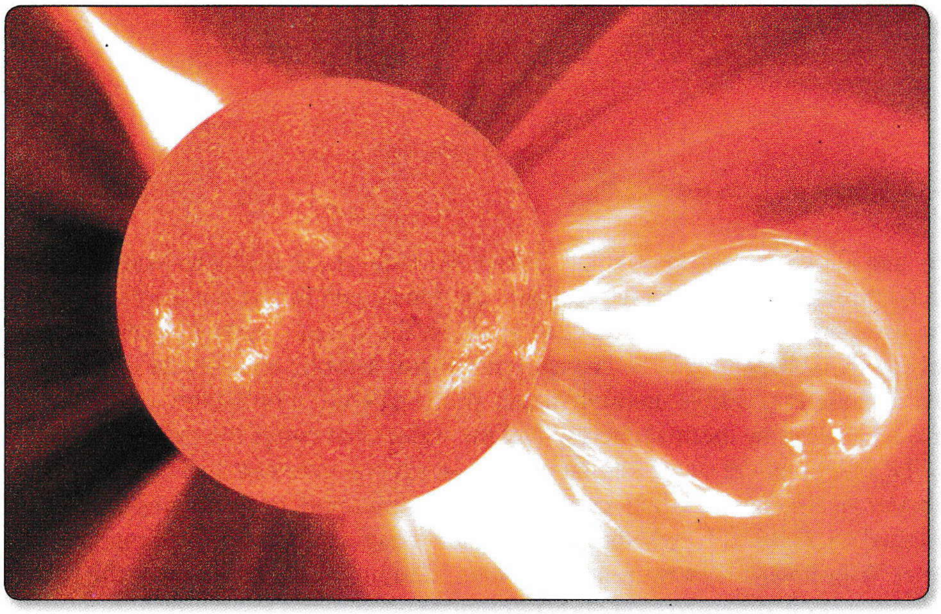
16B THE SECOND AND THIRD LAWS

16.9 Heat Engines and the Second Law

All thermodynamic processes except adiabatic processes involve exchanges of energy between a system and its surroundings. The surroundings must therefore contain either a source of thermal energy, a sink (or receiver) for thermal energy, or both. An easy way to visualize a thermal energy source or sink is to imagine a **heat reservoir** at a specific temperature. The reservoir is so large that no addition or subtraction of energy can change its temperature significantly. A reservoir at a higher temperature than the system, called a *hot reservoir*, is a source of thermal energy for the system. A reservoir at a lower temperature than the system, called a *cold reservoir*, is a thermal energy sink for the system. Both a hot reservoir and a cold reservoir are used to operate a heat engine.



16-12 The sun, a vast heat reservoir, occasionally releases huge amounts of energy in the form of solar flares or prominences, such as the ones shown here.

A source of thermal energy for a system must be hotter than the system. The reason is that thermal energy flows from a hotter body to a colder body. This principle agrees with human experience. If you place a glass of hot water against a glass of cold water, the cold water warms, while the hot water cools. What would you think if, after a few minutes of contact, the cold water froze and the hot water boiled? One form of the **second law of thermodynamics** is the principle that energy flows from an area of higher concentration to an area of lower concentration.

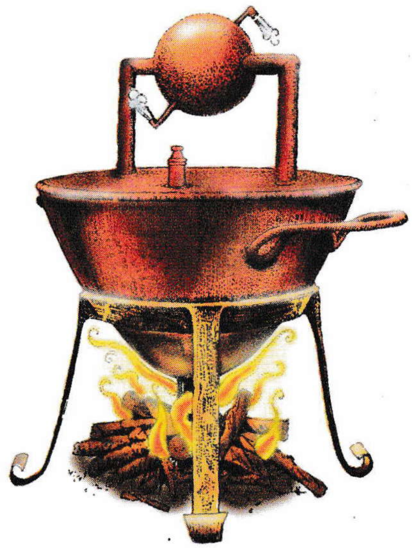
A typical heat engine requires a hot reservoir, a cold reservoir, and a working fluid (a liquid or gas). Thermal energy absorbed from the hot reservoir causes the fluid to expand against a piston or some other movable part. The expansion forces the part to move, performing mechanical work. Then, the fluid gives up thermal energy to the cold reservoir and contracts. The fluid is then ready to be heated and expand again.

There are several ways to state the second law of thermodynamics. One statement of the second law is that energy flows from an area of higher concentration to an area of lower concentration. You observe the second law in action when thermal energy flows from hotter locations to colder ones.

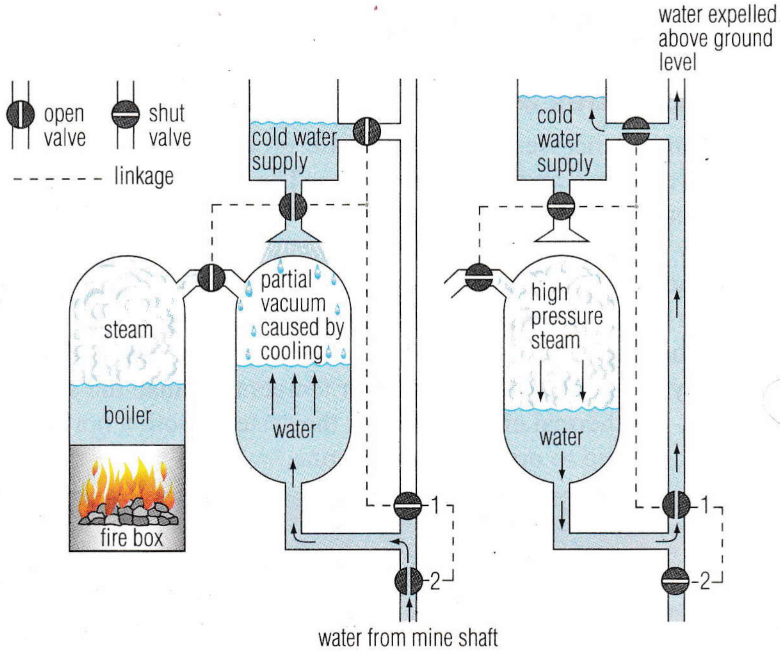
16.10 Early Steam Engines

A steam engine is a heat engine using steam as the working fluid. For centuries men have known that steam can do work. The first steam engine, the *aeolipile*, was described by Hero of Alexandria, who lived about the time of Christ. The aeolipile is a sphere or cylinder with bent outlet pipes (Figure 16-13) that is connected by pipes to a sealed container of boiling water. The connecting pipes are attached in a

Hero of Alexandria (first century AD) was a mathematician and engineer whose writings were an early contribution to mechanics and related sciences.



16-13 The aeolipile



16-14 Schematic of a Savery engine (1698)

way that allows the sphere to rotate. When the water in the container boils, steam is forced through the connecting pipes into the sphere and finally out the outlet pipes. The escaping steam exerts a reaction force on the nozzles that produces a torque, causing the sphere to rotate. The aeolipile is not a cyclic engine; the engine uses only a single irreversible thermodynamic process between two states until its water boils away. All the thermal energy (and the water) that enters the process is lost.

Thomas Savery (1650–1715) was an English engineer and inventor.

Thomas Newcomen (1663–1729) was an English iron magnate and inventor. His was the first practical engine to use a piston in a cylinder.

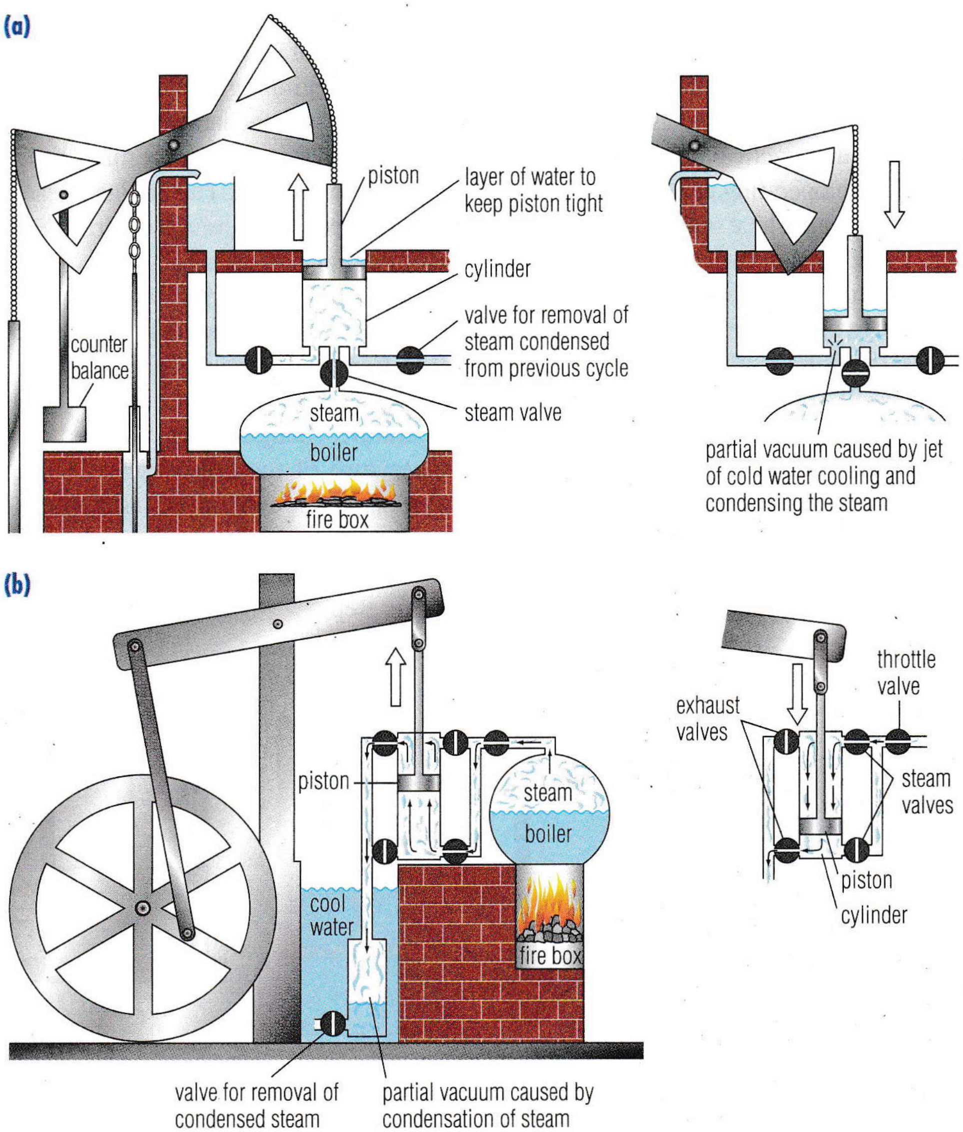
James Watt (1736–1819) was a Scottish engineer who devoted most of his life to designing and building improved steam engines.

The first practical steam engine was a water pump invented by Thomas Savery. A better steam engine, which could be used for pumping or for raising loads, was invented by Thomas Newcomen. Newcomen's engine dominated the market until James Watt invented an even more efficient design. Watt's engine was the first to use separate chambers to heat and cool the steam to avoid the wasteful process of repeatedly heating and then cooling the cylinder walls. Watt's engine was able to power factories and transportation as well as pump water from deep mines. The Industrial Revolution began with Watt's steam engine.

The basic idea behind the steam engine is that steam expands when it is heated and contracts when it is cooled. In the Savery engine (Figure 16-14), the steam expands to push water out of a chamber and through the outlet pipe (right picture). Valve 1 is open; valve 2 is closed. When all the water is out of the chamber, valve 1 is closed and valve 2 is opened. The steam contracts, and the decrease in pressure draws water up through the inlet pipe into the chamber (left picture).

The Newcomen engine, Figure 16-15a, has a movable piston that goes up when the steam expands and down when the steam condenses. It uses a first-class lever to lift the load, so the condensing stroke does the lifting work. The condensed steam is drained from the cylinder before the next cycle begins. One problem that existed with this engine was that the cylinder was made of cast iron. The rough interior surface made it difficult to obtain a good seal with the piston. Another problem was that the cylinder was cooled during the condensation step; the steam entering at the start of the next cycle condensed prematurely as it reheated the cylinder, before any work was done.

The Watt engine, Figure 16-15b, is similar to the Newcomen engine in that it uses a piston. However, the Watt engine relied on the difference in pressure between low-pressure steam and the partial vacuum created by condensing steam



16-15 Schematics of (a) Newcomen's engine (1712) and (b) Watt's double-action rotary engine (1782)

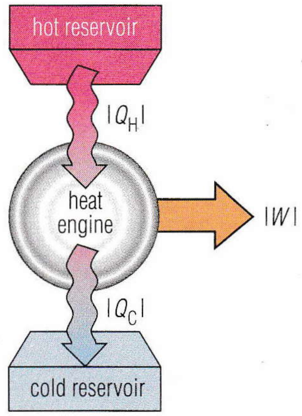
for its power stroke. Also, in later Watt engines, the piston is *double-acting*—force is exerted on both the forward and reverse strokes of the piston through the automatic operation of appropriate steam supply and exhaust valves. The exhausted steam is directed to a second chamber (the condenser), cooled by water, to condense the steam, forming a partial vacuum that increases the net pressure applied by the steam on the piston. Watt's addition of a separate condenser greatly improved the efficiency of his engine compared to earlier designs. The Watt engine also had the advantage of a machine-bored cylinder. The extra-smooth walls allowed a good seal with the piston, preventing the waste of steam.

The valves indicated in the figures are all mechanically linked to the piston in order to ensure they operate at the proper times in the cycle.

16.11 An Ideal Heat Engine Cycle—The Carnot Cycle

A **reversible process** is a quasi-static process that leaves the system in exactly the same state after occurring twice, once normally and once in reverse. The processes that you study here can be assumed to be reversible unless the text states otherwise. However, no real processes are completely reversible due to the presence of nonconservative effects, although some are more nearly reversible than others.

A thermodynamic process is a thermodynamic change between two states. A cycle is made up of several processes that enclose an area on a P-V diagram. The starting and ending points of a cycle are identical, though the paths between the points may be different.

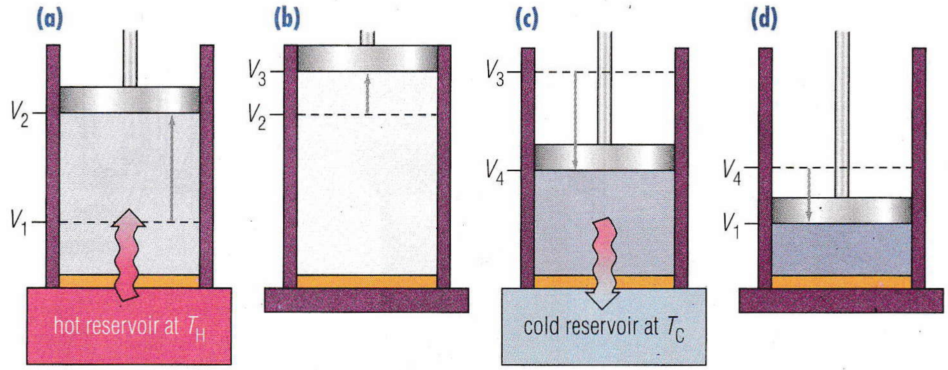


16-16 A conceptual diagram showing how a heat engine works

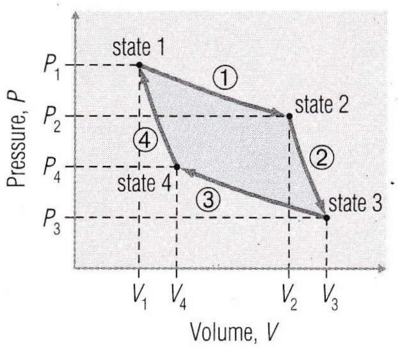
The Carnot cycle is the most efficient ideal heat engine cycle.

A reversible *cycle* leaves the system in the same state as it was before the entire process occurred. The pressure, volume, and temperature of an ideal gas are the same at the end of a reversible cycle as they were at the beginning. Reversible cycles are the most efficient means of converting thermal energy to mechanical work. Cyclic processes are practical because they are very efficient and they can repeat many times without the operating conditions of the engine having to be reset. The engine doesn't continually gain heat until it melts or lose heat until it freezes. There are several idealized cycles that convert thermal energy to work, with varying efficiency.

The most efficient cycle that can operate between two temperatures is the Carnot cycle, a four-step reversible cycle (see Figure 16-17). Step 1 in the Carnot cycle, (a), is an isothermal expansion from V_1 to V_2 at temperature T_H. The system absorbs thermal energy Q_H from the hot reservoir. Step 2, shown in (b), is an adiabatic expansion from V_2 to V_3. The temperature changes from T_H, the temperature of the hot reservoir, to T_C, the temperature of the cold reservoir. The system absorbs no heat in this step. In the third step, (c), an isothermal compression from V_3 to V_4 occurs at T_C. The system gives up thermal energy Q_C to the cold reservoir. Step 4, (d), is an adiabatic compression to the original conditions, T_H and V_1. The system absorbs no thermal energy in this step.



16-17 A Carnot engine completes one cycle. (a) Step 1—isothermal expansion (b) Step 2—adiabatic expansion (c) Step 3—isothermal compression (d) Step 4—adiabatic compression to original conditions



16-18 *P-V* diagram for the Carnot cycle

The curves that represent the isothermal steps 1 and 3 follow *P-V* curves called *isotherms* on the graph. There are potentially an infinite number of isotherms a process may follow. The isotherms followed by an ideal Carnot cycle are the temperatures of the hot and cold reservoirs.

The work done by the system during the cycle can be found from the first law of thermodynamics:

$$Q_{cycle} = \Delta U_{cycle} + W_{cycle}$$

For a cycle, ΔU_{cycle} is zero.

$$Q_{cycle} = 0\text{ J} + W_{cycle}$$

$$Q_{cycle} = W_{cycle}$$

Since the gas does work on its surroundings, W is positive. The sum total of the thermal energy exchanged is Q_{cycle}:

$$|Q_{cycle}| = |Q_H| - |Q_C|$$

The absolute value signs are useful, but not necessary, in order to avoid confusion with signs. By assuming that the gas heat engine does positive work, we assume that Q_H added to the system from the hot reservoir is positive and Q_C lost from the system to the cold reservoir is negative.

Substituting work for the net heat gained by the cycle,

$$|W_{cycle}| = |Q_H| - |Q_C|.$$

The portion of the heat absorbed by the heat engine from the hot reservoir that is converted into useful work is a measure of the efficiency of the engine. The **thermal efficiency** (ε) of a Carnot engine is defined as

$$\varepsilon = \frac{|W_{cycle}|}{|Q_H|} \times 100\%, \text{ or}$$

$$\varepsilon = \frac{|Q_H| - |Q_C|}{|Q_H|} \times 100\%. \quad (16.6)$$

The thermal efficiency (ε) of a Carnot engine is

$$\varepsilon = \frac{|Q_H| - |Q_C|}{|Q_H|} \times 100\%.$$

This result is true for any heat engine cycle that operates between two heat reservoirs. For the portions of the cycle involving isothermal processes at T_H and T_C,

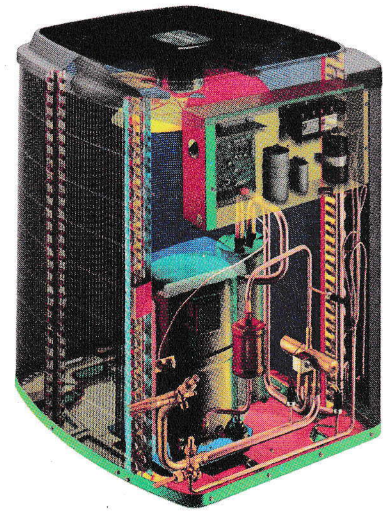
$$\frac{|Q_H| - |Q_C|}{|Q_H|} = \frac{T_H - T_C}{T_H}, \text{ or}$$

$$\varepsilon = \frac{T_H - T_C}{T_H} \times 100\%. \quad (16.7)$$

You can increase the efficiency of a Carnot engine by raising the temperature of the hot reservoir, lowering the temperature of the cold reservoir, or doing both. However, even in theory, the engine cannot be 100% efficient. The efficiency of a real engine will be even lower than that of a theoretical cycle because of friction and other losses.

16.12 Heat Pumps

A heat engine that runs in the counterclockwise direction around the *P-V* diagram, with work added to move thermal energy from the cold reservoir to the hot reservoir, is called a **refrigeration engine** or **heat pump**. The Carnot cycle can be reversed to work as a heat pump. A Carnot heat pump would first adiabatically expand so that the gas's temperature drops below the cold reservoir temperature, then isothermally expand as heat is transferred from the cold reservoir to the heat pump, then adiabatically contract, raising the gas's temperature above the hot reservoir temperature, and finally contract isothermally while it discharges heat to the hot reservoir, thus returning to its original conditions. A refrigerator is a heat pump used to cool a volume. It uses work to move thermal energy from a cold place (inside the refrigerator) to a warm place (the room). An air conditioner is a kind of refrigerator. It cools a room by pumping thermal energy outside. That is the reason that some air conditioners are installed in windows. Heat pumps that function as air conditioners in the summer and as heaters in the winter (by pumping thermal energy from the outside into the room) are also available.



16-19 Domestic heat pumps transfer heat both in summer and winter from the cooler space to the warmer space.

The corresponding method for determining the efficiency of a refrigeration engine or heat pump is to determine its **performance coefficient (*K*)**. This coefficient is defined as

$$K = \frac{|Q_C|}{|W_{cycle}|},$$

where Q_C is the heat removed from the cold reservoir and W_{cycle} is the work done on the engine to move the heat in the unnatural direction from the colder temperature to the warmer. *K* is typically expressed as small numerical values (e.g., 3.00) rather than as a percentage.

16.13 Various Statements of the Second Law and the Third Law

It was stated earlier in this chapter that thermal energy naturally flows from hot bodies to cold bodies. This is one statement of the second law of thermodynamics, a law governing the direction of natural processes. Another statement of the second law is that thermal energy cannot be completely converted to work in a cyclic process. A cycle always loses some energy to a cold reservoir. No exceptions to the second law have been observed.

According to the second law, no engine can be completely efficient. Efficiency for an ideal heat engine is expressed by Equation 16.6,

$$\varepsilon = \frac{|Q_H| - |Q_C|}{|Q_H|} \times 100\%.$$

Statements of the second law:

- Heat flows from a place of higher temperature to one of lower temperature.
- Thermal energy cannot be completely converted to work in a cyclic process.
- No heat engine is 100% efficient.

If no energy were lost to the cold reservoir, Q_C would be zero, and efficiency would be 100%. Complete efficiency is ruled out by the second statement of the second law because some energy is always lost to the cold reservoir.

The ocean is a vast reservoir of thermal energy. Why can't we use this energy to drive a ship across the ocean? The ship could extract energy from the ocean to drive its engine, leaving the ocean a trifle colder than before. Unfortunately, the second law of thermodynamics says that thermal energy does not flow from a cold reservoir—like the ocean—to a hot reservoir—like the ship's engine—unless work is done to force this flow. The work done to extract energy from the ocean would be more than the work the energy could do, so the ship would go nowhere.

The first law says that when converting energy into work you can never get out of a transaction more than you put into it. The second law says that you cannot get as much work out of a machine as you put into it. Both laws forbid *perpetual motion machines*. The first law forbids perpetual motion machines of the first kind, which produce more energy than they consume. The second law forbids perpetual motion machines of the second kind, which are 100% efficient. Many inventors have tried to invent a perpetual motion machine; no one has succeeded.

A heat engine could be 100% efficient only if Q_C were zero:

$$\varepsilon = 100\% = \frac{|Q_H| - 0\text{ J}}{|Q_H|} \times 100\% \tag{16.8}$$

This would mean that all the energy extracted from the hot reservoir was converted to work and none was discharged to the cold reservoir. Since the final legs of the cycle occur at T_C, this temperature would have to be the coldest possible temperature to be able to extract all possible work from the heat. The coldest possible temperature, absolute zero (0 K), has never been attained in the laboratory, though physicists have been able to approach it within a few billionths of a degree under extremely controlled artificial conditions. The coldest natural environment exists in distant interstellar space where the cosmic microwave background radiation indicates a blackbody temperature of 2.725 K.

Scientists are convinced that absolute zero cannot be reached in a particular system because all heat in it would have to be discharged to an even colder reservoir. This is the basis for the third law of thermodynamics, which states that absolute zero is unattainable.

The third law of thermodynamics states that absolute zero is unattainable. Therefore, cold reservoirs at $T_C = 0$ K are not possible.

16.14 Using Thermodynamic Processes to Solve Problems

If human health and commerce rely on cooler temperatures and low humidity, then removing heat and humidity from a location where they have adverse effects to a place where they don't would help solve the problem. Air conditioning is the obvious solution. But what can be done to make this process most efficient?

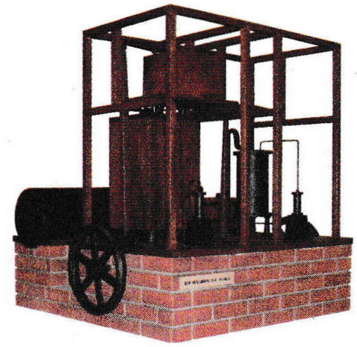
Throughout most of human history, passive methods for cooling buildings have been employed using natural air convection, pools of water, blocks of natural ice, and massive structures to provide thermal inertia. These techniques made living tolerable, but seasonal conditions still ultimately determined whether people actually felt cool. Methods for artificially creating ice began to be developed in the late 1700s. The development of true air chilling, however, began in the 1840s. The first person to effectively experiment with air chilling was a prominent medical doctor in Apalachicola, Florida, named John Gorrie. He noted that yellow fever arrived with hot weather and departed with cool, and he believed, as many people did at that time, that diseases originated from bad or foul air. So he concluded that cool hospital rooms would help patients recover from the disease.

John Gorrie (1802–55) was an American physician, inventor, and public servant. Born in Scotland, he spent most of his life serving the Apalachicola, Florida, community in many capacities. He was motivated to investigate air conditioning out of a humanitarian desire to help his patients.

In 1842, he succeeded in building a machine that operated on principles very similar to the modern refrigerator. Unfortunately, because of the rudimentary state of technology at that time, his machine could not produce the quantity of ice needed to cool entire rooms in a hospital.

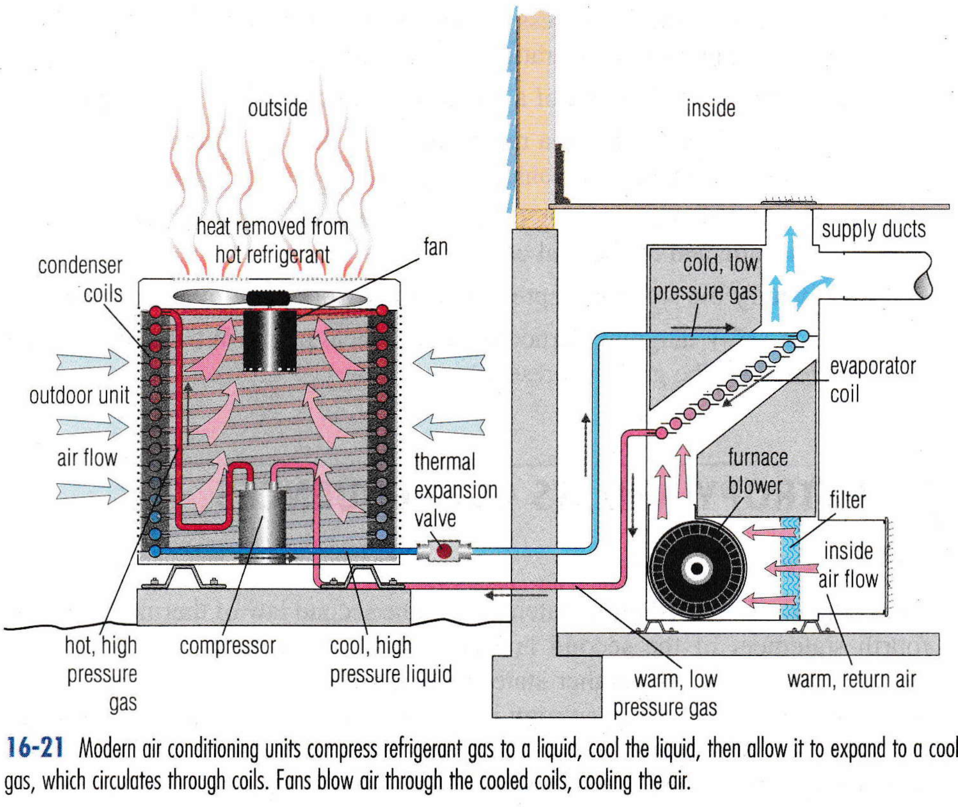
Gorrie's invention set the stage for numerous innovations by many inventors across the world. Instead of compressed air as was used in Gorrie's unit, other fluids with greater heat capacities such as ammonia or carbon dioxide were used with increasing success and efficiency. Large public buildings such as theaters were the earliest beneficiaries of this emerging technology. Then, factory owners realized that productivity could be increased by keeping their workers comfortable.

Some businesses that relied on controlling humidity, such as the photographic film and printing industries, gained significant benefit from using true air conditioning units that controlled relative humidity as well as temperature. In the early 1900s, the American engineer Willis Carrier developed more advanced air conditioning systems and became a successful businessman. He focused on controlling the humidity of air. He sold his inventions to a variety of business clients. Though he was very successful in his work because of his personal expertise, he realized that for the air conditioning industry to become viable, it needed to be based on principles and formulas that could predict the function of a system before it was built. After extensive research and experimentation, Carrier presented a paper in 1911 in which he developed mathematical models to describe the relationship between temperature and humidity, ushering in the science of psychrometrics. Carrier continued to improve his inventions, replacing the piston gas compressors with centrifugal units, and he was the first to use chlorofluorocarbons like DuPont's Freon as the refrigerant. (Freon is a registered trademark of E.I. du Pont de Nemours and Company.) These innovations led to the development of affordable whole-house and room air conditioning units. By the late 1930s, the first car air conditioners were being installed.



16-20 A replica of John Gorrie's ice machine

Psychrometrics or psychrometry is the science of the thermodynamics of gas/liquid mixtures.



16-21 Modern air conditioning units compress refrigerant gas to a liquid, cool the liquid, then allow it to expand to a cool gas, which circulates through coils. Fans blow air through the cooled coils, cooling the air.

American society and culture were subtly and gradually revolutionized by this invention. Sections of the American South and West that were sparsely inhabited saw rapid population growth as the direct result of air conditioning. Today, nearly all cars sold in the United States are air conditioned, and in many places, air conditioning is considered a necessity rather than the luxury it once was.

16B Section Review

1. What are the essential parts of a thermodynamic heat engine?
2. a. What did the Savery engine lack that the Newcomen and Watt engines had?
   b. What was the major improvement of the Watt engine over the Newcomen engine?
3. What two basic reversible thermodynamic processes occur at various points in a Carnot cycle?
4. A steamship's propulsion plant uses the ocean water to absorb its waste heat according to the Carnot cycle. What happens to the propulsion plant's efficiency if the seawater temperature becomes warmer (as in the tropics)?
5. a. What condition would have to exist for an ideal heat engine to be 100% efficient?
   b. What principle states that this condition is not possible?
6. a. Why does your car engine have a radiator?
   b. What principle predicts that a gasoline engine would need one?

DS7. When a gas is compressed (adiabatically) inside a cylinder by a piston, what happens to its thermal energy and temperature? If the high-pressure, compressed gas is cooled, what will happen to its temperature when it is allowed to expand? What can you do with such a process?

DS8. Describe the chilling process within an air conditioning unit. How does this correspond to the operation of a heat pump?

⊙9. a. Sketch a *P-V* diagram of a typical Carnot cycle for a heat engine.
   b. Shade and label the area representing work done during the adiabatic and isothermal expansions.
   c. Shade with a contrasting color and label the work done during the adiabatic and isothermal contractions.
   d. Identify the area that represents the net work done by the engine.

⊙10. Sketch a *P-V* diagram Carnot cycle for a heat pump. What does the area enclosed by the graph represent?

16B Objectives

After completing this section, I can

- ✓ describe how the function of heat engines relies on the second law of thermodynamics.
- ✓ briefly describe the first successful variants of the steam engine.
- ✓ trace the path of a heat engine through a single pass of the Carnot cycle.
- ✓ compute the thermal efficiency of a heat engine.
- ✓ contrast the difference in operation between a heat engine and a heat pump.
- ✓ state the second law of thermodynamics in at least three ways.
- ✓ state the third law of thermodynamics and explain why it must be true.
- ✓ discuss the initial motivation for developing a room- or building-sized air conditioning machine.
- ✓ describe several ways that the air conditioner has changed American culture.

16C ENTROPY AND ITS CONSEQUENCES

16.15 What Is Entropy?

We have already discussed three statements of the second law of thermodynamics. A fourth statement of the second law is that entropy increases in all natural processes. **Entropy (S)** is another state variable of a system, like volume, temperature, or pressure. Because entropy is related to the microscopic properties of the particles of a system, it is similar in some ways to internal energy. Just as with internal energy, the *change* of entropy (ΔS) is more important and more easily

The second law of thermodynamics also states that entropy increases in all natural processes