a. Energy can neither be created nor destroyed in a chemical reaction.
b. If two systems, A and B, are in thermal equilibrium with each another, and B is in thermal equilibrium with a third system, C, then A is also in thermal equilibrium with C.
c. Entropy of any isolated system not in thermal equilibrium always increases.
d. Entropy of a system approaches a constant value as temperature approaches absolute zero.

12.2 First law of Thermodynamics: Thermal Energy and Work

Section Learning Objectives

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

- Describe how pressure, volume, and temperature relate to one another and to work, based on the ideal gas law
- Describe pressure–volume work
- Describe the first law of thermodynamics verbally and mathematically
- Solve problems involving the first law of thermodynamics

Section Key Terms

Boltzmann constant	first law of thermodynamics	ideal gas law	internal energy	pressure

Pressure, Volume, Temperature, and the Ideal Gas Law

Before covering the first law of thermodynamics, it is first important to understand the relationship between **pressure**, volume, and temperature. Pressure, P, is defined as

$$P = \frac{F}{A}, \tag{12.1}$$

where F is a force applied to an area, A, that is perpendicular to the force.

Depending on the area over which it is exerted, a given force can have a significantly different effect, as shown in Figure 12.3.

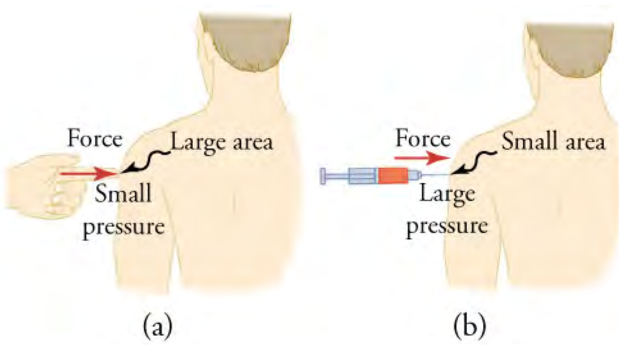

Figure 12.3 (a) Although the person being poked with the finger might be irritated, the force has little lasting effect. (b) In contrast, the same force applied to an area the size of the sharp end of a needle is great enough to break the skin.

The SI unit for pressure is the *pascal*, where $1\ \text{Pa} = 1\ \text{N/m}^2$.

Pressure is defined for all states of matter but is particularly important when discussing fluids (such as air). You have probably heard the word *pressure* being used in relation to blood (high or low blood pressure) and in relation to the weather (high- and low-pressure weather systems). These are only two of many examples of pressures in fluids.

The relationship between the pressure, volume, and temperature for an ideal gas is given by the **ideal gas law**. A gas is considered ideal at low pressure and fairly high temperature, and forces between its component particles can be ignored. The ideal gas law states that

$$PV = NkT. \tag{12.2}$$

where P is the pressure of a gas, V is the volume it occupies, N is the number of particles (atoms or molecules) in the gas, and T is its absolute temperature. The constant k is called the **Boltzmann constant** and has the value $k = 1.38 \times 10^{-23}\,\text{J/K}$, For the purposes of this chapter, we will not go into calculations using the ideal gas law. Instead, it is important for us to notice from the equation that the following are true for a given mass of gas:

- When volume is constant, pressure is directly proportional to temperature.
- When temperature is constant, pressure is inversely proportional to volume.
- When pressure is constant, volume is directly proportional to temperature.

This last point describes *thermal expansion*—the change in size or volume of a given mass with temperature. What is the underlying cause of thermal expansion? An increase in temperature means that there's an increase in the kinetic energy of the individual atoms. Gases are especially affected by thermal expansion, although liquids expand to a lesser extent with similar increases in temperature, and even solids have minor expansions at higher temperatures. This is why railroad tracks and bridges have expansion joints that allow them to freely expand and contract with temperature changes.

To get some idea of how pressure, temperature, and volume of a gas are related to one another, consider what happens when you pump air into a deflated tire. The tire's volume first increases in direct proportion to the amount of air injected, without much increase in the tire pressure. Once the tire has expanded to nearly its full size, the walls limit volume expansion. If you continue to pump air into tire (which now has a nearly constant volume), the pressure increases with increasing temperature (see Figure 12.4).

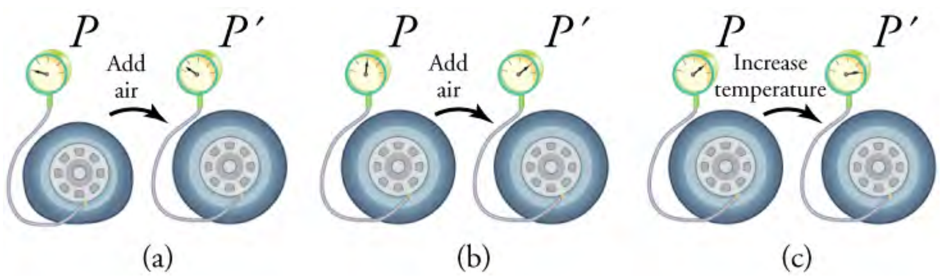

Figure 12.4 (a) When air is pumped into a deflated tire, its volume first increases without much increase in pressure. (b) When the tire is filled to a certain point, the tire walls resist further expansion, and the pressure increases as more air is added. (c) Once the tire is inflated fully, its pressure increases with temperature.

Pressure–Volume Work

Pressure–volume work is the work that is done by the compression or expansion of a fluid. Whenever there is a change in volume and external pressure remains constant, pressure–volume work is taking place. During a compression, a decrease in volume increases the internal pressure of a system as work is done *on* the system. During an expansion (Figure 12.5), an increase in volume decreases the internal pressure of a system as the system *does* work.

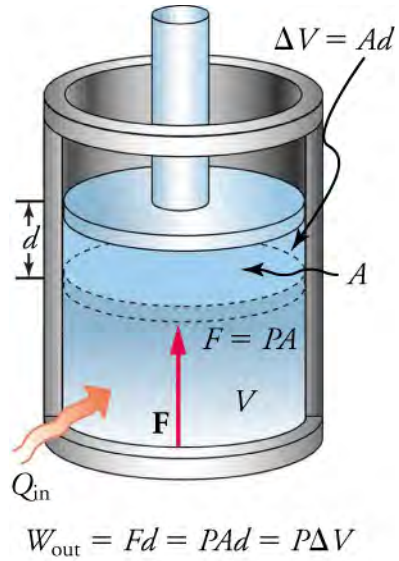

Figure 12.5 An expansion of a gas requires energy transfer to keep the pressure constant. Because pressure is constant, the work done is $P\Delta V$.

Recall that the formula for work is $W = Fd$. We can rearrange the definition of pressure, $P = \frac{F}{A}$, to get an expression for force in terms of pressure.

$$F = PA \tag{12.3}$$

Substituting this expression for force into the definition of work, we get

$$W = PAd. \tag{12.4}$$

Because area multiplied by displacement is the change in volume, $W = P\Delta V$, the mathematical expression for pressure–volume work is

$$W = P\Delta V. \tag{12.5}$$

Just as we say that work is force acting over a distance, for fluids, we can say that work is the pressure acting through the change in volume. For pressure–volume work, pressure is analogous to force, and volume is analogous to distance in the traditional definition of work.

WATCH PHYSICS

Work from Expansion

This video describes work from expansion (or pressure–volume work). Sal combines the equations $W = P\Delta V$ and $\Delta U = Q - W$ to get $\Delta U = Q - P\Delta V$.

[Click to view content (https://www.openstax.org/l/28expansionWork)](https://www.openstax.org/l/28expansionWork)

GRASP CHECK

If the volume of a system increases while pressure remains constant, is the value of work done by the system ***W*** positive or negative? Will this increase or decrease the internal energy of the system?

a. Positive; internal energy will decrease
b. Positive; internal energy will increase
c. Negative; internal energy will decrease
d. Negative; internal energy will increase

The First Law of Thermodynamics

Heat (*Q*) and work (*W*) are the two ways to add or remove energy from a system. The processes are very different. Heat is driven by temperature differences, while work involves a force exerted through a distance. Nevertheless, heat and work can produce identical results. For example, both can cause a temperature increase. Heat transfers energy into a system, such as when the sun warms the air in a bicycle tire and increases the air's temperature. Similarly, work can be done on the system, as when the bicyclist pumps air into the tire. Once the temperature increase has occurred, it is impossible to tell whether it was caused by heat or work. Heat and work are both energy in transit—neither is stored as such in a system. However, both can change the internal energy, U, of a system.

Internal energy is the sum of the kinetic and potential energies of a system's atoms and molecules. It can be divided into many subcategories, such as thermal and chemical energy, and depends only on the state of a system (that is, P, V, and T), not on how the energy enters or leaves the system.

In order to understand the relationship between heat, work, and internal energy, we use the **first law of thermodynamics**. The first law of thermodynamics applies the *conservation of energy* principle to systems where heat and work are the methods of transferring energy into and out of the systems. It can also be used to describe how energy transferred by heat is converted and transferred again by work.

TIPS FOR SUCCESS

Recall that the principle of conservation of energy states that energy cannot be created or destroyed, but it can be altered from one form to another.

The first law of thermodynamics states that the change in internal energy of a closed system equals the net heat transfer *into* the system minus the net work done *by* the system. In equation form, the first law of thermodynamics is

$$\Delta U = Q - W. \tag{12.6}$$

Here, ΔU is the *change in internal energy*, U, of the system. As shown in Figure 12.6, Q is the *net heat transferred into the system*—that is, Q is the sum of all heat transfers into and out of the system. W is the *net work done by the system*—that is, W is the sum of all work done on or by the system. By convention, if Q is positive, then there is a net heat transfer into the system; if W is positive, then there is net work done by the system. So positive Q adds energy to the system by heat, and positive W takes energy from the system by work. Note that if heat transfers more energy into the system than that which is done by work, the difference is stored as internal energy.

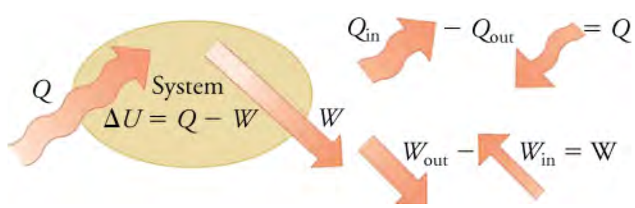

Figure 12.6 The first law of thermodynamics is the *conservation of energy* principle stated for a system, where heat and work are the methods of transferring energy to and from a system. Q represents the net heat transfer—it is the sum of all transfers of energy by heat into and out of the system. Q is positive for net heat transfer *into* the system. W_{out} is the work done *by* the system, and W_{in} is the work done *on* the system. W is the total work done on or *by* the system. W is positive when more work is done *by* the system than *on* it. The change in the internal energy of the system, ΔU, is related to heat and work by the first law of thermodynamics: $\Delta U = Q - W$.

It follows also that negative Q indicates that energy is transferred *away* from the system by heat and so decreases the system's internal energy, whereas negative W is work done *on* the system, which increases the internal energy.

WATCH PHYSICS

First Law of Thermodynamics/Internal Energy

This video explains the first law of thermodynamics, conservation of energy, and internal energy. It goes over an example of energy transforming between kinetic energy, potential energy, and heat transfer due to air resistance.

Click to view content (https://www.openstax.org/l/28FirstThermo)

GRASP CHECK

Consider the example of tossing a ball when there's air resistance. As air resistance increases, what would you expect to happen to the final velocity and final kinetic energy of the ball? Why?

a. Both will decrease. Energy is transferred to the air by heat due to air resistance.
b. Both will increase. Energy is transferred from the air to the ball due to air resistance.
c. Final velocity will increase, but final kinetic energy will decrease. Energy is transferred by heat to the air from the ball through air resistance.
d. Final velocity will decrease, but final kinetic energy will increase. Energy is transferred by heat from the air to the ball through air resistance.

WATCH PHYSICS

More on Internal Energy

This video goes into further detail, explaining internal energy and how to use the equation $\Delta U = Q - W$. Note that Sal uses the equation $\Delta U = Q + W$, where W is the work done *on* the system, whereas we use W to represent work done *by* the system.

Click to view content (https://www.openstax.org/l/28IntrnEnergy)

GRASP CHECK

If 5 J are taken away by heat from the system, and the system does 5 J of work, what is the change in internal energy of the system?

a. -10 J
b. 0 J
c. 10 J
d. 25 J

LINKS TO PHYSICS

Biology: Biological Thermodynamics

We often think about thermodynamics as being useful for inventing or testing machinery, such as engines or steam turbines. However, thermodynamics also applies to living systems, such as our own bodies. This forms the basis of the biological thermodynamics (Figure 12.7).

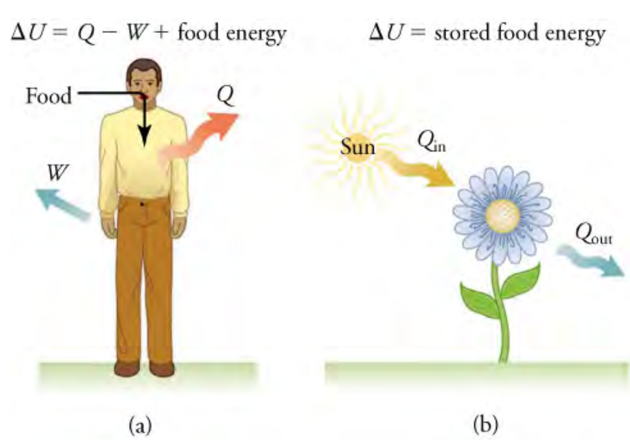

Figure 12.7 (a) The first law of thermodynamics applies to metabolism. Heat transferred out of the body (Q) and work done by the body (W) remove internal energy, whereas food intake replaces it. (Food intake may be considered work done on the body.) (b) Plants convert part of

the radiant energy in sunlight into stored chemical energy, a process called *photosynthesis*.

Life itself depends on the biological transfer of energy. Through photosynthesis, plants absorb solar energy from the sun and use this energy to convert carbon dioxide and water into glucose and oxygen. Photosynthesis takes in one form of energy—light—and converts it into another form—chemical potential energy (glucose and other carbohydrates).

Human metabolism is the conversion of food into energy given off by heat, work done by the body's cells, and stored fat. Metabolism is an interesting example of the first law of thermodynamics in action. Eating increases the internal energy of the body by adding chemical potential energy; this is an unromantic view of a good burrito.

The body metabolizes all the food we consume. Basically, metabolism is an oxidation process in which the chemical potential energy of food is released. This implies that food input is in the form of work. Exercise helps you lose weight, because it provides energy transfer from your body by both heat and work and raises your metabolic rate even when you are at rest.

Biological thermodynamics also involves the study of transductions between cells and living organisms. *Transduction* is a process where genetic material—DNA—is transferred from one cell to another. This often occurs during a viral infection (e.g., influenza) and is how the virus spreads, namely, by transferring its genetic material to an increasing number of previously healthy cells. Once enough cells become infected, you begin to feel the effects of the virus (flu symptoms—muscle weakness, coughing, and congestion).

Energy is transferred along with the genetic material and so obeys the first law of thermodynamics. Energy is transferred—not created or destroyed—in the process. When work is done on a cell or heat transfers energy to a cell, the cell's internal energy increases. When a cell does work or loses heat, its internal energy decreases. If the amount of work done by a cell is the same as the amount of energy transferred in by heat, or the amount of work performed on a cell matches the amount of energy transferred out by heat, there will be no net change in internal energy.

GRASP CHECK

Based on what you know about heat transfer and the first law of thermodynamics, do you need to eat more or less to maintain a constant weight in colder weather? Explain why.

a. more; as more energy is lost by the body in colder weather, the need to eat increases so as to maintain a constant weight
b. more; eating more food means accumulating more fat, which will insulate the body from colder weather and will reduce the energy loss
c. less; as less energy is lost by the body in colder weather, the need to eat decreases so as to maintain a constant weight
d. less; eating less food means accumulating less fat, so less energy will be required to burn the fat, and, as a result, weight will remain constant

Solving Problems Involving the First Law of Thermodynamics

WORKED EXAMPLE

Calculating Change in Internal Energy

Suppose 40.00 J of energy is transferred by heat to a system, while the system does 10.00 J of work. Later, heat transfers 25.00 J out of the system, while 4.00 J is done by work on the system. What is the net change in the system's internal energy?

STRATEGY

You must first calculate the net heat and net work. Then, using the first law of thermodynamics, $\Delta U = Q - W$, find the change in internal energy.

Solution

The net heat is the transfer into the system by heat minus the transfer out of the system by heat, or

$$Q = 40.00\ \text{J} - 25.00\ \text{J} = 15.00\ \text{J}. \tag{12.7}$$

The total work is the work done by the system minus the work done on the system, or

$$W = 10.00\ \text{J} - 4.00\ \text{J} = 6.00\ \text{J}. \tag{12.8}$$

The change in internal energy is given by the first law of thermodynamics.

$$\Delta U = Q - W = 15.00\ \text{J} - 6.00\ \text{J} = 9.00\ \text{J} \tag{12.9}$$

Discussion

A different way to solve this problem is to find the change in internal energy for each of the two steps separately and then add the two changes to get the total change in internal energy. This approach would look as follows:

For 40.00 J of heat in and 10.00 J of work out, the change in internal energy is

$$\Delta U_1 = Q_1 - W_1 = 40.00\ \text{J} - 10.00\ \text{J} = 30.00\ \text{J}. \tag{12.10}$$

For 25.00 J of heat out and 4.00 J of work in, the change in internal energy is

$$\Delta U_2 = Q_2 - W_2 = -25.00\ \text{J} - (-4.00\ \text{J}) = -21.00\ \text{J}. \tag{12.11}$$

The total change is

$$\Delta U = \Delta U_1 + \Delta U_2 = 30.00\ \text{J} + (-21.00\ \text{J}) = 9.00\ \text{J}. \tag{12.12}$$

No matter whether you look at the overall process or break it into steps, the change in internal energy is the same.

WORKED EXAMPLE

Calculating Change in Internal Energy: The Same Change in *U* is Produced by Two Different Processes

What is the change in the internal energy of a system when a total of 150.00 J is transferred by heat from the system and 159.00 J is done by work on the system?

STRATEGY

The net heat and work are already given, so simply use these values in the equation $\Delta U = Q - W$.

Solution

Here, the net heat and total work are given directly as $Q = -150.00\ \text{J}$ and $W = -159.00\ \text{J}$, so that

$$\Delta U = Q - W = -150.00\ \text{J} - (-159.00\ \text{J}) = 9.00\ \text{J}. \tag{12.13}$$

Discussion

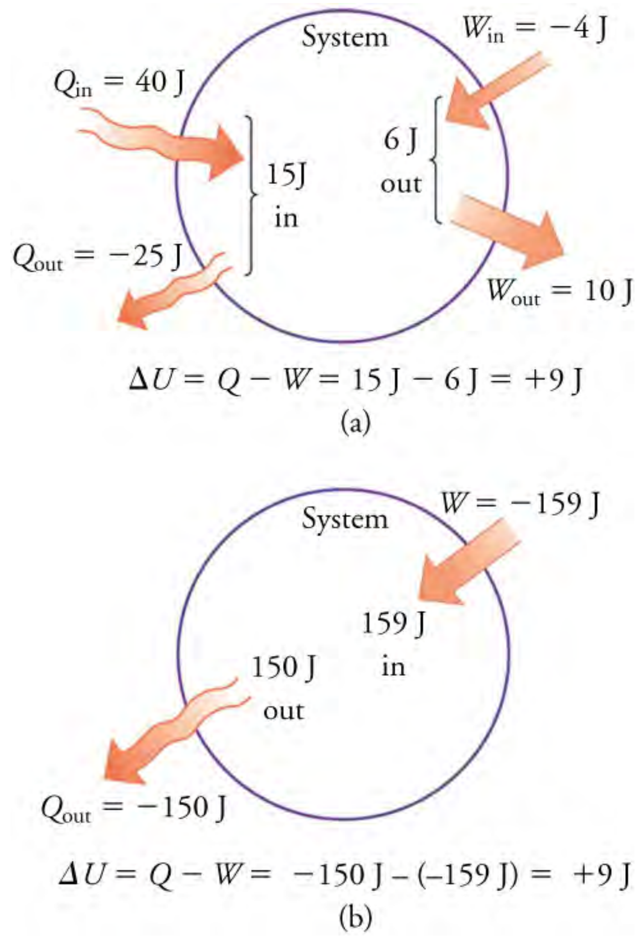

Figure 12.8 Two different processes produce the same change in a system. (a) A total of 15.00 J of heat transfer occurs into the system, while work takes out a total of 6.00 J. The change in internal energy is ΔU = Q – W = 9.00 J. (b) Heat transfer removes 150.00 J from the system while work puts 159.00 J into it, producing an increase of 9.00 J in internal energy. If the system starts out in the same state in (a) and (b), it will end up in the same final state in either case—its final state is related to internal energy, not how that energy was acquired.

A very different process in this second worked example produces the same 9.00 J change in internal energy as in the first worked example. Note that the change in the system in both parts is related to ΔU and not to the individual Q's or W's involved. The system ends up in the *same* state in both problems. Note that, as usual, in Figure 12.8 above, W_{out} is work done *by* the system, and W_{in} is work done *on* the system.

Practice Problems

3. What is the pressure-volume work done by a system if a pressure of $20\ \text{Pa}$ causes a change in volume of $3.0\ \text{m}^3$?
   a. $0.15\ \text{J}$
   b. $6.7\ \text{J}$
   c. $23\ \text{J}$
   d. $60\ \text{J}$

4. What is the net heat out of the system when $25\ \text{J}$ is transferred by heat into the system and $45\ \text{J}$ is transferred out of it?
   a. $-70\ \text{J}$
   b. $-20\ \text{J}$
   c. $20\ \text{J}$
   d. $70\ \text{J}$

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.