

15 THERMODYNAMICS



Figure 15.1 A steam engine uses heat transfer to do work. Tourists regularly ride this narrow-gauge steam engine train near the San Juan Skyway in Durango, Colorado, part of the National Scenic Byways Program. (credit: Dennis Adams)

Chapter Outline

15.1. The First Law of Thermodynamics

- Define the first law of thermodynamics.
- Describe how conservation of energy relates to the first law of thermodynamics.
- Identify instances of the first law of thermodynamics working in everyday situations, including biological metabolism.
- Calculate changes in the internal energy of a system, after accounting for heat transfer and work done.

15.2. The First Law of Thermodynamics and Some Simple Processes

- 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.

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

- 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*.

15.4. Carnot's Perfect Heat Engine: The Second Law of Thermodynamics Restated

- Identify a *Carnot cycle*.
- Calculate maximum theoretical efficiency of a nuclear reactor.
- Explain how dissipative processes affect the ideal *Carnot engine*.

15.5. Applications of Thermodynamics: Heat Pumps and Refrigerators

- Describe the use of heat engines in heat pumps and refrigerators.
- Demonstrate how a heat pump works to warm an interior space.
- Explain the differences between heat pumps and refrigerators.
- Calculate a heat pump's coefficient of performance.

15.6. Entropy and the Second Law of Thermodynamics: Disorder and the Unavailability of Energy

- Define entropy and calculate the increase of entropy in a system with reversible and irreversible processes.
- Explain the expected fate of the universe in entropic terms.
- Calculate the increasing disorder of a system.

15.7. Statistical Interpretation of Entropy and the Second Law of Thermodynamics: The Underlying Explanation

- Identify probabilities in entropy.
- Analyze statistical probabilities in entropic systems.

Introduction to Thermodynamics

Heat transfer is energy in transit, and it can be used to do work. It can also be converted to any other form of energy. A car engine, for example, burns fuel for heat transfer into a gas. Work is done by the gas as it exerts a force through a distance,

15.1 The First Law of Thermodynamics



Figure 15.2 This boiling tea kettle represents energy in motion. The water in the kettle is turning to water vapor because heat is being transferred from the stove to the kettle. As the entire system gets hotter, work is done—from the evaporation of the water to the whistling of the kettle. (credit: Gina Hamilton)

If we are interested in how heat transfer is converted into doing work, then the conservation of energy principle is important. The first law of thermodynamics applies the conservation of energy principle to systems where heat transfer and doing work are the methods of transferring energy into and out of the system. The **first law of thermodynamics** states that the change in internal energy of a system equals the net heat transfer *into* the system **plus** the net work done **on** the system. In equation form, the first law of thermodynamics is

$$\Delta U = Q + W. \quad (15.1)$$

Here ΔU is the *change in internal energy* U of the system. Q is the *net heat transferred into the system*—that is, Q is the sum of all heat transfer 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. We use the following sign conventions: if Q is positive, then there is a net heat transfer into the system; if W is positive, then there is net work done **on** the system. So positive Q adds energy to the system and positive W **adds** energy **to** the system. Thus $\Delta U = Q + W$.

We will now examine Q , W , and ΔU further.

Making Connections: Law of Thermodynamics and Law of Conservation of Energy

The first law of thermodynamics is actually the law of conservation of energy stated in a form most useful in thermodynamics. The first law gives the relationship between heat transfer, work done, and the change in internal energy of a system.

Heat Q and Work W

Heat transfer (Q) and doing work (W) are the two everyday means of bringing energy into or taking energy out of a system.

The processes are quite different. Heat transfer, a less organized process, is driven by temperature differences. Work, a quite organized process, involves a macroscopic force exerted through a distance. Nevertheless, heat and work can produce identical results. For example, both can cause a temperature increase. Heat transfer into a system, such as when the Sun warms the air in a bicycle tire, can increase its temperature, and so can work 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 transfer or by doing work. This uncertainty is an important point. Heat transfer 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 a form of energy completely different from either heat or work.

Internal Energy U

We can think about the internal energy of a system in two different but consistent ways. The first is the atomic and molecular view, which examines the system on the atomic and molecular scale. The **internal energy** U of a system is the sum of the kinetic and potential energies of its atoms and molecules. Recall that kinetic plus potential energy is called mechanical energy. Thus internal energy is the sum of atomic and molecular mechanical energy. Because it is impossible to keep track of all individual atoms and molecules, we must deal with averages and distributions. A second way to view the internal energy of a system is in terms of its macroscopic characteristics, which are very similar to atomic and molecular average values.

Macroscopically, we define the change in internal energy ΔU to be that given by the first law of thermodynamics:

$$\Delta U = Q + W. \quad (15.2)$$

Many detailed experiments have verified that $\Delta U = Q + W$, where ΔU is the change in total kinetic and potential energy of all atoms and molecules in a system. It has also been determined experimentally that the internal energy U of a system depends only on the state of the system and *not how it reached that state*. More specifically, U is found to be a function of a few macroscopic quantities (pressure, volume, and temperature, for example), independent of past history such as whether there has been heat transfer or work done. This independence means that if we know the state of a system, we can calculate changes in its internal energy U from a few macroscopic variables.

Making Connections: Macroscopic and Microscopic

In thermodynamics, we often use the macroscopic picture when making calculations of how a system behaves, while the atomic and molecular picture gives underlying explanations in terms of averages and distributions. We shall see this again in later sections of this chapter.

To get a better idea of how to think about the internal energy of a system, let us examine a system going from State 1 to State 2. The system has internal energy U_1 in State 1, and it has internal energy U_2 in State 2, no matter how it got to either state. So the change in internal energy $\Delta U = U_2 - U_1$ is independent of what caused the change. In other words, ΔU is *independent of path*. By path, we mean the method of getting from the starting point to the ending point. Why is this independence important? Note that $\Delta U = Q + W$. Both Q and W depend on path, but ΔU does not. This path independence means that internal energy U is easier to consider than either heat transfer or work done.

Example 15.1 Calculating Change in Internal Energy: The Same Change in U is Produced by Two Different Processes

(a) Suppose there is heat transfer of 40.00 J to a system, while the system does 10.00 J of work. Later, there is heat transfer of 25.00 J out of the system while 4.00 J of work is done on the system. What is the net change in internal energy of the system?

(b) What is the change in internal energy of a system when a total of 150.00 J of heat transfer occurs out of (from) the system and 159.00 J of work is done on the system? (See [Figure 15.4](#)).

Strategy

In part (a), we must first find the net heat transfer and net work done from the given information. Then the first law of thermodynamics ($\Delta U = Q + W$) can be used to find the change in internal energy. In part (b), the net heat transfer and work done are given, so the equation can be used directly.

Solution for (a)

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

$$Q = 40.00 \text{ J} - 25.00 \text{ J} = 15.00 \text{ J}. \quad (15.3)$$

Similarly, the total work is the work done **on** the system minus the work done **by** the system, or

$$W = 4.00 \text{ J} - 10.00 \text{ J} = -6.00 \text{ J}. \quad (15.4)$$

Thus the change in internal energy is given by the first law of thermodynamics:

$$\Delta U = Q + W = 15.00 \text{ J} + (-6.00 \text{ J}) = 9.00 \text{ J}. \quad (15.5)$$

We can also find the change in internal energy for each of the two steps. First, consider 40.00 J of heat transfer in and 10.00 J of work out, or

$$\Delta U_1 = Q_1 + W_1 = 40.00 \text{ J} + (-10.00 \text{ J}) = 30.00 \text{ J}. \quad (15.6)$$

Now consider 25.00 J of heat transfer out and 4.00 J of work in, or

$$\Delta U_2 = Q_2 + W_2 = -25.00 \text{ J} + 4.00 \text{ J} = -21.00 \text{ J}. \quad (15.7)$$

The total change is the sum of these two steps, or

$$\Delta U = \Delta U_1 + \Delta U_2 = 30.00 \text{ J} + (-21.00 \text{ J}) = 9.00 \text{ J}. \quad (15.8)$$

Discussion on (a)

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

Solution for (b)

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

$$\Delta U = Q + W = -150.00 \text{ J} + 159.00 \text{ J} = 9.00 \text{ J}. \quad (15.9)$$

Discussion on (b)

A very different process in part (b) produces the same 9.00-J change in internal energy as in part (a). 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 (a) and (b). Parts (a) and (b) present two different paths for the system to follow between the same starting and ending points, and the change in internal energy for each is the same—it is independent of path.

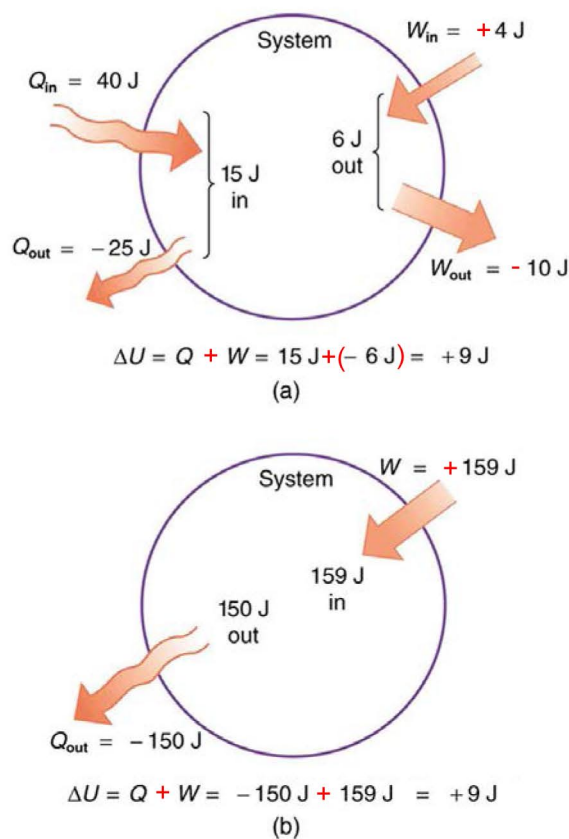


Figure 15.4 Two different processes produce the same change in a system. (a) A total of 15.00 J of heat transfer occurs into the system, while work takes out a total of 6.00 J . The change in internal energy is $\Delta U = Q + W = 9.00\text{ J}$. (b) Heat transfer removes 150.00 J from the system while 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.

15.2 The First Law of Thermodynamics and Some Simple Processes

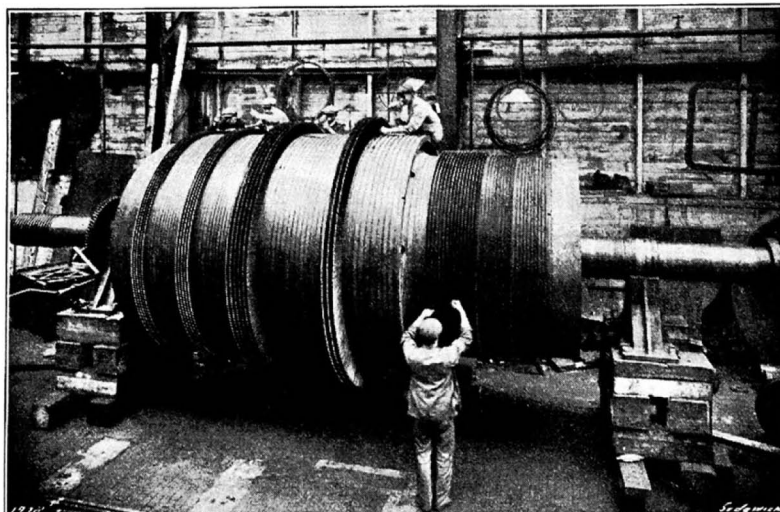


Figure 15.6 Beginning with the Industrial Revolution, humans have harnessed power through the use of the first law of thermodynamics, before we even understood it completely. This photo, of a steam engine at the Turbinia Works, dates from 1911, a mere 61 years after the first explicit statement of the 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.

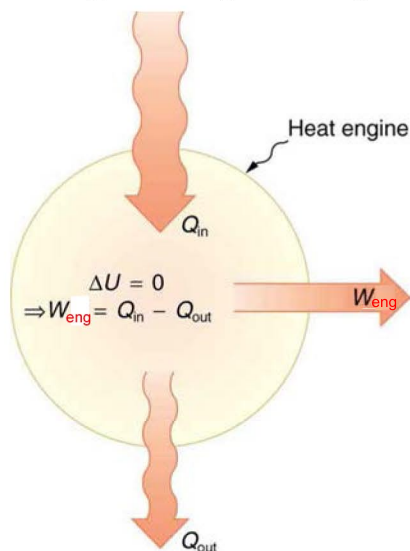


Figure 15.7 Schematic representation of a heat engine, governed, of course, by the first law of thermodynamics. It is impossible to devise a system where $Q_{\text{out}} = 0$, that is, in which no heat transfer occurs to the environment.

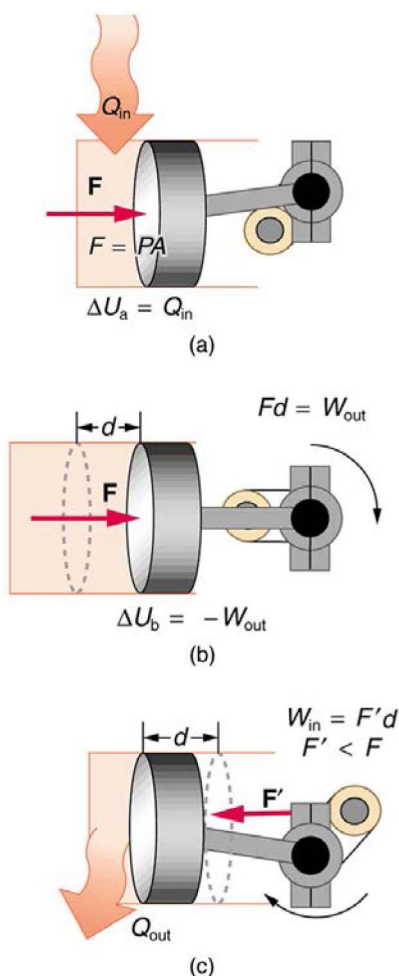


Figure 15.8 (a) Heat transfer to the gas in a cylinder increases the internal energy of the gas, creating higher pressure and temperature. (b) The force exerted on the movable cylinder does work as the gas expands. Gas pressure and temperature decrease when it expands, indicating that the gas's internal 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 **piston does work on a gas** 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

$$-P\Delta V. \quad (15.10)$$

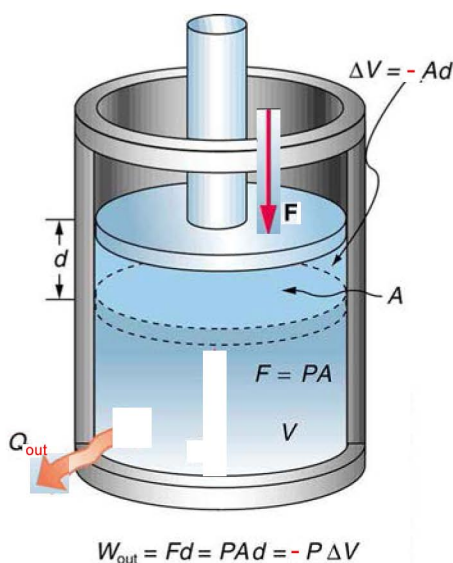


Figure 15.9 An isobaric **compression** of a gas requires heat transfer to keep the pressure constant. Since pressure is constant, the work done is $-P\Delta V$.

$$W = Fd \quad (15.11)$$

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

$$W = PA d. \quad (15.12)$$

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 (**negative, since compression causes the volume to decrease**); thus,

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

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

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.*

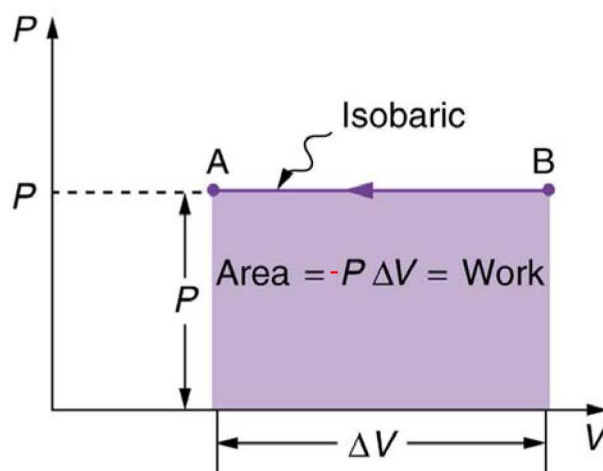


Figure 15.10 A graph of pressure versus volume for a constant-pressure, or isobaric, process, such as the one shown in **Figure 15.9**. The area under the curve equals the work done on the gas, since $W = -P\Delta V$.

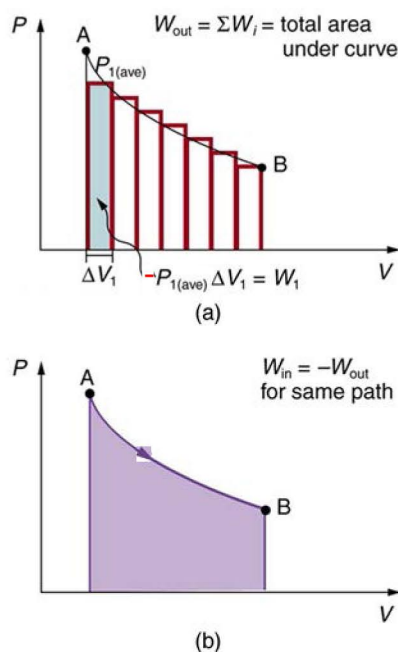


Figure 15.11 (a) A PV diagram in which pressure varies as well as volume. The work done for each interval is its average pressure times the change in volume, or the area under the curve over that interval. Thus the total area under the curve equals the total work done. (b) Work must be done by the system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

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 by the system.

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 **B** to **D** by the path via point **A** than by the path via point **C**. 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 **BADC**, as in **Figure 15.12**(b), then the total work done is the area inside the loop. The negative area below path **DC** 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 **counterclockwise** direction for work to be positive—that is, for there to be a net work done on the system.

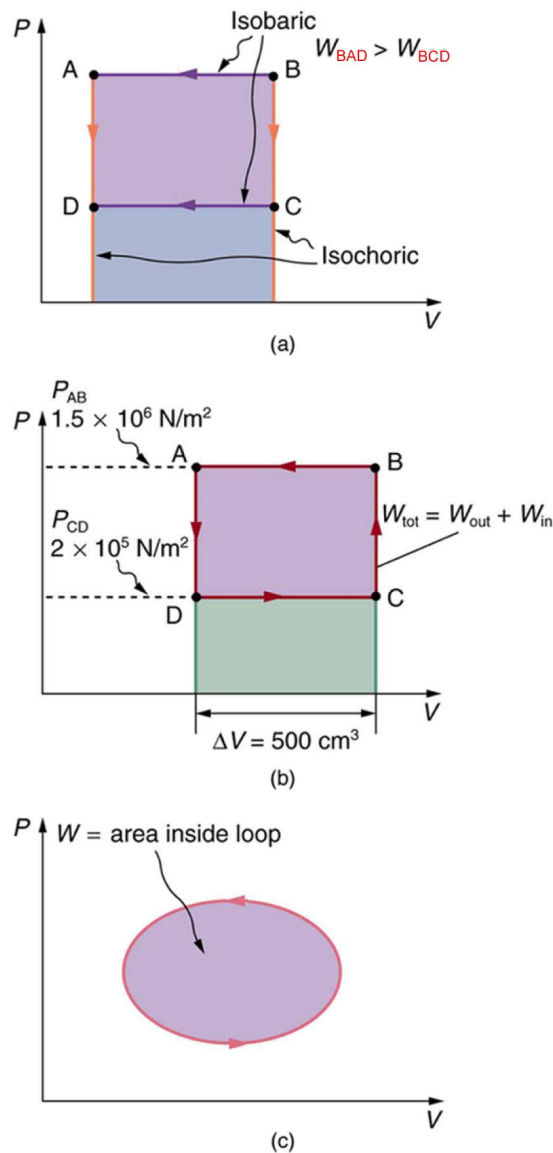


Figure 15.12 (a) The work done in going from **B** to **D** depends on path. The work is greater for the path **BAD** than for the path **BCD**, because the former is at higher pressure. In both cases, the work done is the area under the path. This area is greater for path **BAD**. (b) The total work done in the cyclical process **BADCB** 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 **negative**—it is work done on the outside environment. If the loop is traveled in a counter-clockwise direction, W is **positive**—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 **BADCB** 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 **BADCB**.

Strategy

To find the work along any path on a PV diagram, you use the fact that work is

$W = -P\Delta V$. 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 **BA** is

$$\begin{aligned} W_{BA} &= -P_{BA} \Delta V_{BA} \\ &= -(1.50 \times 10^6 \text{ N/m}^2)(-5.00 \times 10^{-4} \text{ m}^3) = 750 \text{ J}. \end{aligned} \quad (15.14)$$

Since the path **AD** is isochoric, $\Delta V_{AD} = 0$, and so $W_{AD} = 0$. The work along path **DC** is negative, since ΔV_{DC} is **positive** (the volume **increases**). The work is

$$\begin{aligned} W_{DC} &= -P_{DC} \Delta V_{DC} \\ &= -(2.00 \times 10^5 \text{ N/m}^2)(5.00 \times 10^{-4} \text{ m}^3) = -100 \text{ J}. \end{aligned} \quad (15.15)$$

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

$$\begin{aligned} W &= W_{BA} + W_{AD} + W_{DC} + W_{CB} \\ &= 750 \text{ J} + 0 + (-100 \text{ J}) + 0 = 650 \text{ J}. \end{aligned} \quad (15.16)$$

Solution for (b)

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

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

Thus,

$$\text{area} = 650 \text{ J} = W. \quad (15.18)$$

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 **on** the system **by** the outside environment; a negative W represents work done **on** the environment **by** 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

$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} kT. \quad (15.19)$$

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

$$U = N \frac{1}{2} m \bar{v}^2 = \frac{3}{2} NkT, \quad (\text{monatomic ideal gas}), \quad (15.20)$$

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.

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 process, since work is done at the expense of internal energy:

$$U = \frac{3}{2} NkT. \quad (15.21)$$

(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 **by the system**.

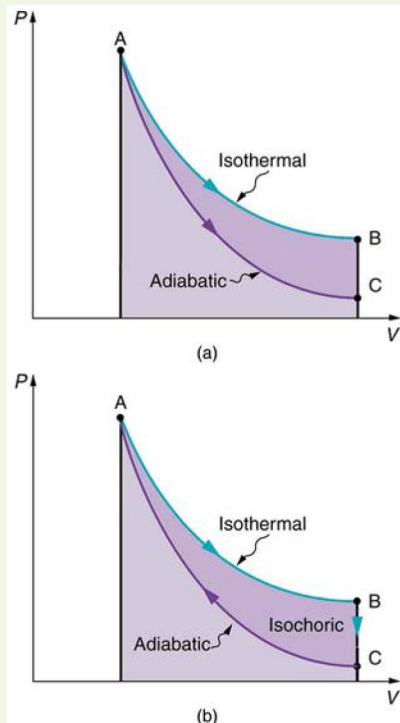


Figure 15.13 (a) The upper curve is an isothermal process ($\Delta T = 0$), whereas the lower curve is an adiabatic process ($Q = 0$). Both start from the same point A, but the isothermal process does more work than the adiabatic because heat transfer into the gas takes place to keep its temperature 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 **done by the system**.

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.

Table 15.2 Summary of Simple Thermodynamic Processes

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

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.



PhET Interactive Simulation

Figure 15.14 States of Matter (http://cnx.org/content/m42233/1.5/states-of-matter_en.jar)

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



Figure 15.15 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 the distinctive alligator-like shape they formed when the picture was taken in the summer of 2009. (credit: Patrick Kelley, U.S. Coast Guard, U.S. Geological Survey)

The second law of thermodynamics deals with the direction taken by spontaneous processes. Many processes occur spontaneously in one direction only—that is, they are irreversible, under a given set of conditions. Although irreversibility is seen in day-to-day life—a broken glass does not resume its original state, for instance—complete irreversibility is a statistical statement that cannot be seen during the lifetime of the universe. More precisely, an **irreversible process** is one that depends on path. If the process can go in only one direction, then the reverse path differs fundamentally and the process cannot be reversible. For example, as noted in the previous section, heat involves the transfer of energy from higher to lower temperature. A cold object in contact with a hot one never gets colder, transferring heat to the hot object and making it hotter. Furthermore, mechanical energy, such as kinetic energy, can be completely converted to thermal energy by friction, but the reverse is impossible. A hot stationary object never spontaneously cools off and starts moving. Yet 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 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. (See Figure 15.16.)

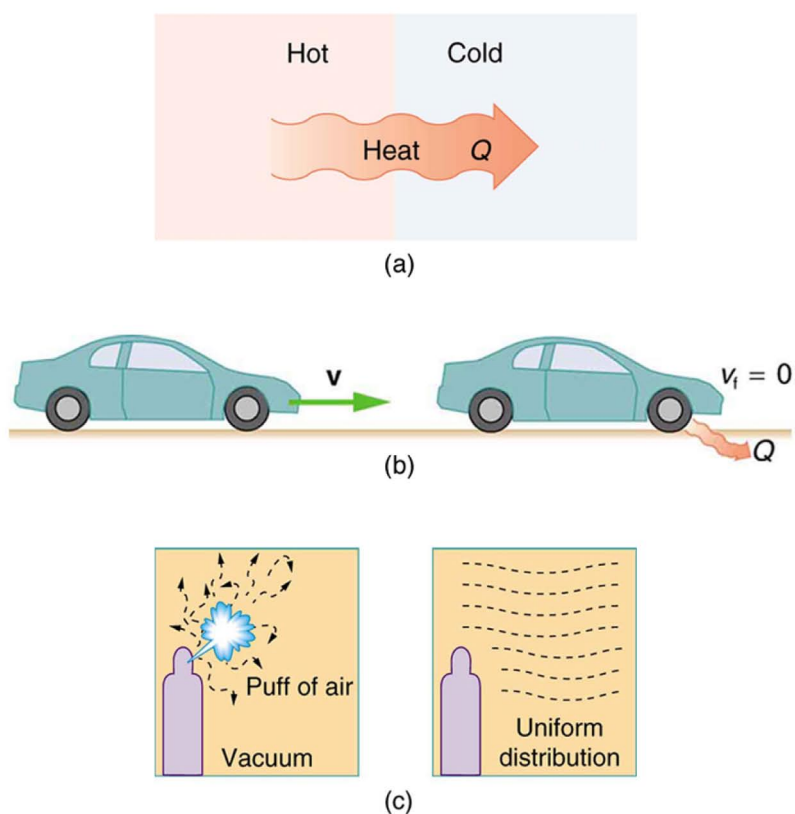


Figure 15.16 Examples of one-way processes in nature. (a) Heat transfer occurs spontaneously from hot to cold and not from cold to hot. (b) The brakes of this car convert its kinetic energy to heat transfer to the environment. The reverse process is impossible. (c) The burst of gas let into this vacuum chamber quickly expands to uniformly fill every part of the chamber. The random motions of the gas molecules will never return them to the corner.

The fact that certain processes never occur suggests that there is a law forbidding them to occur. The first law of thermodynamics would allow them to occur—none of those processes violate conservation of energy. The law that forbids these processes is called the second law of thermodynamics. We shall see that the second law can be stated in many ways that may seem different, but which in fact are equivalent. Like all natural laws, the second law of thermodynamics gives insights into nature, and its several statements imply that it is broadly applicable, fundamentally affecting many apparently disparate processes.

The already familiar direction of heat transfer from hot to cold is the basis of our first version of the **second law of thermodynamics**.

The Second Law of Thermodynamics (first expression)

Heat transfer occurs spontaneously from higher- to lower-temperature bodies but never spontaneously in the reverse direction.

Another way of stating this: It is impossible for any process to have as its sole result heat transfer from a cooler to a hotter object.

Heat Engines

Now let us consider a device that uses heat transfer to do work. As noted in the previous section, such a device is called a heat engine, and one is shown schematically in **Figure 15.17(b)**. Gasoline and diesel engines, jet engines, and steam turbines are all heat engines that do work by using part of the heat transfer from some source. Heat transfer from the hot object (or hot reservoir) is denoted as Q_h , while heat transfer into the cold object (or cold reservoir) is Q_c , and the work done by the engine is W_{eng} . The temperatures of the hot and cold reservoirs are T_h and T_c , respectively.

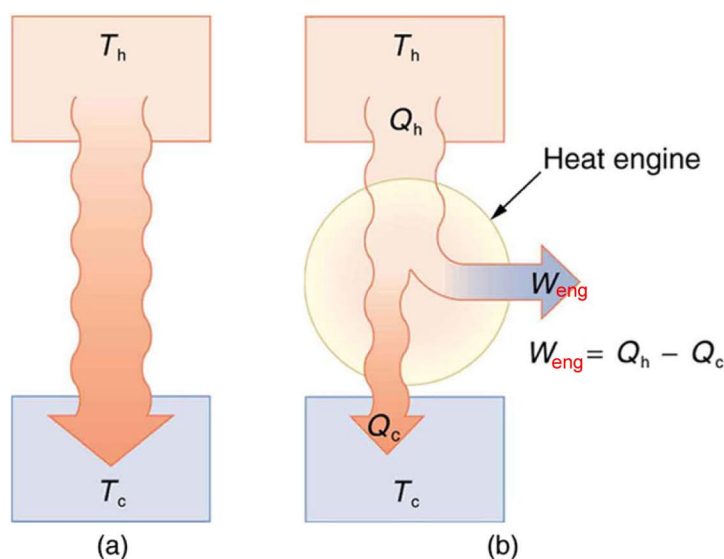


Figure 15.17 (a) Heat transfer occurs spontaneously from a hot object to a cold one, consistent with the second law of thermodynamics. (b) A heat engine, represented here by a circle, uses part of the heat transfer to do work. The hot and cold objects are called the hot and cold reservoirs. Q_h is the heat transfer out of the hot reservoir, W_{eng} is the work output, and Q_c is the heat transfer into the cold reservoir.

Because the hot reservoir is heated externally, which is energy intensive, it is important that the work is done as efficiently as possible. In fact, we would like W_{eng} to equal Q_h , and for there to be no heat transfer to the environment ($Q_c = 0$).

Unfortunately, this is impossible. The **second law of thermodynamics** also states, with regard to using heat transfer to do work (the second expression of the second law):

The Second Law of Thermodynamics (second expression)

It is impossible in any system for heat transfer from a reservoir to completely convert to work in a cyclical process in which the system returns to its initial state.

A **cyclical process** brings a system, such as the gas in a cylinder, back to its original state at the end of every cycle. Most heat engines, such as reciprocating piston engines and rotating turbines, use cyclical processes. The second law, just stated in its second form, clearly states that such engines cannot have perfect conversion of heat transfer into work done. Before going into the underlying reasons for the limits on converting heat transfer into work, we need to explore the relationships among W_{eng} , Q_h , and Q_c , and to define the efficiency of a cyclical heat engine. As noted, a cyclical process brings the system back to its original condition at the end of every cycle. Such a system's internal energy U is the same at the beginning and end of every cycle—that is, $\Delta U = 0$. The first law of thermodynamics states that

$$\Delta U = Q + W, \quad (15.22)$$

where Q is the *net* heat transfer during the cycle ($Q = Q_h - Q_c$) and W is the net work done **on** the system. Since $\Delta U = 0$ for a complete cycle, we have

$$0 = Q + W, \quad (15.23)$$

so that **the work W_{eng} done by the engine,**

$$W_{eng} = -W = Q. \quad (15.24)$$

Thus the net work done by the system equals the net heat transfer into the system, or

$$W_{eng} = Q_h - Q_c \text{ (cyclical process),} \quad (15.25)$$

just as shown schematically in **Figure 15.17(b)**. The problem is that in all processes, there is some heat transfer Q_c to the environment—and usually a very significant amount at that.

In the conversion of energy to work, we are always faced with the problem of getting less out than we put in. We define *conversion efficiency* Eff to be the ratio of useful work output to the energy input (or, in other words, the ratio of what we get to what we spend). In that spirit, we define the efficiency of a heat engine to be its net work output W_{eng} divided by heat transfer to the engine Q_h ; that is,

$$Eff = \frac{W_{eng}}{Q_h} \quad (15.26)$$

Since $W_{eng} = Q_h - Q_c$ in a cyclical process, we can also express this as

$$Eff = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} \text{ (cyclical process),} \quad (15.27)$$

making it clear that an efficiency of 1, or 100%, is possible only if there is no heat transfer to the environment ($Q_c = 0$). Note that all Q s are positive. The direction of heat transfer is indicated by a plus or minus sign. For example, Q_c is out of the system and so is preceded by a minus sign.

Example 15.3 Daily Work Done by a Coal-Fired Power Station, Its Efficiency and Carbon Dioxide Emissions

A coal-fired power station is a huge heat engine. It uses heat transfer from burning coal to do work to turn turbines, which are used to generate electricity. In a single day, a large coal power station has 2.50×10^{14} J of heat transfer from coal and 1.48×10^{14} J of heat transfer into the environment. (a) What is the work done by the power station? (b) What is the efficiency of the power station? (c) In the combustion process, the following chemical reaction occurs: $C + O_2 \rightarrow CO_2$. This implies that every 12 kg of coal puts 12 kg + 16 kg + 16 kg = 44 kg of carbon dioxide into the atmosphere. Assuming that 1 kg of coal can provide 2.5×10^6 J of heat transfer upon combustion, how much CO_2 is emitted per day by this power plant?

Strategy for (a)

We can use $W_{eng} = Q_h - Q_c$ to find the work output W_{eng} , assuming a cyclical process is used in the power station. In this process, water is boiled under pressure to form high-temperature steam, which is used to run steam turbine-generators, and then condensed back to water to start the cycle again.

Solution for (a)

Work output is given by:

$$W_{eng} = Q_h - Q_c. \quad (15.28)$$

Substituting the given values:

$$\begin{aligned} W_{eng} &= 2.50 \times 10^{14} \text{ J} - 1.48 \times 10^{14} \text{ J} \\ &= 1.02 \times 10^{14} \text{ J}. \end{aligned} \quad (15.29)$$

Strategy for (b)

The efficiency can be calculated with $Eff = \frac{W_{eng}}{Q_h}$ since Q_h is given and work W_{eng} was found in the first part of this example.

Solution for (b)

Efficiency is given by: $Eff = \frac{W_{eng}}{Q_h}$. The work W_{eng} was just found to be 1.02×10^{14} J, and Q_h is given, so the efficiency is

$$\begin{aligned} Eff &= \frac{1.02 \times 10^{14} \text{ J}}{2.50 \times 10^{14} \text{ J}} \\ &= 0.408, \text{ or } 40.8\% \end{aligned} \quad (15.30)$$

Strategy for (c)

The daily consumption of coal is calculated using the information that each day there is 2.50×10^{14} J of heat transfer from coal. In the combustion process, we have $C + O_2 \rightarrow CO_2$. So every 12 kg of coal puts 12 kg + 16 kg + 16 kg = 44 kg of CO_2 into the atmosphere.

Solution for (c)

The daily coal consumption is

$$\frac{2.50 \times 10^{14} \text{ J}}{2.50 \times 10^6 \text{ J/kg}} = 1.0 \times 10^8 \text{ kg.} \quad (15.31)$$

Assuming that the coal is pure and that all the coal goes toward producing carbon dioxide, the carbon dioxide produced per day is

$$1.0 \times 10^8 \text{ kg coal} \times \frac{44 \text{ kg CO}_2}{12 \text{ kg coal}} = 3.7 \times 10^8 \text{ kg CO}_2. \quad (15.32)$$

This is 370,000 metric tons of CO_2 produced every day.

Discussion

If all the work output is converted to electricity in a period of one day, the average power output is 1180 MW (this is left to you as an end-of-chapter problem). This value is about the size of a large-scale conventional power plant. The efficiency found is acceptably close to the value of 42% given for coal power stations. It means that fully 59.2% of the energy is heat transfer to the environment, which usually results in warming lakes, rivers, or the ocean near the power station, and is implicated in a warming planet generally. While the laws of thermodynamics limit the efficiency of such plants—including plants fired by nuclear fuel, oil, and natural gas—the heat transfer to the environment could be, and sometimes is, used for heating homes or for industrial processes. The generally low cost of energy has not made it economical to make better use of the waste heat transfer from most heat engines. Coal-fired power plants produce the greatest amount of CO_2 per unit energy output (compared to natural gas or oil), making coal the least efficient fossil fuel.

15.4 Carnot's Perfect Heat Engine: The Second Law of Thermodynamics Restated

We know from the second law of thermodynamics that a heat engine cannot be 100% efficient, since there must always be some heat transfer Q_c to the environment, which is often called waste heat. How efficient, then, can a heat engine be? This question was answered at a theoretical level in 1824 by a young French engineer, Sadi Carnot (1796–1832), in his study of the then-emerging heat engine technology crucial to the Industrial Revolution. He devised a theoretical cycle, now called the **Carnot cycle**, which is the most efficient cyclical process possible. The second law of thermodynamics can be restated in terms of the Carnot cycle, and so what Carnot actually discovered was this fundamental law. Any heat engine employing the Carnot cycle is called a **Carnot engine**.

What is crucial to the Carnot cycle—and, in fact, defines it—is that only reversible processes are used. Irreversible processes involve dissipative factors, such as friction and turbulence. This increases heat transfer Q_c to the environment and reduces the efficiency of the engine. Obviously, then, reversible processes are superior.

Carnot Engine

Stated in terms of reversible processes, the **second law of thermodynamics** has a third form:

A Carnot engine operating between two given temperatures has the greatest possible efficiency of any heat engine operating between these two temperatures. Furthermore, all engines employing only reversible processes have this same maximum efficiency when operating between the same given temperatures.

Carnot also determined the efficiency of a perfect heat engine—that is, a Carnot engine. It is always true that the efficiency of a cyclical heat engine is given by:

$$Eff = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}. \quad (15.33)$$

What Carnot found was that for a perfect heat engine, the ratio Q_c/Q_h equals the ratio of the absolute temperatures of the heat reservoirs. That is, $Q_c/Q_h = T_c/T_h$ for a Carnot engine, so that the maximum or **Carnot efficiency** Eff_C is given by

$$Eff_C = 1 - \frac{T_c}{T_h}, \quad (15.34)$$

where T_h and T_c are in kelvins (or any other absolute temperature scale). No real heat engine can do as well as the Carnot efficiency—an actual efficiency of about 0.7 of this maximum is usually the best that can be accomplished.

Example 15.4 Maximum Theoretical Efficiency for a Nuclear Reactor

A nuclear power reactor has pressurized water at 300°C . (Higher temperatures are theoretically possible but practically not, due to limitations with materials used in the reactor.) Heat transfer from this water is a complex process (see **Figure 15.23**). Steam, produced in the steam generator, is used to drive the turbine-generators. Eventually the steam is condensed to water at 27°C and then heated again to start the cycle over. Calculate the maximum theoretical efficiency for a heat engine operating between these two temperatures.

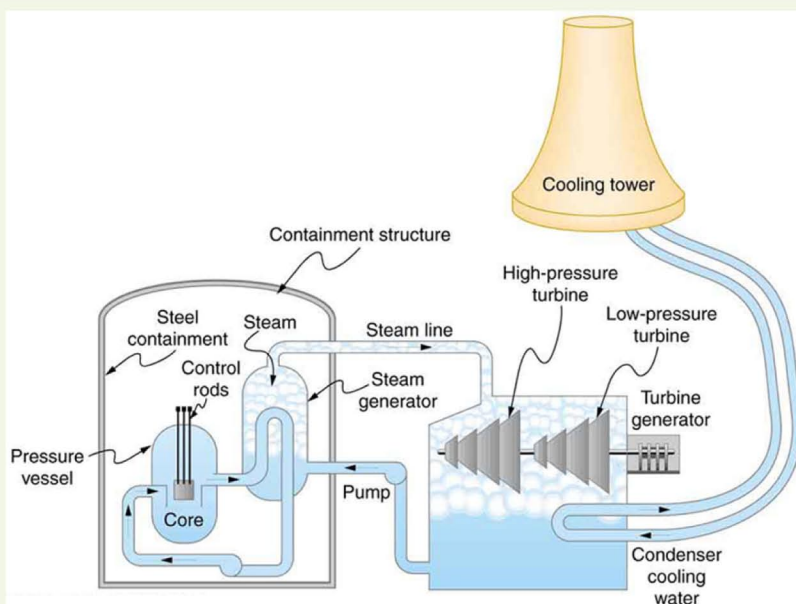


Figure 15.23 Schematic diagram of a pressurized water nuclear reactor and the steam turbines that convert work into electrical energy. Heat exchange is used to generate steam, in part to avoid contamination of the generators with radioactivity. Two turbines are used because this is less expensive than operating a single generator that produces the same amount of electrical energy. The steam is condensed to liquid before being returned to the heat exchanger, to keep exit steam pressure low and aid the flow of steam through the turbines (equivalent to using a lower-temperature cold reservoir). The considerable energy associated with condensation must be dissipated into the local environment; in this example, a cooling tower is used so there is no direct heat transfer to an aquatic environment. (Note that the water going to the cooling tower does not come into contact with the steam flowing over the turbines.)

Strategy

Since temperatures are given for the hot and cold reservoirs of this heat engine, $Eff_C = 1 - \frac{T_c}{T_h}$ can be used to calculate the Carnot (maximum theoretical) efficiency. Those temperatures must first be converted to kelvins.

Solution

The hot and cold reservoir temperatures are given as 300°C and 27.0°C , respectively. In kelvins, then, $T_h = 573\text{ K}$ and $T_c = 300\text{ K}$, so that the maximum efficiency is

$$Eff_C = 1 - \frac{T_c}{T_h}. \quad (15.35)$$

Thus,

$$\begin{aligned} Eff_C &= 1 - \frac{300\text{ K}}{573\text{ K}} \\ &= 0.476, \text{ or } 47.6\%. \end{aligned} \quad (15.36)$$

Discussion

A typical nuclear power station's actual efficiency is about 35%, a little better than 0.7 times the maximum possible value, a tribute to superior engineering. Electrical power stations fired by coal, oil, and natural gas have greater actual efficiencies (about 42%), because their boilers can reach higher temperatures and pressures. The cold reservoir temperature in any of these power stations is limited by the local environment. **Figure 15.24** shows (a) the exterior of a nuclear power station and (b) the exterior of a coal-fired power station. Both have cooling towers into which water from the condenser enters the tower near the top and is sprayed downward, cooled by evaporation.



(a)



(b)

Figure 15.24 (a) A nuclear power station (credit: BlatantWorld.com) and (b) a coal-fired power station. Both have cooling towers in which water evaporates into the environment, representing Q_c . The nuclear reactor, which supplies Q_h , is housed inside the dome-shaped containment buildings. (credit: Robert & Mihaela Vicol, publicphoto.org)