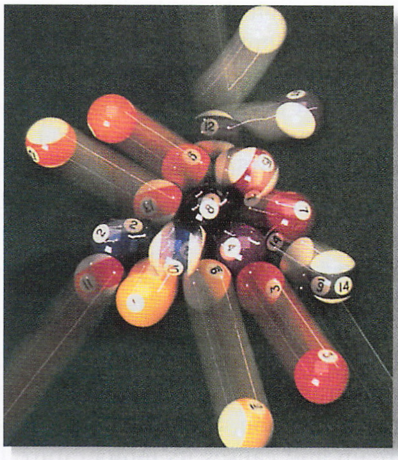
Energy tends to transform spontaneously from more useful to less useful forms.

PHYSICS AROUND US . . . The Cafeteria

Next time you're in the cafeteria, as you go through the food line, think about how each course is prepared. Then try to imagine these processes in reverse. You can peel a piece of fruit, but you can't put it back together. It's easy to scramble eggs, but impossible to unscramble them. You can cook vegetables, but there's no way to uncook them. And once popcorn is popped, it can't be unpopped. Why is this so? Nothing in Newton's laws of motion or the law of gravity suggests that events work in only one way. Nothing that we have learned about energy, including the first law of thermodynamics, suggests that nature works in only one direction.

At the cafeteria you've probably noticed that foods and drinks that are very hot get cooler, while those that are very cold get warmer. A glass of ice water gradually gets warmer, while a plate of hot pasta gets cooler. Ice cream gradually melts, while hot fudge sauce hardens. These everyday events are so familiar that we don't give them a second thought, yet underlying the popping of popcorn and the cooling of a hot drink is one of nature's most subtle and fascinating laws—the second law of thermodynamics.

NATURE'S DIRECTION



(a)

The first law of thermodynamics states that the total amount of energy is constant, but it says nothing about the many ways that energy can shift from one form to another. In everyday life we experience severe limitations on energy transfers. Think again about the behavior of a hot bowl of soup. A hot bowl of soup becomes cooler, releasing heat to its surroundings, but it never spontaneously heats up further, absorbing additional heat from its surroundings. Either way, energy is conserved, yet one example is commonplace and the other seems to be impossible.

Another example: you know that gasoline burns in your automobile to produce heat and exhaust gases, which power the car. However, heat and exhaust gases never spontaneously combine to form gasoline. Again, the first law is obeyed either way, but nature seems to block some kinds of energy transfer.

Many familiar experiences can't be reversed. A pottery bowl falls to the ground and shatters into fragments. Your dorm room seems to get messy in the course of the week all by itself. And everyone and everything gets older—there is no turning back the clock (Figure 13-1). Evidently, there are restrictions on the flow of energy. Since the first law of thermodynamics does not explain these restrictions, we need a second law of thermodynamics.

(b)

(c)

FIGURE 13-1. Many events work in only one direction. (a) As a pool game begins, the cue ball contains all the kinetic energy, but this energy soon becomes distributed evenly through all the balls. (b) A building collapses, transforming the highly ordered structure into a disordered pile of rubble. (c) A flower, once cut, begins to wilt and decay.

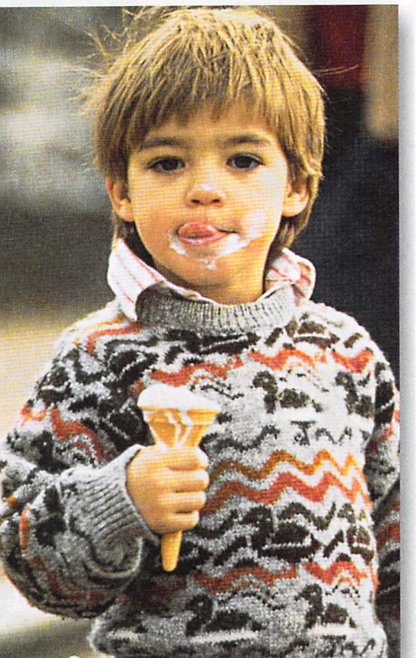
STATEMENTS OF THE SECOND LAW

The influential British scientist and novelist C. P. Snow once called the second law of thermodynamics the scientific equivalent of the works of Shakespeare. That's a pretty strong statement. What exactly is this second law of thermodynamics, and why is it so important?

Throughout the universe, the behavior of energy is regular and predictable. According to the first law of thermodynamics, the total amount of energy is constant, although it may change from one form to another over and over again. Energy in the form of heat flows from one place to another by conduction, convection, and radiation. But the net energy flow goes in only one direction. Hot things tend to cool off; cold things tend to warm up; and an egg, once broken, can never be reassembled. These examples illustrate the concept of the second law of thermodynamics—one of the most fascinating and powerful ideas in science.

The **second law of thermodynamics** places restrictions on the ways heat and other forms of energy can be transferred and used to do work. We explore here three different statements of this law. The first and most intuitive of these statements is that heat does not flow spontaneously from a cold body to a hot body. The second statement follows from the first: you cannot construct an engine that does nothing but convert heat completely to useful work. The third, more subtle statement of the second law is that every isolated system becomes more disordered with time. We consider these ideas in the following section of the chapter.

Although these three statements appear to be very different, they are actually equivalent. Given any one statement of the second law of thermodynamics, you can derive either of the other two as a consequence. For example, given the statement that heat flows only from hot to cold objects, a physicist can produce a set of mathematical steps that show that no engine can convert heat to work with 100% efficiency, which is another way of saying the second statement. In this sense, the three statements of the second law all say the same thing.



The second law of thermodynamics says that heat always flows from a warm body (the air) to a cold one (the ice cream).

Heat Does Not Flow Spontaneously from a Cold Body to a Hot Body

The first statement of the second law of thermodynamics refers to the relative temperatures of two objects. If you take an ice cream cone outside on a hot summer afternoon, it melts. Heat flows from the warm atmosphere to the cold ice cream and causes its temperature to rise above the melting point. By the same token, if you take a cup of hot chocolate outside on a cold day, it cools as heat energy flows from the cup to the surroundings.

From the point of view of energy conservation, there is no reason why energy should necessarily work this way. Energy would be conserved if thermal energy stayed put or even if heat flowed from an ice cream cone to the warm atmosphere, making the ice cream colder than it was at the beginning. Our experience (and many an experimental confirmation) convinces us that heat flows spontaneously in only one direction—from hot to cold. It does not go the other way on its own. This everyday observation may seem trivial, but in this statement is hidden all the mystery of those changes that make the future different from the past: the directionality of time in the universe.

If you think about energy at the molecular level, the explanation of this version of the second law is easy to see. If two moving objects of the same mass collide and one of them is moving faster than the other, chances are that the slower object will speed up and the faster object will slow down. It's possible, but very unlikely, that events will go the other way. Thus, as we saw in the discussion of heat conduction, faster-moving molecules tend to transfer some of their energy to slower-moving ones. On the macroscopic scale, this process is seen as heat flowing from the warm regions to cold ones by conduction.

For the second law to be violated, the molecules in a substance would have to collide in such a way that slower-moving molecules slowed down even more, giving up their energy to faster molecules so they could go even faster. Our experience tells us that this situation doesn't happen. The second law of thermodynamics takes this experience and makes it into a general law of nature.

The second law does *not* state that it's impossible for heat to flow from a colder object to a hotter object. Indeed, you know that's exactly what happens in a refrigerator. When the refrigerator is operating, it removes heat energy from the colder inside to the warmer outside (Figure 13-2). You can verify this fact by putting your hand behind the refrigerator and feeling the warm air. The second law merely states that this action cannot take place *spontaneously,* of its own accord. If you wish to cool something in this way, you must supply energy. In fact, an alternative statement of the second law of thermodynamics could be, "a refrigerator won't work unless it's plugged in."

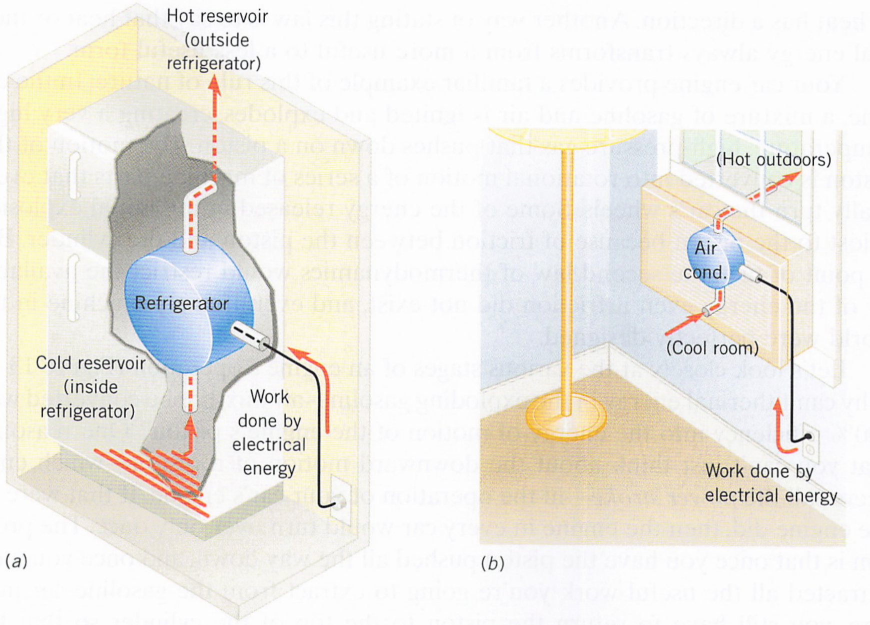


FIGURE 13-2. (*a*) A refrigerator uses electric energy to remove heat from the inside cold reservoir and deposit it in the outside hot reservoir. (*b*) A window air conditioner works the same way to remove heat from a room and send it outside. In both cases the heat output is equal to the sum of the heat input plus the work done.

The second law doesn't tell you that you can't make ice cubes, only that you can't make ice cubes without expending energy. Paying the electric bill, of course, is another piece of our everyday experience.

You Cannot Construct an Engine That Does Nothing but Convert Heat Completely to Useful Work

The second statement of the second law of thermodynamics restricts the way we use energy. Recall that *energy* is defined as the ability to do work. This second statement of the second law tells us that whenever energy is transformed from heat to some other type of energy—from heat to electric energy, for example—some of that heat must be dumped into the environment and is unavailable to do work. The energy is neither lost nor destroyed, but it can't be used to make electricity to play your radio or fuel to drive your car.

Physicists and engineers use the term *efficiency* to quantify the percentage of useful energy an engine can deliver. **Efficiency** is the amount of work you get from an engine, divided by the amount of energy you put into it. In Chapter 12 we learned that different forms of energy are interchangeable and that the total amount of energy is conserved. According to the first law of thermodynamics, there is no reason why energy in the form of thermal energy can't be converted to electric energy with 100% efficiency. However, the second law of thermodynamics tells us that such a process isn't possible. The flow of energy in the form of heat has a direction. Another way of stating this law is to say that heat or thermal energy always transforms from a more useful to a less useful form.

Your car engine provides a familiar example of this rule of nature. In the engine, a mixture of gasoline and air is ignited and explodes, creating a very high-temperature, high-pressure gas that pushes down on a piston. The motion of this piston is converted into rotational motion of a series of machine parts that eventually turn the car's wheels. Some of the energy released in the initial explosion is lost to the piston because of friction between the piston and the cylinder. But in point of fact, the second law of thermodynamics would restrict the availability of the energy even if friction did not exist, and even if every machine in the world were perfectly designed.

Let's look closely at the various stages of an engine's operation (Figure 13-3). Why can't thermal energy in the exploding gasoline–air mixture be converted with 100% efficiency into the energy of motion of the engine's piston? One reason is that you can't just think about the downward motion of a piston—which engineers call the *power stroke*—in the operation of your car's engine. If that were all the engine did, then the engine in every car would turn over only once. The problem is that once you have the piston pushed all the way down, and once you have extracted all the useful work you're going to extract from the gasoline–air mixture, you still have to return the piston to the top of the cylinder so that the cycle can be repeated. (In actuality, the pistons in modern cars go down, up, and down again before they get back to the point where they can return energy

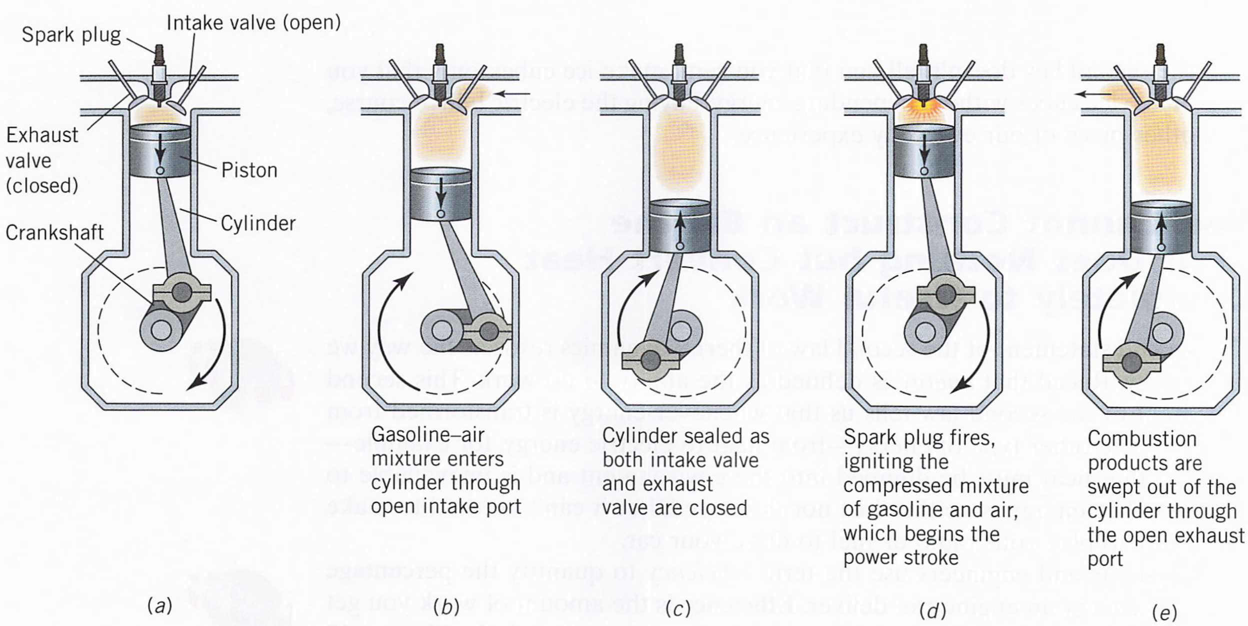


FIGURE 13-3. The cycle of an automobile engine's piston. (*a*) The beginning of the intake stroke; (*b*) the middle of the intake stroke as a gasoline–air mixture enters the cylinder; (*c*) the beginning of the compression stroke; (*d*) the beginning of the power stroke when the spark plug fires, igniting the compressed mixture of gasoline and air; (*e*) the beginning of the exhaust stroke when combustion products are swept out. Note that each cycle involves two complete rotations of the crankshaft.

to the system.) In order to reset the engine to its original position so that more useful work can be done, some heat has to be dumped into the environment.

Ignore for a moment the fact that a real engine is more complicated than the one we're discussing. Suppose that all you had to do was to lift the piston up after the work had been done. The cylinder is full of air and, consequently, when you lift the piston up, the air is compressed and heated. In order to return the engine to the precise state it was in before the explosion, the heat from this compressed air has to be removed. In practice, it is expelled into the atmosphere as exhaust.

When the hot gas is absorbed into the atmosphere, the temperature of the atmosphere doesn't change significantly. After all, there's a lot more atmosphere than there is exhaust gas from a car. In such a situation, physicists call the atmosphere a "low-temperature reservoir," since it doesn't change its temperature. In a car engine, the hot gasoline–air mixture is constantly renewed at the same temperature; as a result, we can say it acts as a "high-temperature reservoir," losing some energy without lowering its temperature. The second law of thermodynamics says that any engine operating between two temperatures must dump some energy in the form of heat into the low-temperature reservoir. This heat is energy that flows through the engine, but that energy can't be used to do work. You can see how this works in the gasoline engine when the hot air produced in resetting the piston must be expelled as exhaust.

The consequence of this situation is that some of the energy stored in the gasoline can be used to run the car, but some must be dumped into the low-temperature reservoir of the atmosphere. Once that heat energy has gone into the atmosphere, it can no longer be used to run the engine. That energy simply dissipates and is no longer available. Thus, this version of the second law tells us that any real engine, or even an engine in which there is no friction, must waste some of the energy that goes into it. The engine works better if the difference between its hot input temperature and cold output temperature is as large as possible, but, no matter how large the difference, perfect efficiency is simply not possible.

This version of the second law of thermodynamics explains why petroleum reserves and coal deposits play such an important role in the world economy. They are high-grade and nonrenewable sources of energy that can be burned to produce very-high-temperature reservoirs. But no matter what we do, when these fossil fuels are burned to produce that high-temperature reservoir and generate electricity, a large portion of energy is then wasted.

Although the second law applies to engines that work in cycles, it does not apply to many other uses of energy. No engine is involved if you burn natural gas to heat your home or use solar energy to heat water, for example. In other words, burning fossil fuels or employing solar energy to heat your home directly can be considerably more efficient than using these fuels to generate electricity and then heating your home with electricity.

Develop Your Intuition: Materials for Jet Engines

Jet engines do not generally use simple steel or aluminum parts. Instead, they are made with special alloys and ceramic materials that can withstand very high temperatures, over 1000°C. Why is such high-temperature resistance necessary?

The exhaust gases of a jet engine are emitted to the atmosphere, so the output temperature cannot be adjusted. Therefore, for increased engine efficiency, the temperatures inside the engine should be as high as possible. Specially designed materials are needed to operate at these high temperatures without melting or becoming soft.

LOOKING DEEPER

Efficiency

The second law of thermodynamics can be used to calculate the maximum possible efficiency of an engine. Let's say that the high-temperature reservoir is at a temperature T_{hot} and the low-temperature reservoir is at a temperature T_{cold} (where all temperatures are measured using the Kelvin scale). Then the maximum theoretical efficiency—the percentage of energy available to do useful work—of any engine in the real world can be calculated as follows:

1. In words:

Efficiency is obtained by comparing the temperature difference between the high-temperature and low-temperature reservoirs, with the temperature of the high-temperature reservoir.

2. In an equation with words:

Efficiency (in percent) =

$$\frac{\text{Temperature}_{hot} - \text{Temperature}_{cold}}{\text{Temperature}_{hot}} \times 100$$

3. In an equation with symbols:

$$e = \frac{T_{hot} - T_{cold}}{T_{hot}} \times 100\%$$

In a real machine, any loss of energy due to friction in pulleys, gears, or wheels will make the actual efficiency less than this theoretical maximum. This maximum possible efficiency is a very stringent constraint on real engines.

Consider the efficiency of a normal coal-fired generating plant. The temperature of the high-energy steam (the hot reservoir) is about 550 kelvins, while the temperature of the air into which waste heat must be dumped (the low-temperature reservoir) is around room temperature, or 300 kelvins. The maximum possible efficiency of such a plant is given by the second law as

$$\text{Efficiency (in percent)} = \frac{T_{hot} - T_{cold}}{T_{hot}} \times 100$$

$$= \frac{550 - 300}{550} \times 100$$

$$= 45.5\%$$

In other words, more than half of the energy produced in a typical coal-burning power plant must be dumped into the atmosphere as waste heat. This fundamental limit is independent of the engineers' ability to design the plant to operate efficiently. In fact, engineers have succeeded in making most generating plants operate within a few percent of the optimum efficiency allowed by the second law of thermodynamics. Figure 13-4 shows the maximum possible efficiency of an engine when the low temperature reservoir is at a temperature of 300 K.

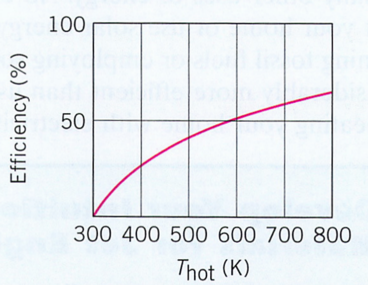


FIGURE 13-4. The maximum possible efficiency of an engine when the low temperature reservoir is the outside air at a temperature of 300 K.

EXAMPLE 13-1

Power Generation in Space

What improvement in efficiency might you obtain for a coal-burning power plant on the Moon, where the cold reservoir is 105 K?

SOLUTION AND REASONING: Apply the equation for efficiency.

$$\text{Efficiency (in percent)} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}} \times 100$$

$$= \frac{550 - 105}{550} \times 100$$

$$= 80.9\%$$

This is 35.4 percent higher than the maximum possible efficiency of a coal-burning power plant on Earth. On the Moon the efficiency of such a power plant would be much higher than on Earth because less energy is wasted as exhaust heat. ●

EXAMPLE 13-2

Steam Engines

What is the maximum efficiency of a steam engine that employs boiling water and dumps its waste heat into ice water?

SOLUTION AND REASONING: Again, apply the equation for efficiency, making sure to use temperature in the Kelvin scale (the temperatures of freezing and boiling water are 273 and 373 K, respectively).

$$\text{Efficiency (in percent)} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}} \times 100$$

$$= \frac{373 - 273}{373} \times 100$$

$$= 26.8\%$$

Today, even the best steam engines use less than one-third of the potential energy stored in coal or gas. But before these thermodynamic principles were understood, typical steam engine efficiencies were a meager 6%. Here's a clear case where the theoretical understanding of energy has led to dramatic benefits to society by showing that better efficiency was possible. ●

Every Isolated System Becomes More Disordered with Time

The third statement of the second law of thermodynamics, that every isolated system becomes more disordered with time, is in many ways the most profound. It tells us something about the order of the universe itself. Consequently, this idea of increasing disorder in the universe is perhaps the most familiar way of looking at the second law.

Order and Disorder To understand what the third statement of the second law means, you have to understand what a physicist means by the terms "order" and

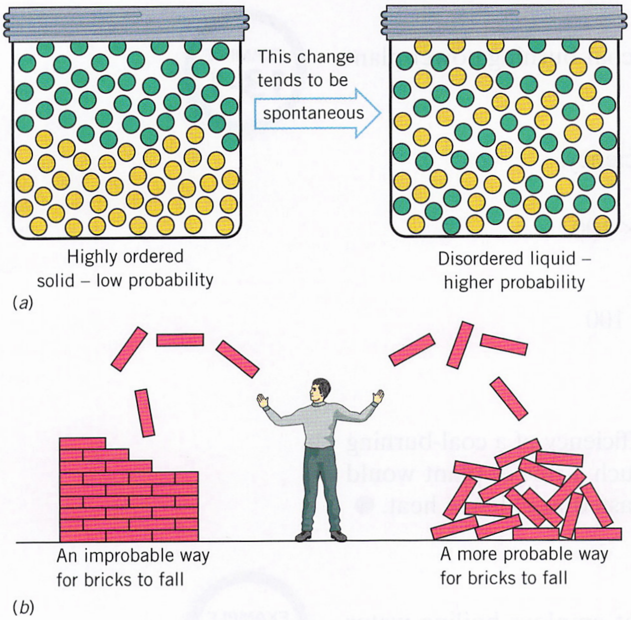


FIGURE 13-5. Highly ordered, regular patterns of objects are less likely to occur than disordered, irregular patterns.

"disorder" (Figure 13-5). An ordered system is one in which some number of objects, be they atoms or automobiles, are positioned in a completely regular and predictable pattern. For example, atoms in a perfect crystal or automobiles in a perfect line are highly ordered systems. A disordered system, on the other hand, contains objects that are randomly situated, without any obvious pattern. Atoms in a gas or automobiles after a multicar pile-up on the freeway are good examples of more disordered systems.

We can devise countless simple experiments to illustrate the phenomenon of increasing disorder. For instance, take a deck of cards and put all the cards in order, by suit and by number. Then shuffle the deck of cards and see what happens. It becomes disordered—never the other way around. You can shuffle these cards a million million times, and chances are that they will not become reordered. In fact, even if you deal out only five cards, the chances of having a winning hand in poker are pretty slim (see Table 13-1).

Another simple experiment involves carefully layering two different colors of marbles or candy in a jar. Gently shake the jar and see what happens. The colors quickly become mixed up—never the other way around. You could shake the jar for a million years, and chances are the two colors would not separate into layers.

Highly ordered arrangements of cards are much less likely than disordered arrangements.

TABLE 13-1 Probabilities of Types of Poker Hands Dealt in the First Five Cards

Type of Hand	Probability
No pair	1 in 2
One pair	1 in 2.5
Two pair	1 in 21
Three of a kind	1 in 47
Straight	1 in 255
Flush	1 in 509
Full house	1 in 694
Four of a kind	1 in 4165
Straight flush	1 in 72,193
Royal flush	1 in 649,740

Note: Number of possible poker hands = 2,598,960

Yet another version of this simple experiment can be done with food coloring and water. Plop a drop of food color into a jar of water. Gradually, the molecules of the food coloring disperse through the water. The same thing is true of perfume or cologne: you put it on in the morning and by evening it's all gone, dispersed into the air. The molecules of perfume never spontaneously coalesce into a droplet.

This behavior of molecules, which spontaneously disperse, also applies to the distribution of velocities of particles in a gas. Imagine what happens when you mix two reservoirs of gas that are initially at different temperatures; for example, one gas at 0°C and a second gas at 100°C. The separation of gas particles into two distinct populations is a more ordered state, just like the separation of red and white marbles in a jar or the separation of pure water and a drop of food coloring. It's also an inherently unstable situation. As the gases mix, the temperature averages out—the system becomes more disordered.

Food dye disperses in water; it never stays clumped together or goes back to being a single drop.

Entropy Defined **Entropy** is a measure of the disorder in a physical system. In terms of entropy, the statement of the second law reads:

The entropy of an isolated system remains constant or increases.

In other words, any system left to itself will change in the direction of the most disordered state. Without careful chemical controls, atoms and molecules tend to become more intermixed; without careful driving, automobile traffic also tends to become more disordered.

The example of food coloring and water reveals how such a process works. In the most likely situation, when molecules of water and food coloring are randomly mixed, the entropy is maximized. In the much less probable case of food coloring molecules coalescing in the water, the entropy is lower because the molecules are more ordered. Another way of saying this is that systems tend to avoid states of high improbability.

Probabilities in Nature The definition of entropy as a measure of disorder may seem a bit fuzzy, but the Austrian physicist Ludwig Boltzmann (1844–1906) placed it on a firm quantitative footing in the late nineteenth century. Boltzmann was born in Vienna and studied at the University of Vienna, where he spent most of his professional life as professor of theoretical physics. He was said to be an imposing man of physical strength combined with sensitivity and humor. But he also suffered from severe bouts of depression, and it was during one of those spells that he took his own life in 1906. Boltzmann used probability theory to demonstrate that, for any given configuration of atoms, the mathematical value of entropy is related to the number of possible ways you can achieve that configuration.

To get a feel for this idea, consider three orange balls numbered 1, 2, and 3, and three green balls numbered 4, 5, and 6. Ask yourself how many different ways there are to arrange these six balls in a row (Figure 13-6). There are six different possibilities for the location of the first ball, then five possibilities for the second, four for the third, and so on. If you multiply that out, you get

$$6 \times 5 \times 4 \times 3 \times 2 \times 1 = 720$$

It turns out that there are 720 ways to arrange these six numbered balls in a row—720 different possible configurations.

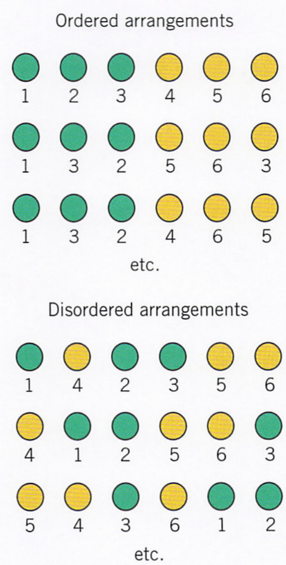


FIGURE 13-6. Ordered and disordered arrangements of six numbered balls (three orange and three green).

Now, how many of those arrangements have the ordered state with three orange balls followed by three green balls? There are exactly six different ways to arrange three orange balls ($3 \times 2 \times 1$), and then six different ways to arrange the three green balls. Altogether, that's 6×6, or 36, different configurations with three orange balls followed by three green balls out of 720 total configurations. Only 5% of all possible arrangements (36/720) are ordered in this way. All of the remaining 684 configurations are different. So, by a 19:1 margin, these other arrangements are much more probable, because there are many more ways to achieve a disordered state than an ordered one.

You can repeat this exercise for other numbers of balls (see Problems 5–7 at the end of the chapter). For a sequence of ten balls (five orange and five green), it turns out that there are more than 3.6 million different configurations, but only 120 of those sequences have five orange followed by five green balls. That's only 0.003% of all possible arrangements!

As the number of objects increases from 6 to 10 to trillions of trillions (as we find in even a few grams of atoms), the fraction of arrangements that is highly ordered becomes infinitesimally small. In other words, highly ordered configurations are improbable because almost every possible configuration is disordered.

The second law of thermodynamics and the behavior of entropy can thus be traced, ultimately, to the laws of probability. If you hold a glass of water in your hand, for example, its atoms are moving at more or less the same average velocity. It is extremely unlikely that the atoms will ever arrange themselves in such a way that one atom moves very fast in a collection of very slow ones. Over the course of time, any unlikely initial state like this evolves into a more probable state.

The concept of probability explains a number of paradoxes that puzzled scientists around the turn of the twentieth century. For example, it's possible that all the air molecules in the room in which you are sitting could suddenly rush over to one side of the room, leaving you in a perfect vacuum. You don't worry about this happening because you know that this event is highly unlikely. In fact, the probability is so low as to make it extremely unlikely you would see it happen even if you waited the entire lifetime of the universe.

Decreasing Entropy While systems tend to become more disordered, the second law does not require *every* system to approach a state of lower order. Think about water, a substance of high disorder because water molecules are arranged at random. If you put water into a freezer, it becomes an ice cube, a much more ordered state in which water molecules have formed a regular crystalline structure. By placing water in the freezer you have caused a system to evolve to a state of higher order. How can this ordering be reconciled with the statement that isolated systems become more disordered?

The answer to this paradox is that this statement refers *only* to systems that are isolated. The refrigerator in which you make the ice cubes is not an isolated system because it has a power cord plugged into the wall socket that is ultimately connected to a generating plant. The isolated system in this case is the refrigerator, the generating plant, and their immediate environments. The second law of thermodynamics says that in this particular isolated system, the total entropy must increase. However, it does not say that the entropy has to increase in all the subparts of the system.

In this example, one part of the system (the ice cube) becomes more ordered, while another part of the system (burning fuel and the surrounding air at the generating plant) becomes more disordered. All that the second law requires is that the amount of disorder at the generating plant be greater than the amount of order at the ice cube. As long as this requirement is met, the second law is not violated. In fact, in this particular example the disorder at the generating plant greatly exceeds any possible order that could take place inside the refrigerator.

Physics in the Making

The Heat Death of the Universe

Some intellectuals viewed the nineteenth-century discovery of the second law of thermodynamics as a gloomy event. The prevailing philosophy of the time was that life, society, and the universe in general were on a never-ending upward spiral of progress. Darwin's 1859 publication of *On the Origin of Species,* which proposed that more complex forms of life could evolve from less complex forms, reinforced this particular notion of an ever-improving world. In this optimistic climate, the discovery that the energy in the universe was being steadily and irrevocably degraded was difficult for nineteenth-century scientists and philosophers to accept.

In fact, they felt that the second law inevitably meant that all the energy in the universe would eventually be degraded into waste heat and that everything in the universe would eventually be at the same temperature. They called this depressing end the "heat death" of the universe, and they saw it as the ultimate effect of the laws of thermodynamics. For example, the hero of the famous story *The Time Machine,* written by H. G. Wells in 1895, travels to a far distant future in which the Sun and the stars have all burned themselves out and the cold, dark Earth remains. Today, we realize that even if the universe does end in frozen desolation, such a demise will not occur for many hundreds of billions of years. ●

CONSEQUENCES OF THE SECOND LAW

The Arrow of Time

We live in a world of four dimensions. Three of these dimensions define space and have no restrictions on the directions that you can travel. You can go east or west, north or south, and up or down in our universe. But the fourth dimension, time, behaves differently. Time has direction; we can never revisit the past.

Take one of your favorite home movies or just about any videotape and play it in reverse. Chances are that before too long you'll see something silly—something that couldn't possibly happen that will make you laugh. Springboard divers fly out of the water and land completely dry on the diving board. From a complete stop, golf balls roll along the ground and then fly off toward the tee. Ocean spray coalesces into smooth waves that recede from shore. Most physical laws, such as Newton's laws of motion or the first law of thermodynamics, say nothing about the direction of time. The motions predicted by Newton and the conservation of energy are independent of time—they work just as well if you play a video forward or backward.

The second law of thermodynamics is different: it takes into account a *sequence* of events. For example, heat flows from hot to cold, fuels burn to produce waste heat, the disorder of isolated systems never spontaneously decreases, and we all must get older. Time has a direction. We experience the passage of events as dictated by the second law. Scientists cannot answer the deeper philosophical question of why the arrow of time goes in only one direction, but through the second law they can describe how the effects of that directionality come about.

The tendency of all systems to change from an improbable to a more probable state accounts for this directionality of time that we see in the universe. From the point of view of the first law of thermodynamics, there is no reason that improbable situations can't occur. Fifteen slow-moving billiard balls have enough energy to produce one fast-moving ball. The fact that this situation doesn't occur in nature is an important clue as to how things work at the atomic level (see Figure 13-1).

Built-In Limitations of the Universe

The second law of thermodynamics has both practical and philosophical consequences. It poses severe limits on the ways in which humans can manipulate nature and on the way that nature itself operates. It tells us that some things cannot happen in our universe. In terms of energy, the first law says you can't get something for nothing. The second law says you can't break even.

At the practical level, the second law tells us that if we continue to generate electricity by burning fossil fuels or by nuclear fission, we are using up a good deal of the energy that is locked up in those concentrated nonrenewable resources. These limitations are not a question of sloppy engineering or poor design—they're simply built into the laws of nature. If you could design an engine or other device that extracted energy from coal and oil with higher efficiency than the second law allows, then you could also design a refrigerator that worked when it wasn't plugged in. Over the years, many inventors have tried to do just this, creating machines that supposedly could provide more work as output than they take in as heat or other energy. None of these so-called perpetual motion machines work this way and, according to the laws of thermodynamics, you simply cannot make such a machine. Some attempts have been quite ingenious, but there is always a flaw in the design that requires more energy than the machine can produce.

At the philosophical level, the second law tells us that nature has a built-in hierarchy of more useful and less useful forms of energy. The lowest or least useful state of energy is the reservoir into which all energy eventually gets dumped. Once the energy is in that reservoir, it can no longer be used to do work. For Earth, energy passes through the region that supports life, the *biosphere,* but is eventually lost as it is radiated into the black void of space.

Physics in the Making

America's First Theoretical Physicist

Most of the great names in American physics have been experimentalists. Starting with Benjamin Franklin (Chapter 16) and Benjamin Thompson (Chapter 11), American physicists were a practical lot, looking for ideas that would lead to specific improvements in machines or would resolve particular problems. The major exception was one of the leading theoretical scientists of the nineteenth century, Josiah Willard Gibbs (1839–1903).

Gibbs came from an old New England family and lived quietly in New Haven, Connecticut, all his life. He started out as an engineer and was the first American ever to receive a Ph.D. in engineering. However, afterward he spent two years studying in Europe and became more interested in mathematical and theoretical physics. He was appointed Professor of Mathematical Physics at Yale in 1871, at the age of 32.

Gibbs studied how matter changes, in the most general ways. He developed the idea that is now called the "Gibbs free energy," one of the key concepts in determining whether a given chemical reaction will take place spontaneously. The Gibbs free energy combines two quantities: the first quantity is related to the chemical potential energy of the reactants and the second quantity is related to the entropy of the reactants. Gibbs showed that a reaction is determined by entropy considerations as much as by energy differences.

Despite the fundamental importance of his work, Gibbs was notoriously modest about himself. He published his work in the local *Transactions of the Connecticut Academy of Science,* which was seldom read by anyone outside the Yale community. However, Gibbs mailed copies of his articles to scientists around the world whose work might be affected by his own findings. Most other scientists could not follow his subtle and mathematically demanding work, but two of the great physicists of the time—James Clerk Maxwell and William Thomson, Lord Kelvin—recognized the brilliant work Gibbs was doing and gave lectures on his results to other European scientists.

Gibbs is now considered the founder of physical chemistry, establishing the physical principles that govern all chemical reactions. He also helped to establish the area of physics known as "statistical mechanics," which connects the laws of thermodynamics to the behavior of systems with large numbers of particles. It has been said that of all the great theories advanced in the nineteenth century, only the work of Gibbs continues to stand without serious changes after the new ideas of physics came along in the twentieth century. ●

THINKING MORE ABOUT

The Second Law: Evolution and Entropy

Entropy is such an important concept, so fundamental to the working of the universe, that it appears in many discussions that seem to have little to do with heat transfer. Economists, for example, use it to discuss disordered aspects of the economy, and communications engineers routinely use it to discuss the information (i.e., order) in radio and other transmissions. But perhaps the most interesting place where entropy crops up is in the intense debate about the origin of life on Earth.

Creationists, who believe that life appeared as the result of a single miraculous creation a few thousand years ago, point out that every life form is a highly ordered system—a system in which trillions of atoms and molecules must occur in exactly the right sequence. They argue that life could not possibly have arisen spontaneously without violating the second law. How, they ask, could a natural system go spontaneously from a disordered state of nonlife to the ordered state containing life?

This argument fails to take into account the fact that Earth is not itself an isolated system. The energy that drives living systems is sunlight, so that the isolated system that the second law speaks of comprises Earth *plus the Sun.* To make the evolution of life consistent with the second law, the increased order observed in living things must be offset by an even greater amount of disorder in the Sun. Once again, as with the earlier example of the ice cube, this requirement is easily met by the Sun and Earth taken together.

Science cannot yet describe in detail how life arose, and some aspects of the process may never be known for sure. The scientific method, for example, is not an appropriate way to answer the question whether God was involved in the origin of life (see Chapter 1). However, science can help explain how the development of life, as a natural process, is consistent with the universal laws of thermodynamics.

Summary

The first law of thermodynamics promises that the total amount of energy never changes, no matter how you shift it from one form to another. The **second law of thermodynamics** places restrictions on how energy can be shifted. Three different but equivalent statements of the second law underscore these restrictions:

1. Heat does not flow spontaneously from a colder body to a hotter body.
2. It is impossible to construct a machine that does nothing but convert heat completely into useful work. That is, no engine can operate with 100% **efficiency.**
3. The **entropy** (measure of disorder) of an isolated system never decreases.

Key Terms

efficiency A measure of how much useful work you can get from an engine; it is equal to the work done by an engine divided by the heat input to the engine. (p. 273)

entropy A measure of the disorder in a system. (p. 278)

second law of thermodynamics The law of physics that places restrictions on the ways heat and other forms of energy can be transformed and used to do work. (p. 271)

Key Equation

$$\text{Efficiency (in percent)} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}} \times 100$$

Review

1. What is the first law of thermodynamics? What is meant by the directionality of energy flow? Does the first law of thermodynamics deal with the directionality of energy flow?
2. State the second law of thermodynamics in three different ways. Do they all say essentially the same thing?
3. Does the fact that heat does not flow spontaneously from a cold to a hot body violate the first law of thermodynamics in any way? Explain.
4. Give a molecular-level explanation of why heat does not flow spontaneously from a cold body to a hot body.
5. Why does a refrigerator that facilitates the flow of heat from a cool interior to a warm exterior not violate the second law? What must be supplied for this to happen?
6. If energy is defined as the ability to do work, can you construct an engine that does nothing but completely convert the energy in heat to useful work? Explain.
7. What is meant by the efficiency of an engine? Does the first law of thermodynamics preclude the construction of a 100% efficient engine? What about the second law?
8. Explain in terms of the motion of a piston why 100% efficiency in an engine is not possible.
9. What is the high-temperature reservoir in your car's engine? What is the low-temperature reservoir?
10. Why are petroleum reserves and coal deposits so important in producing a relatively efficient use of energy?
11. Does the second law apply to other uses of energy, such as heating your home with natural gas? Explain.
12. Identify three examples of the second law of thermodynamics in action that have occurred since you woke up this morning.
13. Why would a power plant in outer space be potentially very efficient?

14. What do physicists mean by the terms order and disorder?
15. Which type of system does the second law say the universe is going toward, a more ordered or a more disordered one?
16. What is entropy? What does the second law say about entropy?
17. What was Boltzmann's contribution toward the understanding of entropy?
18. Why are highly ordered configurations of objects improbable?
19. How do the laws of probability explain the behavior of entropy and the second law of thermodynamics? How likely is it that objects will be in an ordered state given the nearly infinite possible configurations available to systems with many objects in them? Explain.
20. Does the second law require *every* system to approach a state of lower order? Explain.
21. Give examples of ordered systems in nature. Give examples of disordered systems.
22. Do Newton's laws of motion have a direction in time? Why or why not?
23. Does the first law of thermodynamics have a direction in time? Why or why not?
24. What does the second law have to say about the directionality of time? How is probability involved?
25. Does the second law support a creationist view of the origin of the universe? Explain.

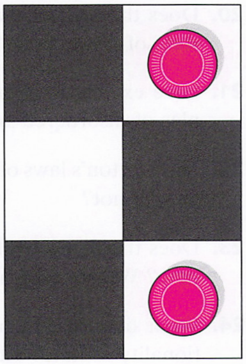
Questions

1. Why don't all the atoms in the room you're sitting in move to one side, leaving you in a vacuum?
2. Why are there big cooling stacks around nuclear reactors and coal-fired generating plants?
3. "Cogeneration" is a term used to describe systems in which waste heat from electric generating plants is used to heat nearby homes. Such systems achieve efficiencies much greater than 50%. Does cogeneration violate the second law? Why or why not?
4. Why is a perpetual motion machine impossible?
5. Seawater is full of moving molecules that possess kinetic energy. Could we extract this energy from seawater? Why or why not?
6. When ice freezes, water goes from a state of larger disorder to one with more order. Does this violate the second law of thermodynamics? Explain.
7. In the equation defining efficiency, why must you always use the Kelvin temperature scale? (*Hint:* Consider the effects of a temperature's sign and also of dividing by 0.)
8. Two systems contain vastly different amounts of internal energy. For the sake of definiteness, let's assume that system A contains 1,000,000 joules of internal energy and system B contains 100 joules of internal energy. Is it possible to say which direction heat will flow if these two systems are placed in thermal contact? Why or why not?
9. A cube of aluminum metal is placed in contact with a cube of copper metal. The average speed of the atoms in each metal is the same. Which way does heat flow? Explain. (*Hint:* Look at the periodic table to find the atomic masses of aluminum and copper. Which cube is at a higher temperature?)
10. During a complete cycle of an engine, the net internal energy change is 0. During that cycle, an amount of heat Q_{in} enters the engine, an amount Q_{out} leaves the engine, and an amount of work W is done. The following table lists these quantities (in joules) for a variety of engines. Which of these engines violates the first law of thermodynamics (energy in equals energy out)? Which of these engines violates the second law of thermodynamics?

Engine	Q_{in}	Q_{out}	W
A	100	100	0
B	100	50	50
C	100	0	100
D	100	20	60
E	100	100	50

11. Imagine that it were possible to construct a reservoir at -5 K (below absolute zero). Suppose you ran an engine and used the -5 K reservoir as the cold reservoir. Why would such an engine violate the second law of thermodynamics?
12. An ice cube melts on the warm sidewalk on a hot summer day. What happens to the entropy of the ice cube? What happens to the entropy of the pavement? What happens to the entropy of the ice cube–sidewalk system?
13. You roll two six-sided dice. Why are you much more likely to roll a total of 7 than a total of 2?
14. A large parking lot contains 50 identical cars. Which is a higher entropy situation: when the cars are allowed to park anywhere, or when the cars are forced to park in between the lines in designated spaces? Explain in terms of the number of possible configurations of the system.
15. How many different ways are there to arrange five coins in a row if one is heads-up and the other four are tails-up (see figure)? What if two were heads-up and three were tails-up?

16. Two identical poker chips are placed on a board that is divided into a 2 × 3 checkerboard arrangement (see figure). If they are allowed to be on any two squares on the left half of the board, how many arrangements are there? What if they are allowed to be on any two squares on the board? What does this question have to do with entropy? (*Hint:* It may help to sketch all of the possible arrangements.)



17. Why do we say that the liquid state is more disordered than the solid state? Explain in terms of the number of possible arrangements of the atoms or molecules.

Problems

1. What is the theoretical efficiency of an engine that has a hot reservoir of 600 kelvins and a low-temperature reservoir of 300 kelvins?
2. If a steam engine has a high-temperature reservoir of 100°C and a low-temperature reservoir of 10°C, what is its maximum possible efficiency? What would be the efficiency if the low-temperature reservoir had a temperature of 278 K?
3. Calculate the maximum possible efficiency of a power plant that burns natural gas at a temperature of 600 kelvins, with low-temperature surroundings at 300 kelvins. How much more efficient would the plant be if it were built in the Arctic, where the low-temperature reservoir is at 250 kelvins? Why don't we build all power plants in the Arctic?
4. The Ocean Thermal Electric Conversion system (OTEC) is an example of a high-tech electric generator. It takes advantage of the fact that in the tropics, deep ocean water is at a temperature of 4°C, while the surface is at a temperature around 25°C. The idea is to find a material that boils between these temperatures. The material in the fluid form is brought up through a large pipe from the depths, and the expansion associated with its boiling is used to drive an electrical turbine. The gas is then pumped back to the depths, where it condenses back into a liquid and the whole process repeats.
   a. What is the maximum efficiency with which OTEC can produce electricity? (Hint: Remember to convert all temperatures to the Kelvin scale.)
   b. Why do you suppose engineers are willing to pursue the scheme, given your answer in (a)?
   c. What is the ultimate source of the energy generated by OTEC?
5. You have a collection of eight numbered balls; 1 through 4 are orange and 5 through 8 are green. How many different arrangements of these balls in a line are possible?
6. What percentage of those arrangements in Problem 5 have four orange balls followed by four green balls?
7. Repeat problems 5 and 6 for a collection of twelve numbered balls (six orange and six green).
8. In Problems 5–7, what happens to the probability of an ordered configuration as the total number of balls increases?

Investigations

1. Play a home movie or videotape backward. How many violations of the second law of thermodynamics can you spot?
2. Research the development of the steam engine. How efficient were the first steam engines and how was the efficiency eventually improved over time? Who were the people responsible for these improvements? Alternatively, do the same research for the automobile engine.
3. Spend a bit of time writing down all the ordered and disordered groups of objects or systems you see in a typical day. Write a very brief hypothesis for each group or system about the likelihood of the ordered and disordered items becoming, respectively, disordered and ordered. Estimate the time within which this will occur. Check this diary at a later date to see if your hypotheses were correct. Are your expectations consistent with what you learned in this chapter?
4. Investigate the history of perpetual motion machines. What were some of the different types of machines imagined and built, and what were the problems associated with them?
5. Investigate and research the Carnot cycle, which is a more formal explanation of the version of the second law that says you cannot construct an engine that does nothing but

convert heat completely to useful work. As part of your research, find and read a short biography of the French scientist Sadi Carnot, who was a key figure in the improvement of heat engines.

6. Investigate the design of waterwheels, which are machines that convert the gravitational potential energy of water into mechanical energy. What factors prevent such a wheel from operating with 100% efficiency?

WWW Resources

See the *Physics Matters* home page at **www.wiley.com/college/trefil** for valuable web links.

1. **http://www.stirlingengine.com** A discussion of the stirling engine.
2. **http://electron4.phys.utk.edu/141/nov19/November%2019.html** A discussion of entropy and ocean currents.
3. **http://filebox.vt.edu/eng/mech/scott/index.html** A collection of thermodynamic cycles, including steam engines and refrigerators.
4. **http://www.taftan.com/thermodynamics/** Another collection of applied thermodynamics examples and descriptions, together with the laws of thermodynamics.