Carnot Cycle

In 1824, Sadi Carnot (1796-1832) published a short book, *Reflections on the Motive Power of Fire*. (The book is now free online. You should try it out.) To construct an engine, Carnot noted, at least two reservoirs of energy of different temperatures are needed. He further noted that the engine loses efficiency whenever the working fluid of the engine exchanges energy with the rest of the world across a finite difference in temperature. To avoid such exchange of energy, he described a specific cycle—later known as the Carnot cycle—consisting of isothermal and adiabatic processes. Whenever the working fluid exchanges energy with either reservoir, the temperature of the working fluid is kept the same as that of the reservoir. Whenever the temperature of working fluid differs from the temperatures of the reservoirs, the working fluid is thermally insulated. He argued that this cycle is the most efficient of all cycles that convert heat to work by operating between two constant-temperature reservoirs of energy.

In the mid-1800s, the Carnot cycle was used by Kelvin and Clausius to formulate the second law of thermodynamics, leading to the discovery of a new function of state: entropy. The fundamental postulate was formulated much later, in the late 1800s and the beginning of 1900s.

Our textbook recounts this history in Chapters 7 and 8. Our lecture, however, will not follow this historical development. As they say, thermodynamics is difficult enough without troubling the students with its history. We will take the two great principles—the fundamental postulate and the conservation of energy—as given, and use them to analyze the Carnot cycle.

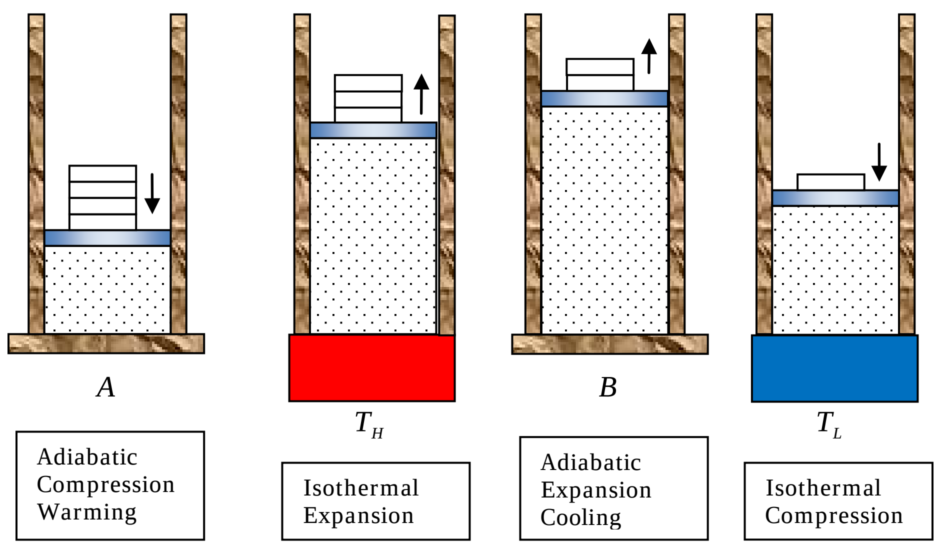
You are strongly urged to read Chapters 7 and 8 of the textbook for illumination, to appreciate how people grope for understanding in darkness. I will assign homework from the textbook. After all, how to apply the concept of entropy to analyze engines and refrigerators and heat pumps is independent of how the concept is introduced. Indeed, Carnot himself analyzed these devices in his book without clear understanding of entropy.

Steam engines. Before Carnot published his book, steam engines had already become a driving force for the Industrial Revolution. A steam engine is a device that converts the heat from burning coal into work. Carnot wanted to determine the maximal efficiency of an engine—that is, the maximal amount of work produced by burning a unit amount of coal. To this end, Carnot noted the following.

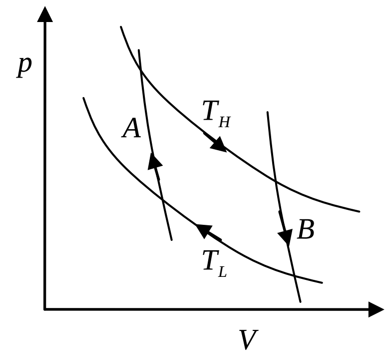
First, to construct an engine, at least two reservoirs of energy, of different temperatures, are needed. For example, when a fluid in a piston-cylinder setup is in thermal contact with one reservoir, heat can flow into the fluid, causing the fluid to expand and raise the weight on the piston. This process, however, stops when the fluid and the reservoir reach thermal equilibrium. That is, no more work can be produced when the temperature of the fluid becomes the same as that of the reservoir. To continue the process, the fluid must be made in contact with another reservoir with a different temperature.

Second, the engine loses efficiency whenever the working fluid of the engine exchanges energy with the rest of the world by heat across a finite difference in temperature. As an extreme example, if an engine is so constructed that the two reservoirs are in direct thermal contact, the energy will transfer by heat from the high-temperature reservoir to the low-temperature reservoir, and the engine will do no work.

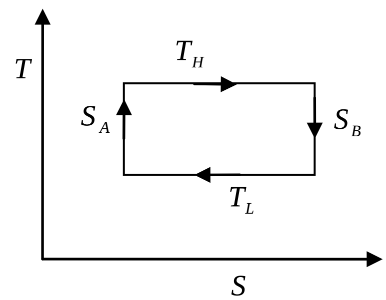
Carnot cycle. To avoid any wasteful exchange of energy, Carnot described a specific cycle—later known as the Carnot cycle—consisting of isothermal and adiabatic processes. Whenever the working fluid exchanges energy with either reservoir, the temperature of the working fluid is kept the same as that of the reservoir. Whenever the temperature of working fluid differs from the temperatures of the reservoirs, the working fluid is thermally insulated. He argued that this cycle is the most efficient of all cycles that convert heat to work by using two reservoirs of different temperatures.



Here is the specific cycle described by Carnot. A working fluid is enclosed in a cylinder-piston setup. The fluid forms a closed system—that is, the fluid does not exchange matter with the rest of the world. The fluid, however, exchanges energy with the rest of the world in two ways: the pressure of the fluid does work by moving the piston, and heat transfers across the base of the cylinder. No heat transfers across the wall of the cylinder or across the piston.



The working fluid cycles through four **reversible processes**:



- *Adiabatic compression*. The system is fully insulated, and the weight compresses the fluid. The energy of the fluid increases, and the temperature of the fluid increases.
- *Isothermal expansion*. The base of the cylinder is in thermal contact with a reservoir of temperature T_H, and the fluid expands.
- *Adiabatic expansion*. The system is fully insulated, and fluid expands. The energy of the fluid decreases, and the temperature of the fluid decreases.
- *Isothermal compression*. The base of the cylinder is in thermal contact with a reservoir of temperature T_L, and the fluid is compressed.

The Carnot cycle is represented on the (p,V) diagram, and on the (T,S) diagram.

Two propositions concerning the Carnot cycle. Although the cycle proposed by Carnot relies on a specific setup, the significance of this cycle is appreciated in terms of two propositions.

The first proposition. It is impossible to construct an engine that operates between two given reservoirs and is more efficient than a reversible engine operating between the same two reservoirs.

The second proposition. All engines that operate on the Carnot cycle between two given constant-temperature reservoirs have the same efficiency.

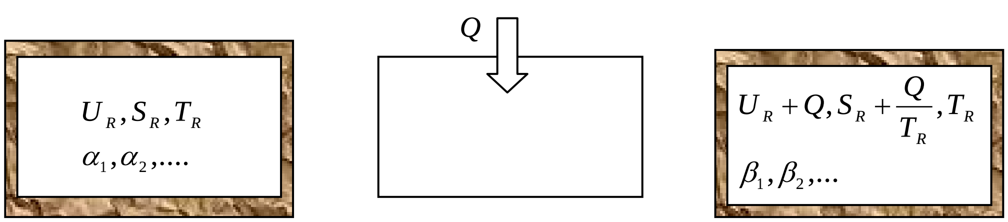
We next analyze cycles of any kind operating between two constant-temperature reservoirs of energy by using the two great principles, the conservation of energy and the fundamental postulate.

Ideal reservoir of energy. We model a heat source or a heat sink by a device called a reservoir of energy, or a heat reservoir, or a heat bath. The reservoir of energy, unless otherwise stated, is idealized as follows:

- The reservoir exchanges energy with the rest of the world by heat, not by work.
- The reservoir is a closed system—it does not exchange matter with the rest of the world.
- When the reservoir is in thermal contact with another system, the two systems exchange energy, but the temperature of the reservoir is fixed.
- The transfer of energy is so slow that the reservoir changes its thermodynamic state by a quasi-equilibrium process.

For example, a saturated mixture of two phases of a pure substance can serve as an ideal reservoir. When energy is added to the mixture by heat, one phase grows at the expense of the other, while the temperature of the mixture is maintained at the saturation temperature. The mixture changes its state—that is, changes the amounts of the two phases—by a quasi-equilibrium process so long as the transfer of energy is slow.

As another example, a large body—such as a pond—is a reservoir of energy. In thermal contact with a smaller body, the amount of energy exchanged between the two bodies is so small that the temperature of the large body remains unchanged. The large body changes its state by a quasi-equilibrium process so long as the transfer of energy is slow.



Isolate a reservoir of energy at energy U_R

Add energy to the reservoir by a quantity of heat Q

Isolate the reservoir at energy $U_R + Q$

Ideal reservoir of energy analyzed by the principle of the conservation of energy. An ideal reservoir of energy is a thermodynamic system of one independent variation. Let U_R be the energy of the reservoir. When the reservoir receives a quantity of heat Q, according to the principle of the conservation of energy, the energy of the reservoir increases to $U_R + Q$. That is, the energy of one state differs from the energy in the other state by

$$\Delta U_R = Q .$$

Ideal reservoir of energy analyzed by the fundamental postulate. In addition to the energy U_R, we are interested in two other functions of state of the reservoir: the entropy S_R, and the temperature T_R. For an ideal reservoir of energy, the temperature of the reservoir, T_R, is fixed while the reservoir exchanges energy with the rest of the world. According to the fundamental postulate, the entropy of the reservoir changes by $\Delta S_R = \Delta U_R / T_R$. Consequently, when the reservoir receives a quantity of heat Q, the entropy of the ideal reservoir of energy increases by

$$\Delta S_R = \frac{Q}{T_R} .$$

What does this expression mean? We can always translate entropy back to the number of quantum states by recalling the definition of entropy, $S = \log \Omega$. When the energy is fixed at U_R, the reservoir is an isolated system, flipping among a set of quantum states, $\{\alpha_1, \alpha_2, ...\}$; the number of the quantum states in this set is $\Omega_R(U_R)$, and the entropy of the set is $\log \Omega_R(U_R)$. When the energy is fixed at $U_R + Q$, the reservoir is another isolated system, flipping among another set of quantum states, $\{\beta_1, \beta_2, ...\}$; The number of the quantum states in this set is $\Omega_R(U_R + Q)$, and the entropy of the set is $\log \Omega_R(U_R + Q)$. Thus, the above expression is written as

$$\log \frac{\Omega(U_R + Q)}{\Omega(U_R)} = \frac{Q}{T_R} .$$

When all other interactions between the reservoir and the rest of the world are blocked, adding energy to the reservoir by heat increases the number of quantum states of the reservoir.

Arbitrary cycles analyzed by the principle of conservation of energy. Consider an engine operates in a cycle between two ideal reservoirs of energy of different temperatures. During one cycle, let the working fluid gains energy Q_H from the high-temperature reservoir, and loses energy Q_L to the low-energy reservoir. During the cycle, let the working fluid does work W. After the working fluid completes the cycle, every function of state returns to its initial value. In particular, the internal energy of the working fluid returns to its initial value after the fluid completes a cycle. According to the principle of the conservation of energy, we write

$$W = Q_H - Q_L .$$

When the engine operates in a cycle, the work done by the energy equals the energy grained from the high-temperature reservoir minus the energy lost to the low-temperature reservoir.

Arbitrary cycles analyzed by the fundamental postulate. Both reservoirs of energy are ideal; they are of different temperatures, T_H and T_L. On losing energy Q_H, the high-temperature reservoir changes entropy by

$$\Delta S_H = -\frac{Q_H}{T_H} .$$

On gaining energy Q_L, the low-temperature reservoir changes entropy by

$$\Delta S_L = +\frac{Q_L}{T_L} .$$

The composite of the working fluid, the weight, and the two reservoirs of energy is an isolated system. The entropy of the composite is the sum of the entropies of all the parts. After the working fluid completes the cycle, the entropy of the fluid returns to its initial value. During the cycle, the weight does not change the number of quantum states—the weight merely goes up and down. Consequently, after a cycle, the entropy of the composite changes by

$$\Delta S_{composite} = \Delta S_L + \Delta S_H .$$

Inserting the above expressions, we obtain that

$$\Delta S_{composite} = \frac{Q_L}{T_L} - \frac{Q_H}{T_H} .$$

That is, only the two reservoirs of energy contribute to the change in the entropy of the composite.

During a cycle, the working fluid of the engine gains heat from one reservoir, loses heat to the other reservoir, and moves the weight. The parts of the composite must interact with one another by removing various constraints to allow the transfer of energy by heat and work. According to the fundamental postulate, upon removing constraints internal to the isolated system, the entropy of the isolated system increases, so that

$$\Delta S_{composite} \geq 0 .$$

The equality holds when the cycle is reversible. That is, after a reversible cycle, the entropy of the composite recovers its initial value. After an irreversible cycle, however, the entropy of the composite increases.

A real engine undergoes irreversible cycles that generate entropy. For example, when the working fluid and a reservoir is in thermal contact, the transfer of energy is irreversible when the temperature of the working fluid differs from that of the reservoir. As another example, when the weight moves, the piston moves against friction. These irreversible processes generate entropy even when the two reservoirs of energy are ideal. This conclusion is consistent with the above inequality.

A combination of the above two expressions gives the inequality

$$\frac{Q_L}{T_L} \geq \frac{Q_H}{T_H} .$$

The equality holds when the cycle is reversible, and the inequality holds when the cycle is irreversible.

The above inequality recovers a familiar special case. When the two ideal reservoirs of energy in direct thermal contact, no work is produced. According to the principle of the conservation of energy, the energy gained by one reservoir equals the energy lost by the other reservoir, $Q_L = Q_H$. In this special case, the above inequality reduces to $T_H > T_L$. That is, when the two reservoirs are in direct thermal contact, energy transfers in the direction from the high-temperature reservoir to the low-temperature reservoir.

Efficiency of an engine. The efficiency of an engine is defined by

$$\frac{W}{Q_H} .$$

According to the principle of the conservation of energy, $W = Q_H - Q_L$, so that the efficiency of the engine is written as

$$\frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H} .$$

Using the thermodynamic inequality, $Q_L / Q_H \geq T_L / T_H$, we obtain that

$$\frac{W}{Q_H} \leq 1 - \frac{T_L}{T_H} .$$

The equality holds for reversible engines.

Carnot cycle running in the opposite direction. The Carnot cycle running in the opposite direction serves the function of refrigeration. An external force does work W to the working fluid in a refrigerator. The refrigerator gains energy Q_L from the low-temperature reservoir, and loses energy Q_H to the high-energy reservoir. For such a cycle, a similar line of reasoning leads to a thermodynamic inequality:

$$\frac{Q_L}{T_L} \leq \frac{Q_H}{T_H}.$$

The equality holds when all the processes are reversible. For example, the heat transfer between the fluid and a reservoir is reversible when the temperature of the fluid equals that of the reservoir. Try to prove this inequality by yourself.

Efficiency of a refrigerator. The efficiency of the refrigerator, also known as the coefficient of performance (COP), is defined as

$$\frac{Q_L}{W}.$$

According to the conservation of energy, $W = Q_H - Q_L$, we write

$$\frac{Q_L}{W} = \frac{1}{Q_H / Q_L - 1}.$$

In the cycle for refrigerators, the thermodynamic inequality becomes $Q_H / Q_L \geq T_H / T_L$, we obtain that

$$\frac{Q_L}{W} \leq \frac{1}{T_H / T_L - 1}.$$

The equality holds for reversible refrigerators.

Efficiency of a heat pump. We can easily convert 100% of work to heat. For example, we can use the joule heating of a metal to convert electrical work fully to heat. Using a heat pump, however, we can use 1 unit of work to add more energy to a hot place, by drawing energy from a cold place.

A heat pump works like a refrigerator, but with a different object. While a refrigerator aims to remove energy from a cold place, a heat pump aims to add more energy to a hot place. An external force does work W to the working fluid, and the heat pump gains energy Q_L from a low-temperature reservoir, and loses energy Q_H to a high-energy reservoir. The efficiency of the heat pump is defined as

$$\frac{Q_H}{W}.$$

According to the conservation of energy, $W = Q_H - Q_L$, so that the efficiency of the heat pump can be written as

$$\frac{Q_H}{W} = \frac{1}{1 - Q_L / Q_H}.$$

Using the thermodynamic inequality $Q_L / Q_H \le T_L / T_H$, we obtain that

$$\frac{Q_H}{W} \le \frac{1}{1 - T_L / T_H}.$$

The equality holds for reversible heat pumps. The efficiency of a heat pump can exceed 100%.

SUPPLEMENTARY MATERIAL

Two ideal reservoirs of energy in thermal contact. Now consider two ideal reservoirs of energy, one being fixed at a low temperature T_L, and the other being fixed at a high temperature T_H. The composite of the two reservoirs is an isolated system. When insulated from each other, the two reservoirs do not exchange energy. The insulation between the two reservoirs is a constraint internal to the isolated system—the constraint prevents the transfer of energy from one reservoir to the other. When the insulation is removed, the two reservoirs are in thermal contact, and energy goes from the high-temperature reservoir to the low-temperature reservoir. We next analyze this everyday experience by using the principle of the conservation of energy and the fundamental postulate.

According to the principle of the conservation of energy, the energy gained by the low-temperature reservoir equal the energy lost by the high temperature reservoir. Let the low-temperature reservoir gain energy *Q*, and the high-temperature reservoir lose energy *Q*.

Upon gaining energy *Q*, the low-temperature reservoir changes entropy by

$$\Delta S_L = +\frac{Q}{T_L}.$$

The higher the energy, the more quantum states. Upon losing energy *Q*, the high-temperature reservoir changes entropy by

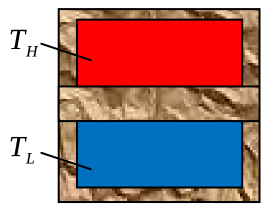
$$\Delta S_H = -\frac{Q}{T_H}.$$

The lower the energy, the fewer quantum states. The entropy of the composite is the sum of the entropies of the two reservoirs, so that

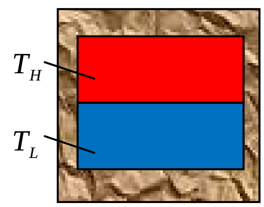
$$\Delta S_{composite} = \Delta S_L + \Delta S_H .$$

The notation $\Delta S_{composite}$ means the entropy of the composite after the removal of the insulation minus that before the removal of the insulation. Inserting the above expressions, we obtain that

$$\Delta S_{composite} = \left(\frac{1}{T_L} - \frac{1}{T_H} \right) Q .$$



Two reservoirs in thermal isolation.



Two reservoirs in thermal contact.

What does this expression mean? Recall the definition of entropy, $S = \log \Omega$. When the two reservoirs is insulated from each other, the number of quantum states of the composite is designated as $\Omega_{insulated}$. When the two reservoirs is thermal contact, the number of quantum states of the composite is designated as $\Omega_{contact}$. The above expression means that

$$\log \frac{\Omega_{contact}}{\Omega_{insulated}} = \left(\frac{1}{T_L} - \frac{1}{T_H} \right) Q .$$

According to the fundamental postulate, upon lifting a constraint internal to an isolated system, the system changes from a macrostate of fewer quantum states to a macrostate of more quantum states:

$$\Omega_{contact} > \Omega_{insulated} ,$$

or

$$\Delta S_{composite} \geq 0 .$$

The inequality is consistent with our everyday experience: energy flows by heat from the high-temperature reservoir to the low-temperature reservoir.

Reversible heat transfer. An isolated system is unlikely to go from a macrostate of more quantum states to a macrostate of fewer quantum states. Consequently, the transfer of energy by heat across a finite difference in temperature is an irreversible process.

A heat-transfer process approaches a reversible process as the difference in the temperatures of the two reservoirs approaches zero. To transfer a finite amount of energy through an infinitesimal difference in temperature would be infinitesimally slow. We can, however, make the difference in the temperatures of the two reservoirs so small that the two reservoirs are nearly in equilibrium. That is, reversible heat transfer is an idealization.

Non-ideal reservoir of energy. Real reservoirs of energy are non-ideal, in ways that may violate any one of the idealizations listed above. Here we analyze an example of non-ideal reservoir of energy. When the reservoir receives a finite amount of energy by heat across the boundary, the temperature at the boundary increases relative to the temperature in the interior of the reservoir, and the finite difference in the temperature motivates heat conduction. Of course, difference in the temperature within the reservoir can be made small by adding energy to the reservoir slowly. In so doing, the non-ideal reservoir approaches an ideal one.

Thermodynamic analysis of a non-ideal reservoir of energy. Inside a non-ideal reservoir, the temperature is inhomogeneous, so we cannot speak of *the* temperature of the non-ideal reservoir. Imagine that the non-ideal reservoir is divided into many small parts, and each part has values of temperature, energy and entropy. We can then sum up the energies of all the parts to obtain the energy of the non-ideal reservoir U_R . We can also sum up the entropies of all the parts to obtain the entropy of the non-ideal reservoir S_R. But we cannot speak of the temperature of the non-ideal reservoir.

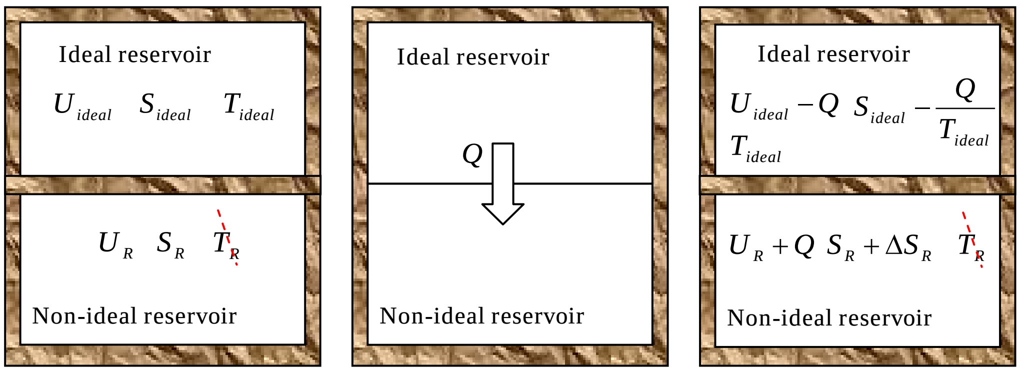
To model the process of adding energy to the non-ideal reservoir, we imagine that the non-ideal reservoir is in thermal contact with a second reservoir of energy. We model the second reservoir as an ideal reservoir, characterized by the temperature T_{ideal}, energy U_{ideal}, and entropy S_{ideal}. The composite of the two reservoirs is an isolated system. We next analyze the composite by using the conservation of energy and the fundamental postulate.

According to the principle of the conservation of energy, the amount of energy gained by one reservoir is the same as that lost by the other reservoir. When the non-ideal reservoir gains energy Q, the ideal reservoir loses energy Q.

Upon losing energy Q by heat, the ideal reservoir changes its entropy by

$$\Delta S_{ideal} = -\frac{Q}{T_{ideal}}.$$

That is, removing energy from a system—while blocking all other interactions between the system and the rest of the world—decreases the number of quantum states of the system.



Let the change of the entropy of the non-ideal reservoir by ΔS_R. Because we cannot speak of the temperature of the non-ideal reservoir, we cannot calculate ΔS_R in the same way as what we did for the ideal reservoir. The change of the entropy of the composite is the sum of the changes in the two reservoirs:

$$\Delta S_{composite} = \Delta S_R + \Delta S_{ideal}.$$

A combination of the above two expressions gives that

$$\Delta S_{composite} = \Delta S_R - \frac{Q}{T_{ideal}}.$$

According to the fundamental postulate, upon lifting constraints internal to an isolated system, the entropy of the isolated system increases. The entropy of the composite increases as energy redistributes within the non-ideal reservoir by heat conduction. Thus,

$$\Delta S_{composite} \geq 0,$$

or

$$\Delta S_R \geq \frac{Q}{T_{ideal}}.$$

Recall that ΔS_R is the change of the entropy of the non-ideal reservoir, T_{ideal} is the fixed temperature of the ideal reservoir, and Q is the energy transferred from the ideal reservoir to the non-ideal reservoir.

The above inequality can be readily understood. When the non-ideal reservoir is in thermal contact with the ideal reservoir, the entropy of the composite increases, so that the increase of the entropy of the non-ideal reservoir is more than the decrease of the entropy of the ideal reservoir.

In the above expressions, the equality holds when the composite undergoes a quasi-equilibrium process—that is, when both reservoirs are ideal, and when they have the same temperature.

Kelvin-Planck statement of the second law of thermodynamics. When a fluid in a piston-cylinder setup is in thermal contact with a reservoir, heat can flow into the fluid, causing the fluid to expand and raise the weight on the piston. This process, however, stops when the fluid and the reservoir reach thermal equilibrium. That is, no more work can be gained when the temperature of the fluid becomes the same as that of the reservoir.

This everyday experience, with some extension, is written as the *Kelvin-Planck statement*:

> It is impossible to construct a device that operates in a cycle and produces no effect other than the raising of a weight and the exchange of heat with a single reservoir.

This statement is a version of the second law of thermodynamics. We next show that the Kelvin-Planck statement is a consequence of the two great principles, the fundamental postulate and conservation of energy.

We regard the composite of the weight, the device and the reservoir as an isolated system. During a cycle, let the device gains energy Q from the reservoir, and does work to increase the potential energy of the weight by W. After the device completes the cycle, every function of state returns to its initial value. In particular, the internal energy of the device returns to its initial value after the cycle. According to the principle of the conservation of energy, we write

$$W = Q .$$

We have adopted the following sign convention: $Q > 0$ means that the device receives energy from the reservoir by heat, and does work to raise the weight.

Let the temperature of the reservoir be T_R. On losing energy Q, the reservoir changes entropy by

$$\Delta S_R = -\frac{Q}{T_R} .$$

The entropy of the composite is the sum of the entropies of the fluid, the weight and the reservoir. After the fluid completes a cycle, the entropy of the fluid—like any other function of thermodynamic state—returns to its initial value. During the cycle, the weight does not change the number of quantum states—the weight merely changes height. Consequently, after a cycle, the entropy of the composite changes by

$$\Delta S_{composite} = -\frac{Q}{T_R}.$$

According to the fundamental postulate, upon removing constraints internal to the isolated system, the entropy of the isolated system increases, so that

$$\Delta S_{composite} \geq 0,$$

or

$$Q \leq 0.$$

The equality holds when all the processes are reversible. For example, the transfer of energy by heat between the fluid and a reservoir is reversible when the temperature of the fluid equals that of the reservoir. The above inequality shows that, when the device is irreversible, the weight must do work to the device, and energy must be transferred into the reservoir. This completes the proof of the Kelvin-Planck statement. The proof works for devices of any constructions.

Perpetual-motion machines. Perpetual-motion machines of the first kind operate in a cycle, doing work without the input of energy. Such machines violate the principle of the conservation of energy.

Perpetual-motion machines of the second kind operate in a cycle, doing work by drawing energy from a single reservoir. Such machines violate the fundamental postulate. If such a machine were constructed, we could hook the machine to the Earth, which is a giant reservoir of energy. We could then produce work in perpetual without violating the principle of the conservation of energy. The fundamental postulate, or more directly, the Kelvin-Planck statement, denies the existence of perpetual-motion machines of the second kind.

Clausius statement of the second law of thermodynamics. The following statement is another version of the second law of thermodynamics.

> It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.

The textbook gives a demonstration of the equivalence of the Kelvin-Planck statement and the Clausius statement. So far as we are concerned, both statements are consequences of the two great principles, the fundamental postulate and the conservation of energy.