Check Your Understanding

5. What is pressure?
   a. Pressure is force divided by length.
   b. Pressure is force divided by area.
   c. Pressure is force divided by volume.
   d. Pressure is force divided by mass.

6. What is the SI unit for pressure?
   a. pascal, or N/m^3
   b. coulomb
   c. newton
   d. pascal, or N/m^2

7. What is pressure-volume work?
   a. It is the work that is done by the compression or expansion of a fluid.
   b. It is the work that is done by a force on an object to produce a certain displacement.
   c. It is the work that is done by the surface molecules of a fluid.
   d. It is the work that is done by the high-energy molecules of a fluid.

8. When is pressure-volume work said to be done ON a system?
   a. When there is an increase in both volume and internal pressure.
   b. When there is a decrease in both volume and internal pressure.
   c. When there is a decrease in volume and an increase in internal pressure.
   d. When there is an increase in volume and a decrease in internal pressure.

9. What are the ways to add energy to or remove energy from a system?
   a. Transferring energy by heat is the only way to add energy to or remove energy from a system.
   b. Doing compression work is the only way to add energy to or remove energy from a system.
   c. Doing expansion work is the only way to add energy to or remove energy from a system.
   d. Transferring energy by heat or by doing work are the ways to add energy to or remove energy from a system.

10. What is internal energy?
    a. It is the sum of the kinetic energies of a system's atoms and molecules.
    b. It is the sum of the potential energies of a system's atoms and molecules.
    c. It is the sum of the kinetic and potential energies of a system's atoms and molecules.
    d. It is the difference between the magnitudes of the kinetic and potential energies of a system's atoms and molecules.

12.3 Second Law of Thermodynamics: Entropy

Section Learning Objectives

By the end of this section, you will be able to do the following:

- Describe entropy
- Describe the second law of thermodynamics
- Solve problems involving the second law of thermodynamics

Section Key Terms

entropy	second law of thermodynamics

Entropy

Recall from the chapter introduction that it is not even theoretically possible for engines to be 100 percent efficient. This phenomenon is explained by the **second law of thermodynamics**, which relies on a concept known as **entropy**. Entropy is a measure of the disorder of a system. Entropy also describes how much energy is *not* available to do work. The more disordered a system and higher the entropy, the less of a system's energy is available to do work.

Although all forms of energy can be used to do work, it is not possible to use the entire available energy for work. Consequently, not all energy transferred by heat can be converted into work, and some of it is lost in the form of waste heat—that is, heat that does not go toward doing work. The unavailability of energy is important in thermodynamics; in fact, the field originated from efforts to convert heat to work, as is done by engines.

The equation for the change in entropy, ΔS, is

$$\Delta S = \frac{Q}{T},$$

where Q is the heat that transfers energy during a process, and T is the absolute temperature at which the process takes place.

Q is positive for energy transferred *into* the system by heat and negative for energy transferred *out of* the system by heat. In SI, entropy is expressed in units of joules per kelvin (J/K). If temperature changes during the process, then it is usually a good approximation (for small changes in temperature) to take T to be the average temperature in order to avoid trickier math (calculus).

TIPS FOR SUCCESS

Absolute temperature is the temperature measured in Kelvins. The Kelvin scale is an absolute temperature scale that is measured in terms of the number of degrees above absolute zero. All temperatures are therefore positive. Using temperatures from another, nonabsolute scale, such as Fahrenheit or Celsius, will give the wrong answer.

Second Law of Thermodynamics

Have you ever played the card game 52 pickup? If so, you have been on the receiving end of a practical joke and, in the process, learned a valuable lesson about the nature of the universe as described by the second law of thermodynamics. In the game of 52 pickup, the prankster tosses an entire deck of playing cards onto the floor, and you get to pick them up. In the process of picking up the cards, you may have noticed that the amount of work required to restore the cards to an orderly state in the deck is much greater than the amount of work required to toss the cards and create the disorder.

The second law of thermodynamics states that *the total entropy of a system either increases or remains constant in any spontaneous process; it never decreases.* An important implication of this law is that heat transfers energy spontaneously from higher- to lower-temperature objects, but never spontaneously in the reverse direction. This is because entropy increases for heat transfer of energy from hot to cold (Figure 12.9). Because the change in entropy is Q/T, there is a larger change in ΔS at lower temperatures (smaller T). The decrease in entropy of the hot (larger T) object is therefore less than the increase in entropy of the cold (smaller T) object, producing an overall increase in entropy for the system.

Figure 12.9 The ice in this drink is slowly melting. Eventually, the components of the liquid will reach thermal equilibrium, as predicted by the second law of thermodynamics—that is, after heat transfers energy from the warmer liquid to the colder ice. (Jon Sullivan, PDPhoto.org)

Another way of thinking about this is that it is impossible for any process to have, as its sole result, heat transferring energy from a cooler to a hotter object. Heat cannot transfer energy spontaneously from colder to hotter, because the entropy of the overall system would decrease.

Suppose we mix equal masses of water that are originally at two different temperatures, say $20.0\ ^\circ\text{C}$ and $40.0\ ^\circ\text{C}$. The result will be water at an intermediate temperature of $30.0\ ^\circ\text{C}$. Three outcomes have resulted: entropy has increased, some energy has become unavailable to do work, and the system has become less orderly. Let us think about each of these results.

First, why has entropy increased? Mixing the two bodies of water has the same effect as the heat transfer of energy from the higher-temperature substance to the lower-temperature substance. The mixing decreases the entropy of the hotter water but increases the entropy of the colder water by a greater amount, producing an overall increase in entropy.

Second, once the two masses of water are mixed, there is no more temperature difference left to drive energy transfer by heat and therefore to do work. The energy is still in the water, but it is now *unavailable* to do work.

Third, the mixture is less orderly, or to use another term, less structured. Rather than having two masses at different temperatures and with different distributions of molecular speeds, we now have a single mass with a broad distribution of molecular speeds, the average of which yields an intermediate temperature.

These three results—entropy, unavailability of energy, and disorder—not only are related but are, in fact, essentially equivalent. Heat transfer of energy from hot to cold is related to the tendency in nature for systems to become disordered and for less energy to be available for use as work.

Based on this law, what cannot happen? A cold object in contact with a hot one never spontaneously transfers energy by heat to the hot object, getting colder while the hot object gets hotter. Nor does a hot, stationary automobile ever spontaneously cool off and start moving.

Another example is the expansion of a puff of gas introduced into one corner of a vacuum chamber. The gas expands to fill the chamber, but it never regroups on its own in the corner. The random motion of the gas molecules could take them all back to the corner, but this is never observed to happen (Figure 12.10).

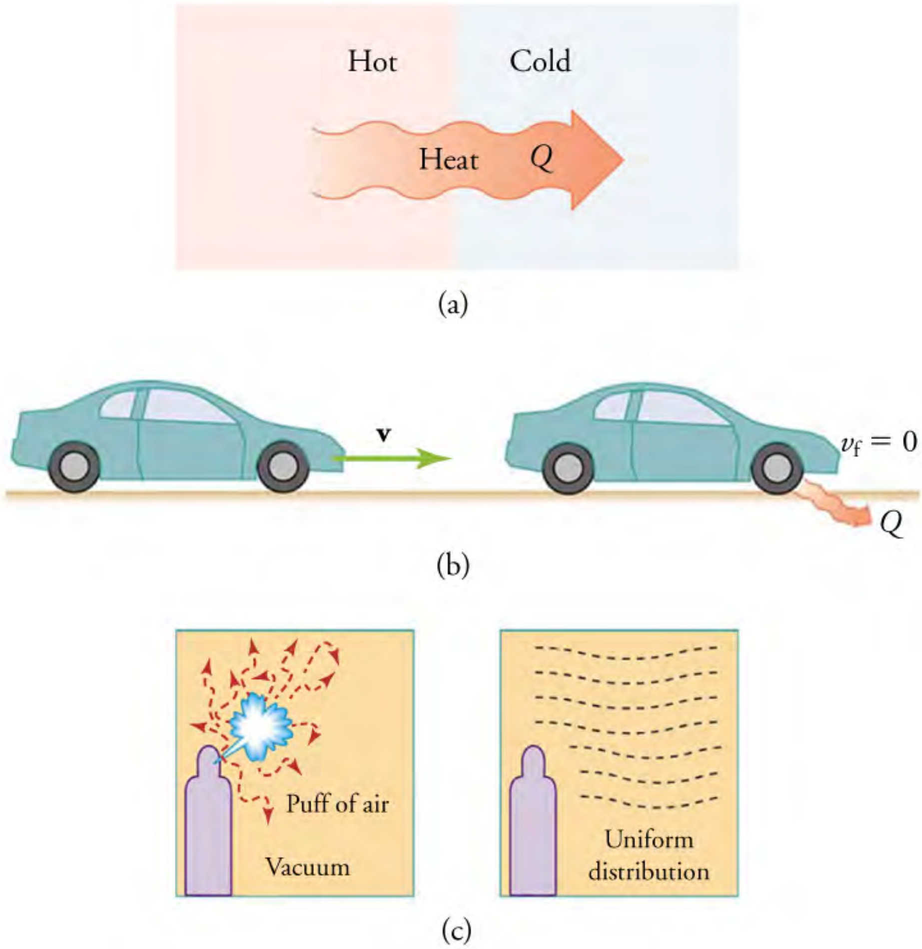

Figure 12.10 Examples of one-way processes in nature. (a) Heat transfer occurs spontaneously from hot to cold, but not from cold to hot. (b) The brakes of this car convert its kinetic energy to increase their internal energy (temperature), and heat transfers this energy to the environment. The reverse process is impossible. (c) The burst of gas released into this vacuum chamber quickly expands to uniformly fill every part of the chamber. The random motions of the gas molecules will prevent them from returning altogether to the corner.

We've explained that heat never transfers energy spontaneously from a colder to a hotter object. The key word here is *spontaneously*. If we *do work* on a system, it *is* possible to transfer energy by heat from a colder to hotter object. We'll learn more about this in the next section, covering refrigerators as one of the applications of the laws of thermodynamics.

Sometimes people misunderstand the second law of thermodynamics, thinking that based on this law, it is impossible for entropy to decrease at any particular location. But, it actually *is* possible for the entropy of *one part* of the universe to decrease, as long as the total change in entropy of the universe increases. In equation form, we can write this as

$$\Delta S_{\text{tot}} = \Delta S_{\text{syst}} + \Delta S_{\text{envir}} > 0.$$

Based on this equation, we see that ΔS_{syst} can be negative as long as ΔS_{envir} is positive and greater in magnitude.

How is it possible for the entropy of a system to decrease? Energy transfer is necessary. If you pick up marbles that are scattered about the room and put them into a cup, your work has decreased the entropy of that system. If you gather iron ore from the ground and convert it into steel and build a bridge, your work has decreased the entropy of that system. Energy coming from the sun can decrease the entropy of local systems on Earth—that is, ΔS_{syst} is negative. But the overall entropy of the rest of the universe increases by a greater amount—that is, ΔS_{envir} is positive and greater in magnitude. In the case of the iron ore, although you made the system of the bridge and steel more structured, you did so at the expense of the universe. Altogether, the entropy of the universe is increased by the disorder created by digging up the ore and converting it to steel. Therefore,

$$\Delta S_{\text{tot}} = \Delta S_{\text{syst}} + \Delta S_{\text{envir}} > 0, \tag{12.14}$$

and the second law of thermodynamics is *not* violated.

Every time a plant stores some solar energy in the form of chemical potential energy, or an updraft of warm air lifts a soaring bird, Earth experiences local decreases in entropy as it uses part of the energy transfer from the sun into deep space to do work. There is a large total increase in entropy resulting from this massive energy transfer. A small part of this energy transfer by heat is stored in structured systems on Earth, resulting in much smaller, local decreases in entropy.

Solving Problems Involving the Second Law of Thermodynamics

Entropy is related not only to the unavailability of energy to do work; it is also a measure of disorder. For example, in the case of a melting block of ice, a highly structured and orderly system of water molecules changes into a disorderly liquid, in which molecules have no fixed positions (Figure 12.11). There is a large increase in entropy for this process, as we'll see in the following worked example.

Figure 12.11 These ice floes melt during the Arctic summer. Some of them refreeze in the winter, but the second law of thermodynamics predicts that it would be extremely unlikely for the water molecules contained in these particular floes to reform in the distinctive alligator-like shape they possessed when this picture was taken in the summer of 2009. (Patrick Kelley, U.S. Coast Guard, U.S. Geological Survey)

WORKED EXAMPLE

Entropy Associated with Disorder

Find the increase in entropy of 1.00 kg of ice that is originally at $0\ °\text{C}$ and melts to form water at $0\ °\text{C}$.

STRATEGY

The change in entropy can be calculated from the definition of ΔS once we find the energy, Q, needed to melt the ice.

Solution

The change in entropy is defined as

$$\Delta S = \frac{Q}{T}. \tag{12.15}$$

Here, Q is the heat necessary to melt 1.00 kg of ice and is given by

$$Q = mL_f, \tag{12.16}$$

where m is the mass and L_f is the latent heat of fusion. $L_f = 334\text{ kJ/kg}$ for water, so

$$Q = (1.00\text{ kg})(334\text{ kJ/kg}) = 3.34 \times 10^5\text{ J}. \tag{12.17}$$

Because Q is the amount of energy heat adds to the ice, its value is positive, and T is the melting temperature of ice, $T = 273\text{ K}$ So the change in entropy is

$$\Delta S = \frac{Q}{T} = \frac{3.34 \times 10^5\text{ J}}{273\text{ K}} = 1.22 \times 10^3\text{ J/K}. \tag{12.18}$$

Discussion

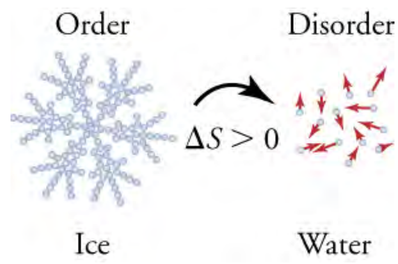

Figure 12.12 When ice melts, it becomes more disordered and less structured. The systematic arrangement of molecules in a crystal structure is replaced by a more random and less orderly movement of molecules without fixed locations or orientations. Its **entropy** increases because heat transfer occurs into it. Entropy is a measure of disorder.

The change in entropy is positive, because heat transfers energy *into* the ice to cause the phase change. This is a significant increase in entropy, because it takes place at a relatively low temperature. It is accompanied by an increase in the disorder of the water molecules.

Practice Problems

11. If 30.0 J are added by heat to water at 12°C, what is the change in entropy?
    a. 0.105 J/K
    b. 2.5 J/K
    c. 0.45 J/K
    d. 9.50 J/K

12. What is the increase in entropy when 3.00 kg of ice at 0°C melt to form water at 0°C?
    a. $1.84 \times 10^3\text{ J/K}$
    b. $3.67 \times 10^3\text{ J/K}$
    c. $1.84 \times 10^8\text{ J/K}$
    d. $3.67 \times 10^8\text{ J/K}$

Check Your Understanding

13. What is entropy?
    a. Entropy is a measure of the potential energy of a system.
    b. Entropy is a measure of the net work done by a system.
    c. Entropy is a measure of the disorder of a system.
    d. Entropy is a measure of the heat transfer of energy into a system.

14. Which forms of energy can be used to do work?
    a. Only work is able to do work.
    b. Only heat is able to do work.
    c. Only internal energy is able to do work.
    d. Heat, work, and internal energy are all able to do work.

15. What is the statement for the second law of thermodynamics?
    a. All the spontaneous processes result in decreased total entropy of a system.
    b. All the spontaneous processes result in increased total entropy of a system.
    c. All the spontaneous processes result in decreased or constant total entropy of a system.
    d. All the spontaneous processes result in increased or constant total entropy of a system.

16. For heat transferring energy from a high to a low temperature, what usually happens to the entropy of the whole system?
    a. It decreases.
    b. It must remain constant.
    c. The entropy of the system cannot be predicted without specific values for the temperatures.

d. It increases.

12.4 Applications of Thermodynamics: Heat Engines, Heat Pumps, and Refrigerators

Section Learning Objectives

By the end of this section, you will be able to do the following:

- Explain how heat engines, heat pumps, and refrigerators work in terms of the laws of thermodynamics
- Describe thermal efficiency
- Solve problems involving thermal efficiency

Section Key Terms

cyclical process	heat engine	heat pump
thermal efficiency		

Heat Engines, Heat Pumps, and Refrigerators

In this section, we'll explore how heat engines, heat pumps, and refrigerators operate in terms of the laws of thermodynamics.

One of the most important things we can do with heat is to use it to do work for us. A **heat engine** does exactly this—it makes use of the properties of thermodynamics to transform heat into work. Gasoline and diesel engines, jet engines, and steam turbines that generate electricity are all examples of heat engines.

Figure 12.13 illustrates one of the ways in which heat transfers energy to do work. Fuel combustion releases chemical energy that heat transfers throughout the gas in a cylinder. This increases the gas temperature, which in turn increases the pressure of the gas and, therefore, the force it exerts on a movable piston. The gas does work on the outside world, as this force moves the piston through some distance. Thus, heat transfer of energy to the gas in the cylinder results in work being done.