$\Delta U = -Q - W +$ food energy $\Delta U =$ stored food energy

FIGURE 15.5 (a) The first law of thermodynamics applied to metabolism. Heat transferred out of the body (Q) and work done by the body (W) remove internal energy, while food intake replaces it. (Food intake may be considered as work done on the body.) (b) Plants convert part of the radiant heat transfer in sunlight to stored chemical energy, a process called photosynthesis.

Term	Definition
U	Internal energy—the sum of the kinetic and potential energies of a system's atoms and molecules. Can be divided into many subcategories, such as thermal and chemical energy. Depends only on the state of a system (such as its P, V, and T), not on how the energy entered the system. Change in internal energy is path independent.
Q	Heat—energy transferred because of a temperature difference. Characterized by random molecular motion. Highly dependent on path. Q entering a system is positive.
W	Work—energy transferred by a force moving through a distance. An organized, orderly process. Path dependent. W done by a system (either against an external force or to increase the volume of the system) is positive.

TABLE 15.1 Summary of Terms for the First Law of Thermodynamics, $\Delta U = Q - W$

15.2 The First Law of Thermodynamics and Some Simple Processes

LEARNING OBJECTIVES

By the end of this section, you will be able to:
- Describe the processes of a simple heat engine.
- Explain the differences among the simple thermodynamic processes—isobaric, isochoric, isothermal, and adiabatic.
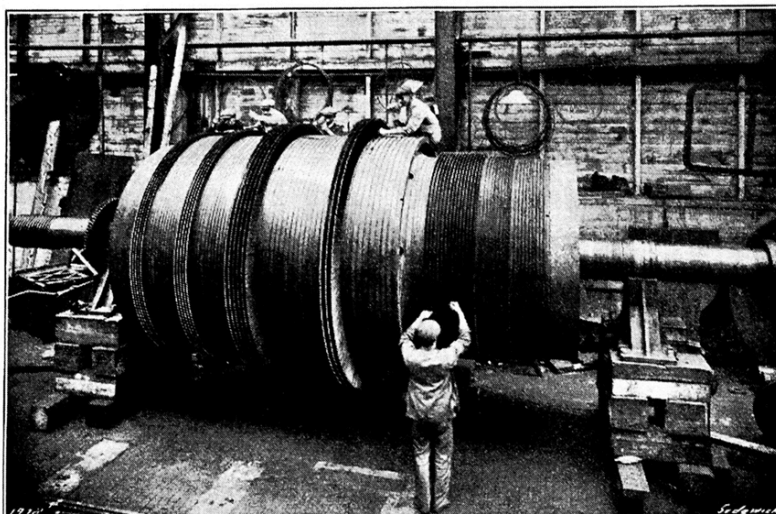- Calculate total work done in a cyclical thermodynamic process.

FIGURE 15.6 Beginning with the Industrial Revolution, humans have harnessed power through the use of the first law of thermodynamics, before we even understood it completely. This photo, of a steam engine at the Turbinia Works, dates from 1911, a mere 61 years after the first explicit statement of the first law of thermodynamics by Rudolph Clausius. (credit: public domain; author unknown)

One of the most important things we can do with heat transfer is to use it to do work for us. Such a device is called a **heat engine**. Car engines and steam turbines that generate electricity are examples of heat engines. Figure 15.7 shows schematically how the first law of thermodynamics applies to the typical heat engine.
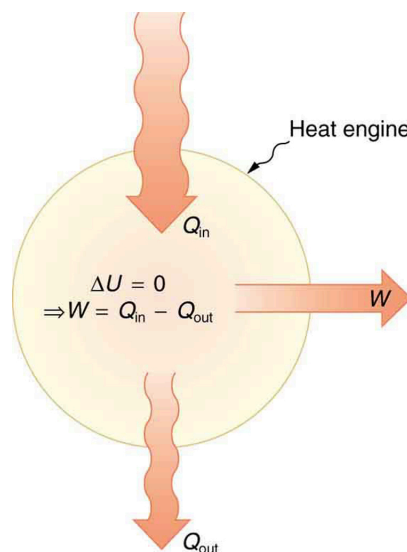

FIGURE 15.7 Schematic representation of a heat engine, governed, of course, by the first law of thermodynamics. It is impossible to devise a system where $Q_{\text{out}} = 0$, that is, in which no heat transfer occurs to the environment.
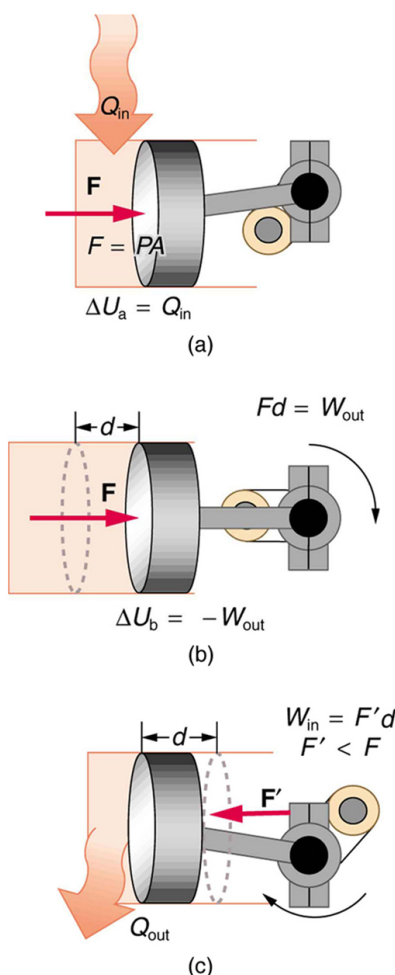
FIGURE 15.8 (a) Heat transfer to the gas in a cylinder increases the internal energy of the gas, creating higher pressure and temperature. (b) The force exerted on the movable cylinder does work as the gas expands. Gas pressure and temperature decrease when it expands, indicating that the gas's internal energy has been decreased by doing work. (c) Heat transfer to the environment further reduces pressure in the gas so that the piston can be more easily returned to its starting position.

The illustrations above show one of the ways in which heat transfer does work. Fuel combustion produces heat transfer to a gas in a cylinder, increasing the pressure of the gas and thereby 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. Heat transfer to the gas cylinder results in work being done. To repeat this process, the piston needs to be returned to its starting point. Heat transfer now occurs from the gas to the surroundings so that its pressure decreases, and a force is exerted by the surroundings to push the piston back through some distance. Variations of this process are employed daily in hundreds of millions of heat engines. We will examine heat engines in detail in the next section. In this section, we consider some of the simpler underlying processes on which heat engines are based.

PV Diagrams and their Relationship to Work Done on or by a Gas

A process by which a gas does work on a piston at constant pressure is called an **isobaric process**. Since the pressure is constant, the force exerted is constant and the work done is given as

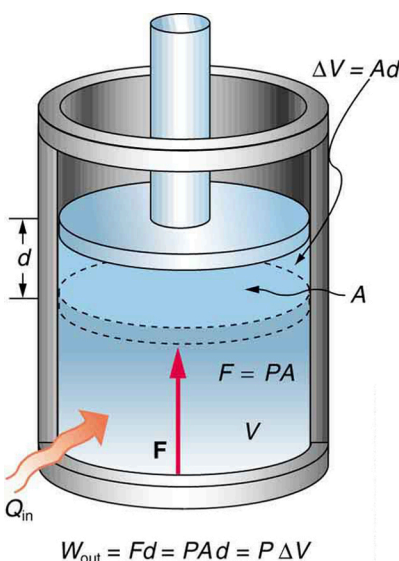$$P\Delta V. \hspace{6cm} \textbf{\textcolor{red}{15.10}}$$

FIGURE 15.9 An isobaric expansion of a gas requires heat transfer to keep the pressure constant. Since pressure is constant, the work done is $P\Delta V$.

$$W = Fd \qquad\qquad \text{15.11}$$

See the symbols as shown in Figure 15.9. Now $F = PA$, and so

$$W = PAd. \qquad\qquad \text{15.12}$$

Because the volume of a cylinder is its cross-sectional area A times its length d, we see that $Ad = \Delta V$, the change in volume; thus,

$$W = P\Delta V \text{ (isobaric process).} \qquad\qquad \text{15.13}$$

Note that if ΔV is positive, then W is positive, meaning that work is done *by* the gas on the outside world.

(Note that the pressure involved in this work that we've called P is the pressure of the gas *inside* the tank. If we call the pressure outside the tank P_{ext}, an expanding gas would be working *against* the external pressure; the work done would therefore be $W = -P_{\text{ext}}\Delta V$ (isobaric process). Many texts use this definition of work, and not the definition based on internal pressure, as the basis of the First Law of Thermodynamics. This definition reverses the sign conventions for work, and results in a statement of the first law that becomes $\Delta U = Q + W$.)

It is not surprising that $W = P\Delta V$, since we have already noted in our treatment of fluids that pressure is a type of potential energy per unit volume and that pressure in fact has units of energy divided by volume. We also noted in our discussion of the ideal gas law that PV has units of energy. In this case, some of the energy associated with pressure becomes work.

Figure 15.10 shows a graph of pressure versus volume (that is, a PV diagram for an isobaric process. You can see in the figure that the work done is the area under the graph. This property of PV diagrams is very useful and broadly applicable: *the work done on or by a system in going from one state to another equals the area under the curve on a PV diagram.*
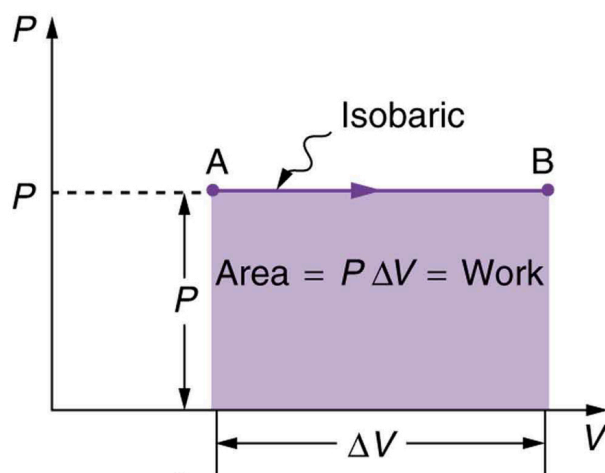
FIGURE 15.10 A graph of pressure versus volume for a constant-pressure, or isobaric, process, such as the one shown in Figure 15.9. The area under the curve equals the work done by the gas, since $W = P\Delta V$.
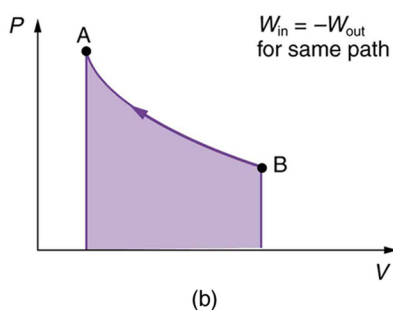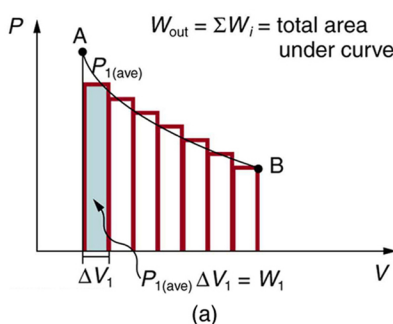

FIGURE 15.11 (a) A PV diagram in which pressure varies as well as volume. The work done for each interval is its average pressure times the change in volume, or the area under the curve over that interval. Thus the total area under the curve equals the total work done. (b) Work must be done on the system to follow the reverse path. This is interpreted as a negative area under the curve.

We can see where this leads by considering Figure 15.11(a), which shows a more general process in which both pressure and volume change. The area under the curve is closely approximated by dividing it into strips, each having an average constant pressure $P_{i(\text{ave})}$. The work done is $W_i = P_{i(\text{ave})}\Delta V_i$ for each strip, and the total work done is the sum of the W_i. Thus the total work done is the total area under the curve. If the path is reversed, as in Figure 15.11(b), then work is done on the system. The area under the curve in that case is negative, because ΔV is negative.

PV diagrams clearly illustrate that *the work done depends on the path taken and not just the endpoints*. This path dependence is seen in Figure 15.12(a), where more work is done in going from A to C by the path via point B than by the path via point D. The vertical paths, where volume is constant, are called **isochoric** processes. Since volume is constant, $\Delta V = 0$, and no work is done in an isochoric process. Now, if the system follows the cyclical path ABCDA, as in Figure 15.12(b), then the total work done is the area inside the loop. The negative area below path CD subtracts, leaving only the area inside the rectangle. In fact, the work done in any cyclical process (one that returns to its starting point) is the area inside the loop it forms on a PV diagram, as Figure 15.12(c) illustrates for a general cyclical process. Note that the loop must be traversed in the clockwise direction for work to be positive—that is, for

there to be a net work output.
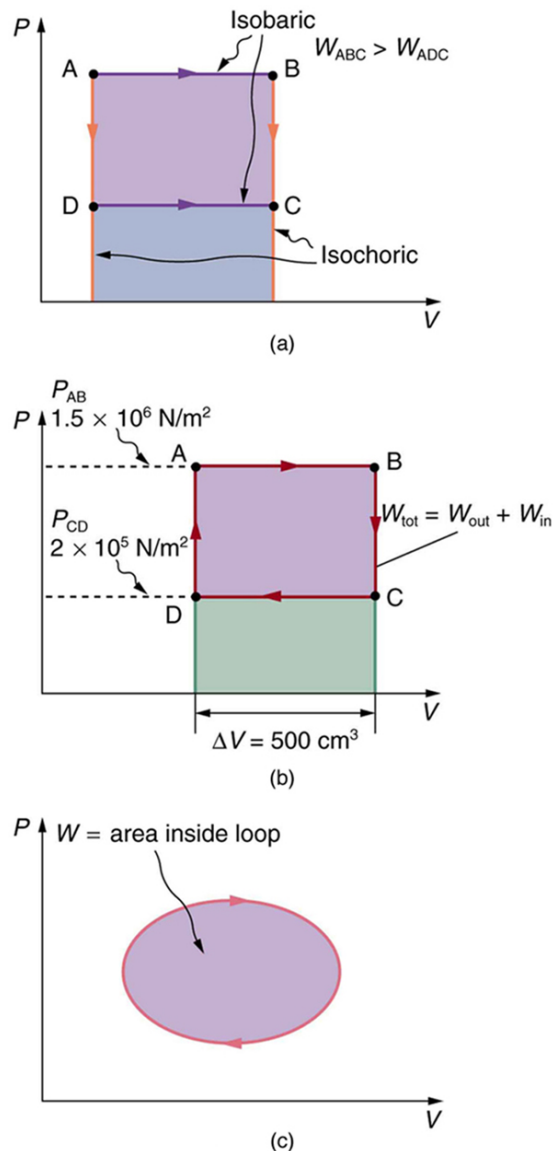

(a)

(b)

(c)

FIGURE 15.12 (a) The work done in going from A to C depends on path. The work is greater for the path ABC than for the path ADC, because the former is at higher pressure. In both cases, the work done is the area under the path. This area is greater for path ABC. (b) The total work done in the cyclical process ABCDA is the area inside the loop, since the negative area below CD subtracts out, leaving just the area inside the rectangle. (The values given for the pressures and the change in volume are intended for use in the example below.) (c) The area inside any closed loop is the work done in the cyclical process. If the loop is traversed in a clockwise direction, W is positive—it is work done on the outside environment. If the loop is traveled in a counter-clockwise direction, W is negative—it is work that is done to the system.

✳ EXAMPLE 15.2

Total Work Done in a Cyclical Process Equals the Area Inside the Closed Loop on a *PV* Diagram

Calculate the total work done in the cyclical process ABCDA shown in Figure 15.12(b) by the following two methods to verify that work equals the area inside the closed loop on the *PV* diagram. (Take the data in the figure to be precise to three significant figures.) (a) Calculate the work done along each segment of the path and add these values to get the total work. (b) Calculate the area inside the rectangle ABCDA.

Strategy

To find the work along any path on a PV diagram, you use the fact that work is pressure times change in volume, or $W = P\Delta V$. So in part (a), this value is calculated for each leg of the path around the closed loop.

Solution for (a)

The work along path AB is

$$
\begin{aligned}
W_{AB} &= P_{AB}\Delta V_{AB} \\
&= (1.50{\times}10^6 \text{ N/m}^2)(5.00{\times}10^{-4} \text{ m}^3) = 750 \text{ J.}
\end{aligned}
$$
<div align="right">15.14</div>

Since the path BC is isochoric, $\Delta V_{BC} = 0$, and so $W_{BC} = 0$. The work along path CD is negative, since ΔV_{CD} is negative (the volume decreases). The work is

$$
\begin{aligned}
W_{CD} &= P_{CD}\Delta V_{CD} \\
&= (2.00{\times}10^5 \text{ N/m}^2)(-5.00{\times}10^{-4} \text{ m}^3) = -100 \text{ J.}
\end{aligned}
$$
<div align="right">15.15</div>

Again, since the path DA is isochoric, $\Delta V_{DA} = 0$, and so $W_{DA} = 0$. Now the total work is

$$
\begin{aligned}
W &= W_{AB} + W_{BC} + W_{CD} + W_{DA} \\
&= 750 \text{ J} + 0 + (-100\text{J}) + 0 = 650 \text{ J.}
\end{aligned}
$$
<div align="right">15.16</div>

Solution for (b)

The area inside the rectangle is its height times its width, or

$$
\begin{aligned}
\text{area} &= (P_{AB} - P_{CD})\Delta V \\
&= \left[(1.50{\times}10^6 \text{ N/m}^2) - (2.00{\times}10^5 \text{ N/m}^2)\right](5.00{\times}10^{-4} \text{ m}^3) \\
&= 650 \text{ J.}
\end{aligned}
$$
<div align="right">15.17</div>

Thus,

$$
\text{area} = 650 \text{ J} = W.
$$
<div align="right">15.18</div>

Discussion

The result, as anticipated, is that the area inside the closed loop equals the work done. The area is often easier to calculate than is the work done along each path. It is also convenient to visualize the area inside different curves on PV diagrams in order to see which processes might produce the most work. Recall that work can be done to the system, or by the system, depending on the sign of W. A positive W is work that is done by the system on the outside environment; a negative W represents work done by the environment on the system.

Figure 15.13(a) shows two other important processes on a PV diagram. For comparison, both are shown starting from the same point A. The upper curve ending at point B is an **isothermal** process—that is, one in which temperature is kept constant. If the gas behaves like an ideal gas, as is often the case, and if no phase change occurs, then $PV = nRT$. Since T is constant, PV is a constant for an isothermal process. We ordinarily expect the temperature of a gas to decrease as it expands, and so we correctly suspect that heat transfer must occur from the surroundings to the gas to keep the temperature constant during an isothermal expansion. To show this more rigorously for the special case of a monatomic ideal gas, we note that the average kinetic energy of an atom in such a gas is given by

$$
\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT.
$$
<div align="right">15.19</div>

The kinetic energy of the atoms in a monatomic ideal gas is its only form of internal energy, and so its total internal energy U is

$$
U = N\frac{1}{2}m\bar{v}^2 = \frac{3}{2}NkT, \text{ (monatomic ideal gas),}
$$
<div align="right">15.20</div>

where N is the number of atoms in the gas. This relationship means that the internal energy of an ideal monatomic gas is constant during an isothermal process—that is, $\Delta U = 0$. If the internal energy does not change, then the net heat transfer into the gas must equal the net work done by the gas. That is, because $\Delta U = Q - W = 0$ here, $Q = W$. We must have just enough heat transfer to replace the work done. An isothermal process is inherently slow, because heat transfer occurs continuously to keep the gas temperature constant at all times and must be allowed to spread through the gas so that there are no hot or cold regions.

Note that diatomic gases, such as those in air, have different formulas for average kinetic energy of an atom and total internal energy.

Also shown in Figure 15.13(a) is a curve AC for an **adiabatic** process, defined to be one in which there is no heat transfer—that is, $Q = 0$. Processes that are nearly adiabatic can be achieved either by using very effective insulation or by performing the process so fast that there is little time for heat transfer. Temperature must decrease during an adiabatic expansion process, since work is done at the expense of internal energy:

$$U = \frac{3}{2}NkT. \tag{15.21}$$

(You might have noted that a gas released into atmospheric pressure from a pressurized cylinder is substantially colder than the gas in the cylinder.) In fact, because $Q = 0$, $\Delta U = -W$ for an adiabatic process. Lower temperature results in lower pressure along the way, so that curve AC is lower than curve AB, and less work is done. If the path ABCA could be followed by cooling the gas from B to C at constant volume (isochorically), Figure 15.13(b), there would be a net work output.
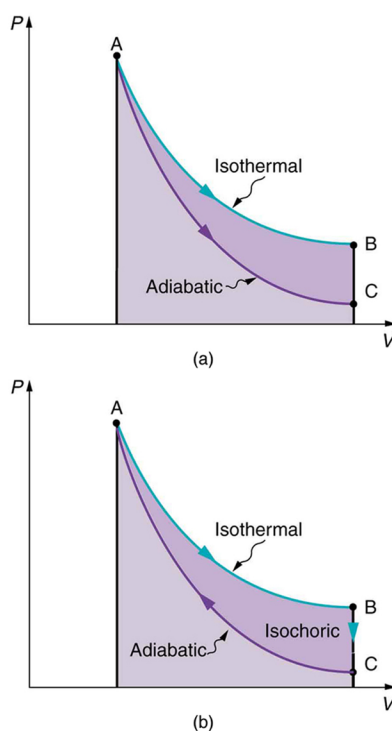

FIGURE 15.13 (a) The upper curve is an isothermal process ($\Delta T = 0$), whereas the lower curve is an adiabatic process ($Q = 0$). Both start from the same point A, but the isothermal process does more work than the adiabatic because heat transfer into the gas takes place to keep its temperature constant. This keeps the pressure higher all along the isothermal path than along the adiabatic path, producing more work. The adiabatic path thus ends up with a lower pressure and temperature at point C, even though the final volume is the same as for the isothermal process. (b) The cycle ABCA produces a net work output.

Reversible Processes

Both isothermal and adiabatic processes such as shown in Figure 15.13 are reversible in principle. A **reversible process** is one in which both the system and its environment can return to exactly the states they were in by following the reverse path. The reverse isothermal and adiabatic paths are BA and CA, respectively. Real

macroscopic processes are never exactly reversible. In the previous examples, our system is a gas (like that in Figure 15.9), and its environment is the piston, cylinder, and the rest of the universe. If there are any energy-dissipating mechanisms, such as friction or turbulence, then heat transfer to the environment occurs for either direction of the piston. So, for example, if the path BA is followed and there is friction, then the gas will be returned to its original state but the environment will not—it will have been heated in both directions. Reversibility requires the direction of heat transfer to reverse for the reverse path. Since dissipative mechanisms cannot be completely eliminated, real processes cannot be reversible.

There must be reasons that real macroscopic processes cannot be reversible. We can imagine them going in reverse. For example, heat transfer occurs spontaneously from hot to cold and never spontaneously the reverse. Yet it would not violate the first law of thermodynamics for this to happen. In fact, all spontaneous processes, such as bubbles bursting, never go in reverse. There is a second thermodynamic law that forbids them from going in reverse. When we study this law, we will learn something about nature and also find that such a law limits the efficiency of heat engines. We will find that heat engines with the greatest possible theoretical efficiency would have to use reversible processes, and even they cannot convert all heat transfer into doing work. Table 15.2 summarizes the simpler thermodynamic processes and their definitions.

Isobaric	Constant pressure $W = P\Delta V$
Isochoric	Constant volume $W = 0$
Isothermal	Constant temperature $Q = W$
Adiabatic	No heat transfer $Q = 0$

TABLE 15.2 Summary of Simple Thermodynamic Processes

PHET EXPLORATIONS

States of Matter
Watch different types of molecules form a solid, liquid, or gas. Add or remove heat and watch the phase change. Change the temperature or volume of a container and see a pressure-temperature diagram respond in real time. Relate the interaction potential to the forces between molecules.

Click to view content (https://openstax.org/books/college-physics-2e/pages/15-2-the-first-law-of-thermodynamics-and-some-simple-processes)

PhET

15.3 Introduction to the Second Law of Thermodynamics: Heat Engines and Their Efficiency

LEARNING OBJECTIVES
By the end of this section, you will be able to:
- State the expressions of the second law of thermodynamics.
- Calculate the efficiency and carbon dioxide emission of a coal-fired electricity plant, using second law characteristics.
- Describe and define the Otto cycle.