Part III
Second Law of Thermodynamics

In this Part, we introduce the **second law of thermodynamics**, which asserts that

- processes occur in a certain direction and that
- energy has quality as well as quantity.
- A process cannot take place unless it satisfies both the first and second laws of thermodynamics.

In this chapter, the thermal energy reservoirs, reversible and irreversible processes, heat engines, refrigerators, and heat pumps are introduced first. Various statements of the second law are followed by a discussion of perpetual-motion machines and the absolute thermodynamic temperature scale. The Carnot cycle is introduced next, and the Carnot principles are examined. Finally, idealized Carnot heat engines, refrigerators, and heat pumps are discussed.

Introduction

In the preceding two chapters, we applied the *first law of thermodynamics,* or the *conservation of energy principle,* to processes involving closed systems. Energy is a conserved property, and no process is known to have taken place in violation of the first law of thermodynamics. Therefore, it is reasonable to conclude that a process must satisfy the first law to occur. However, as explained below, satisfying the first law alone does not ensure that the process will actually take place.

It is common experience that a cup of hot coffee left in a cooler room eventually cools off.

This process satisfies the first law of thermodynamics since the amount of energy lost by the coffee is equal to the amount gained by the surrounding air. Now let us consider the reverse process-the hot coffee getting even hotter in a cooler room as a result of heat transfer from the room air. We all know that this process never takes place. Yet, doing so would not violate the first law as long as the amount of energy lost by the air is equal to the amount gained by the coffee.

It is clear from the above that processes proceed in a *certain direction* and not in the reverse direction. The first law places no restriction on the direction of a process, but satisfying the first law does not ensure that that process will actually occur. This inadequacy of the first law to identify whether a process can take place is remedied by introducing another general principle, the *second law of thermodynamics.* We show later in this chapter that the reverse processes discussed above violate the second law of thermodynamics. This violation is easily detected with the help of a property, called *entropy,* defined in the next part. *A process will not occur unless it satisfies both the first and the second laws of thermodynamics.*

The second law has been stated in several ways.

(i) ***The principle of Thomson (Lord Kelvin)*** states: 'It is impossible by a cyclic process to take heat from a reservoir and to convert it into work without simultaneously transferring heat from a hot to a cold reservoir.' This statement of the second law is related to equilibrium, i.e. work can be obtained from a system only when the system is not already at equilibrium. If a system is at equilibrium, no spontaneous process occurs and no work is produced. Evidently, Kelvin's principle indicates that the spontaneous process is the heat flow from a higher to a lower temperature, and that only from such a spontaneous process can work be obtained.

(ii) ***The principle of Clausius*** states: 'It is impossible to devise an engine which, working in a cycle, shall produce no effect other than the transfer of heat from a colder to a hotter body.' A good example of this principle is the operation of a refrigerator.

(iii) ***The principle of Planck*** states: 'It is impossible to construct an engine which, working in a complete cycle, will produce no effect other than raising of a weight and the cooling of a heat reservoir.'

(iv) ***The Kelvin-Planck principle*** may be obtained by combining the principles of Kelvin and of Planck into one equivalent statement as the Kelvin-Planck statement of the second law. It states: 'No process is possible whose sole result is the absorption of heat from a reservoir and the conversion of this heat into work.'

The second law of thermodynamics is also used in determining the *theoretical limits* for the performance of commonly used engineering systems, such as heat engines and refrigerators, as well as predicting the *degree of completion* of chemical reactions.

The second law is not a deduction from the first law but a separate law of nature, referring to an aspect of nature different from that contemplated by the first law. The first law denies the possibility of creating or destroying energy, whereas the second law denies the possibility of utilizing energy in a particular way. The continuous operation of a machine that creates its own energy and thus violates the first law is called *perpetual motion of the first kind.* A cyclic device which would continuously abstract heat from a single reservoir and convert that heat completely to mechanical work is called a *perpetual-motion machine of the second kind.* Such a machine would not violate the first law (the principle of conservation of energy), since it would not create energy, but economically it would be just as valuable as if it did so. Hence, the second law is sometimes stated as follows: *'A perpetual motion machine of the second kind is impossible.'*

Thermal Energy Reservoir

In the development of the second law of thermodynamics, it is very convenient to have a hypothetical body with a relatively large *thermal energy capacity* (mass x specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature. Such a body is called a **thermal energy reservoir**, or just a reservoir. In practice, large bodies of water such as oceans, lakes, and rivers as well as the atmospheric air can be modeled accurately as thermal energy reservoirs because of their large thermal energy storage capabilities or thermal masses.

A body does not actually have to be very large to be considered a reservoir. Any physical body whose thermal energy capacity is large relative to the amount of energy it supplies or absorbs can be modeled as one. The air in a room, for example, can be treated as a reservoir in the analysis of the heat dissipation from a TV set in the room, since the amount of heat transfer from the TV set to the room air is not large enough to have a noticeable effect on the room air temperature.

A reservoir that supplies energy in the form of heat is called a source, and one that absorbs energy in the form of heat is called a sink (Fig. 5-7). Thermal energy reservoirs are often referred to as heat reservoirs since they supply or absorb energy in the form of heat.

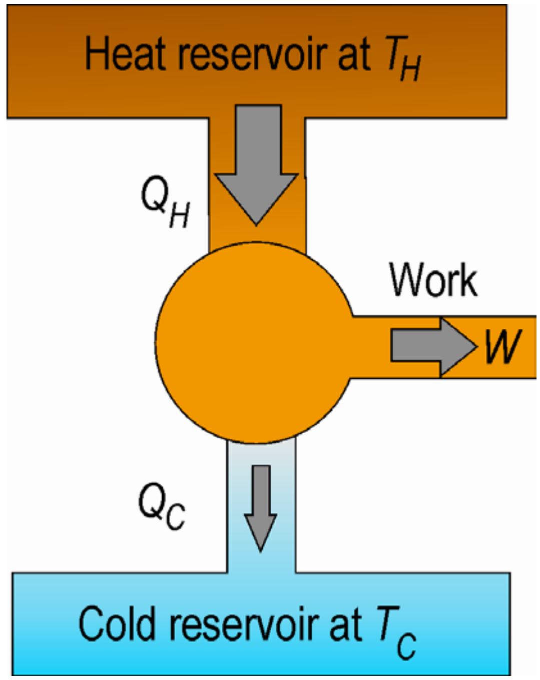
Heat Engines

Work can easily be converted to other forms of energy, but converting other forms of energy to work is not that easy. The mechanical work done by a propeller placed in a bucket of water, for example, is first converted to the internal energy of the water. This energy may then leave the water as heat. We know from experience that any attempt to reverse this process will fail. That is, transferring heat to the water will not cause the shaft to rotate. From this and other observations, we conclude that *work can be converted to heat directly and completely, but converting heat to work requires the use of some special devices. These devices are* ***called heat engines****.*

Heat engines differ considerably from one another, but all can be characterized by the following.

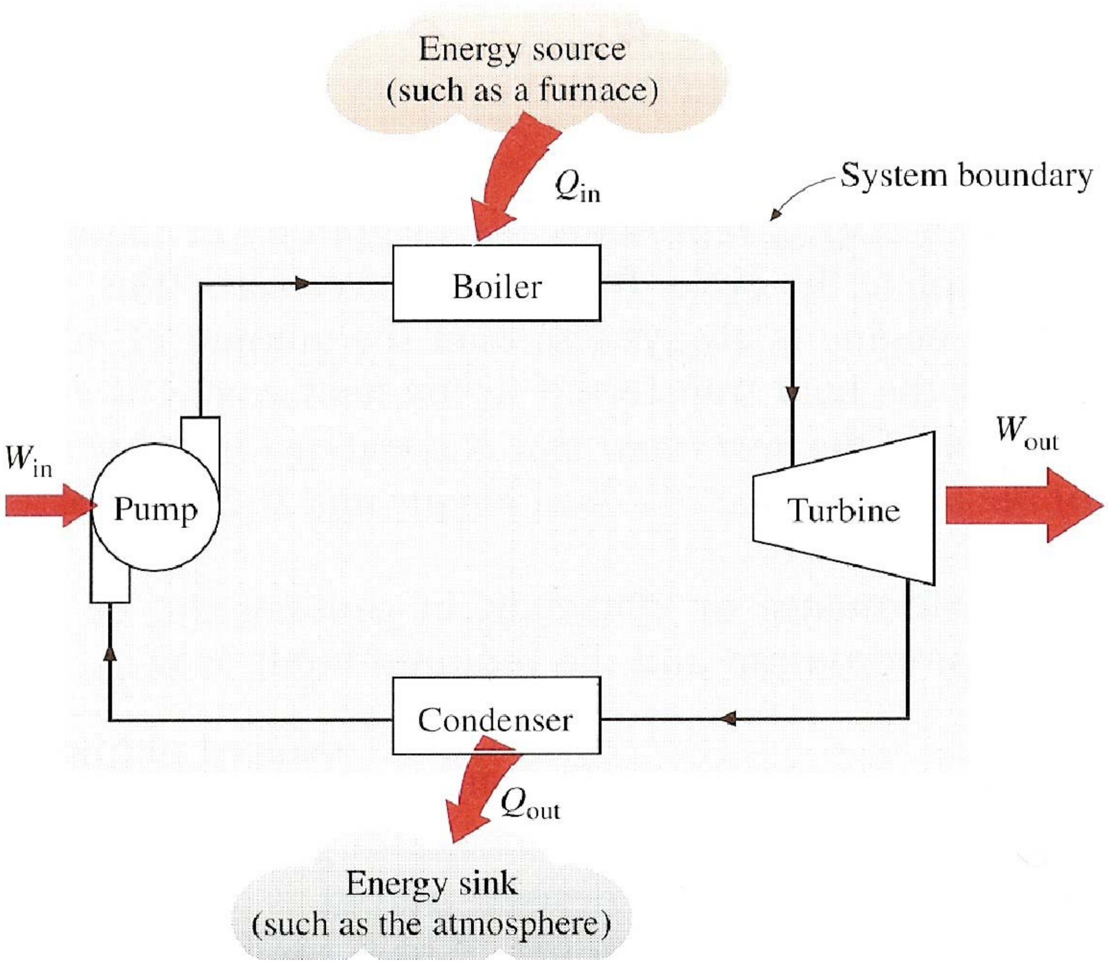
- They receive heat from a high-temperature source (solar energy, oil furnace, nuclear reactor, etc.).
- They convert part of this heat to work (usually in the form of a rotating shaft).
- They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).
- They operate on a cycle

Heat engines and other cyclic devices usually involve a fluid to and from which heat is transferred while undergoing a cycle. This fluid is called the working fluid.



Note: The term *heat engine* is often used in a broader sense to include work-producing devices that do not operate in a thermodynamic cycle. Engines that involve internal combustion such as gas turbines and car engines fall into this category. These devices operate in a mechanical cycle but not in a thermodynamic cycle since the working fluid (the combustion gases) does not undergo a complete cycle. Instead of being cooled to the initial temperature, the exhaust gases are purged and replaced by fresh air-and-fuel mixture at the end of the cycle.

The work-producing device that best fits into the definition of a heat engine is the *steam power plant,* which is an external-combustion engine. That is, the combustion process takes place outside the engine, and the thermal energy released during this process is transferred to the steam as heat. The schematic of a basic steam power plant is shown below



The various quantities shown on this figure are as follows

Q_{in} = amount of heat supplied to steam in boiler from a high temperature source (furnace)
Q_{out} = amount of heat rejected from steam in condenser to a low temperature sink (the atmosphere, a river, etc.)
W_{out} = amount of work delivered by steam as it expands in turbine
W_{in} = amount of work required to compress water to boiler pressure

Above the quantities are indicated with *in* and *out*, and they are all positive
The net work output of this power plant is simply the difference between the total work output of the plant and the total work input.

$$W_{net\ out} = W_{out} - W_{in} \qquad 3\text{-}1$$

The net work can also be determined from the heat transfer data alone. For a closed system undergoing a cycle, the change in internal energy ΔU is zero, and therefore the net work output of the system is also equal to the net heat transfer to the system:

$$W_{net\ out} = Q_{in} - Q_{out} \qquad 3\text{-}2$$

Thermal Efficiency

In Eq. 3-2, Q_{out} represents the magnitude of the energy wasted in order to complete the cycle. But Q_{out} is never zero; thus, the net work output of a heat engine is always less than the amount of heat input. That is, only part of the heat transferred to the heat engine is converted to work. *The fraction of the heat input that is converted to net work output is a measure of the performance of a heat engine and is called the* **thermal efficiency**.

Performance or efficiency, in general, can be expressed in terms of the desired output and the required input as

Performance = desired output / required input 3-3

or,

$$\eta = W_{net\ out} / Q_{in} \qquad 3\text{-}4$$

or

$$\eta = 1 - Q_{out} / Q_{in} \qquad 3\text{-}4$$

Cyclic devices such as heat engines, refrigerators, and heat pumps operate between a high-temperature medium (or reservoir) at temperature T_H and a low-temperature medium (or reservoir) at temperature T_L. To bring uniformity to the treatment of heat engines, refrigerators, and heat pumps, we define the following two quantities

Q_H = *magnitude* of heat transfer between cyclic device and high temperature medium at temperature T_H

Q_L = *magnitude* of heat transfer between cyclic device and low temperature medium at temperature T_L

Note: Q_L and Q_H are defined as *magnitudes* and therefore are *positive quantities.* The direction of Q_H and Q_L is easily determined by inspection, and we do not need to be concerned about their signs. Then the net work output and thermal efficiency relations for any heat engine (shown in Fig. 5-14) can also be expressed as

$$W_{net\ out} = Q_H - Q_L \qquad 3\text{-}5$$

$$\eta = W_{net\ out} / Q_H \qquad 3\text{-}6$$

$$\eta = 1 - Q_L / Q_H \qquad 3\text{-}4$$

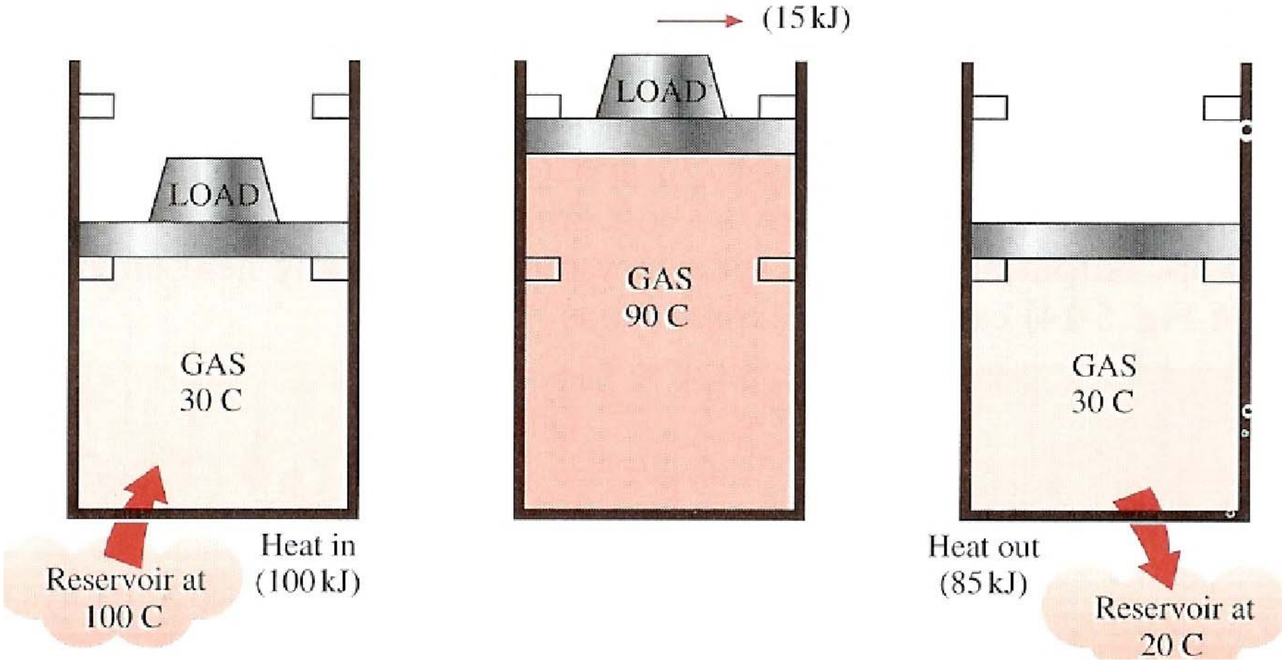
The thermal efficiency of a heat engine is always less than unity since both Q_L and Q_H are defined as positive quantities.

Note: The thermal efficiencies of work-producing devices are amazingly low. Ordinary spark-ignition automobile engines have a thermal efficiency of about 20 percent. That is, an automobile engine converts, at an average, about 20 percent of the chemical energy of the gasoline to mechanical work. This number is about 30 percent for diesel engines and large gas-turbine plants and 40 percent for large steam power plants. Thus, even with the most efficient heat engines available today, more than one-half of the energy supplied ends up in the rivers, lakes, or the atmosphere as waste or unusable energy.

Can We Save Q_{out}?

In a steam power plant, the condenser is the device where large quantities of waste heat is rejected to rivers, lakes, or the atmosphere. Then one may ask, can we not just take the condenser out of the plant and save all that waste energy? The answer to this question is *no* for the simple reason that without the cooling process in a condenser the cycle cannot be completed. (Cyclic devices such as steam power plants cannot run continuously unless the cycle is completed.) This is demonstrated below with the help of a simple heat engine.

Consider the simple heat engine shown below that is used to lift weights. It consists of a piston-cylinder device with two sets of stops. The working fluid is the gas contained within the cylinder. Initially, the gas temperature is 30°C.



The piston, which is loaded with the weights, is resting on top of the lower stops. Now 100 kJ of heat is transferred to the gas in the cylinder from a source at l00^{o}C, causing it to expand and to raise the loaded piston until the piston reaches the upper stops, as shown in the figure. At this point, the load is removed, and the gas temperature is observed to be 90^{0}C

The work done on the load during this expansion process is equal to the increase in its potential energy, say 15 kJ. Even under ideal conditions (weightless piston, no friction, no heat losses, and quasi-equilibrium expansion), the amount of heat supplied to the gas is greater than the work done since part of the heat supplied is used to raise the temperature of the gas.

Now let us try to answer the following question: *Is it possible to transfer the* 85 *kJ of excess heat at 90°C back to the reservoir at 100°C for later use?* If it is, then we will have a heat engine that can have a thermal efficiency of 100 percent under ideal conditions. The answer to this question is again *no,* for the very simple reason that heat always flows from a high-temperature medium to a low-temperature one, and never the other way around. Therefore, we cannot cool this gas from 90 to 300e by transferring heat to a reservoir at 100°C. Instead, we have to bring the system into contact with a low-temperature reservoir, say at 20^{o}C, so that the gas can return to its initial state by rejecting its 85 kJ of excess energy as heat to this reservoir. This energy cannot be recycled, and it is properly called *waste energy.*

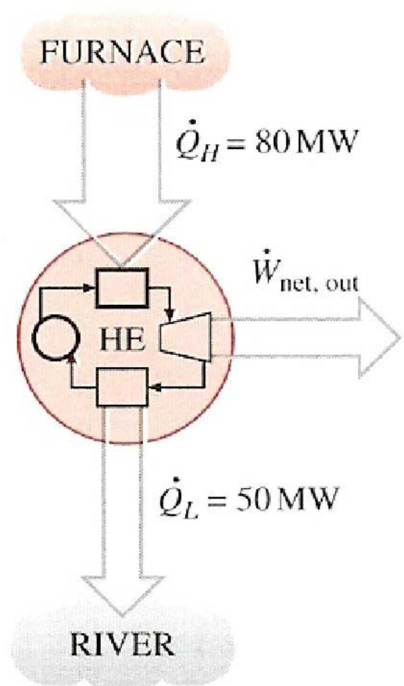
We conclude from the above discussion that every heat engine must *waste* some energy by transferring it to a low-temperature reservoir in order to complete the cycle, even under idealized conditions. The requirement that a heat engine exchange heat with at least two reservoirs for continuous operation forms the basis for the Kelvin-Planck expression of the second law of thermodynamics discussed later in this section.

Example 3.1

Heat is transferred to a heat engine from a furnace at a rate of 80 MW. If the rate of waste heat rejection to a nearby river is 50 MW, determine the net power output and the thermal efficiency for this heat engine.

Solution

A schematic of the heat engine is given below. The furnace serves as the high-temperature reservoir for this heat engine and the river as the low-temperature reservoir. Then the given quantities can be expressed in rate form as



$\dot{Q}_H = 80$ MW $\quad \dot{Q}_L = 50$ MW

The net power output is $\dot{W}_{net.out} = \dot{Q}_H - \dot{Q}_L = 30$ MW

Thus, η = $\dot{W}_{net.out}$ / $\dot{Q}_H$ =0.375

The Second Law of Thermodynamics: Kelvin-Planck Statement

No heat engine can convert all the heat it receives to useful work. This limitation on the thermal efficiency of heat engines forms the basis for the Kelvin-Planck statement of the second law of thermodynamics, which is expressed as follows:

- *It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.*

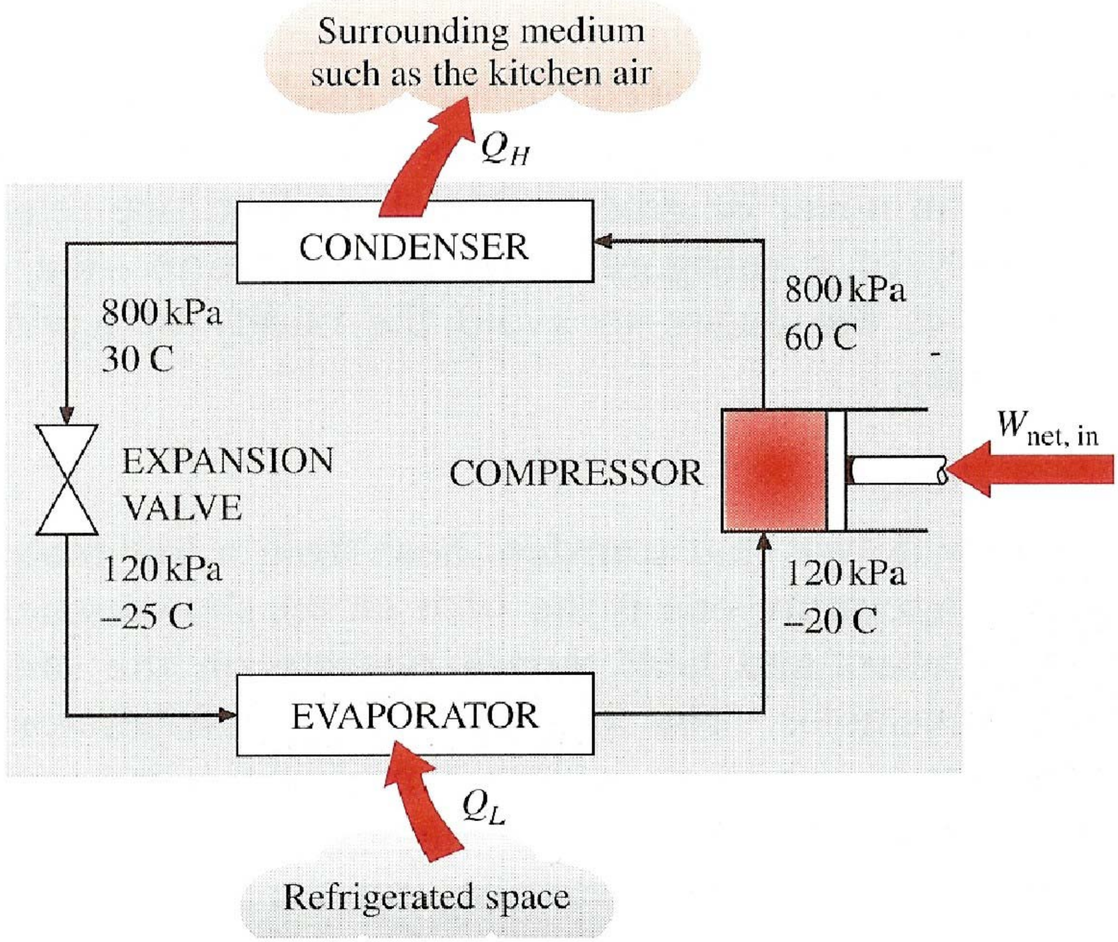
- The Kelvin-Planck statement can also be expressed as follows: *No heat engine can have a thermal efficiency of 100 percent*, or *for a power plant to operate, the working fluid must exchange heat with the environment as well as the furnace.*

Note The impossibility of having a 100 percent efficient heat engine is not due to friction or other dissipative effects. It is a limitation that applies to both the idealized and the actual heat engines.

Refrigerators and Heat Pumps

We all know from experience that heat flows in the direction of decreasing temperature, i.e., from high-temperature mediums to low temperature ones. This heat transfer process occurs in nature without requiring any devices. The reverse process, however, cannot occur by itself. The transfer of heat from a low-temperature medium to a high-temperature one requires special devices called refrigerators.

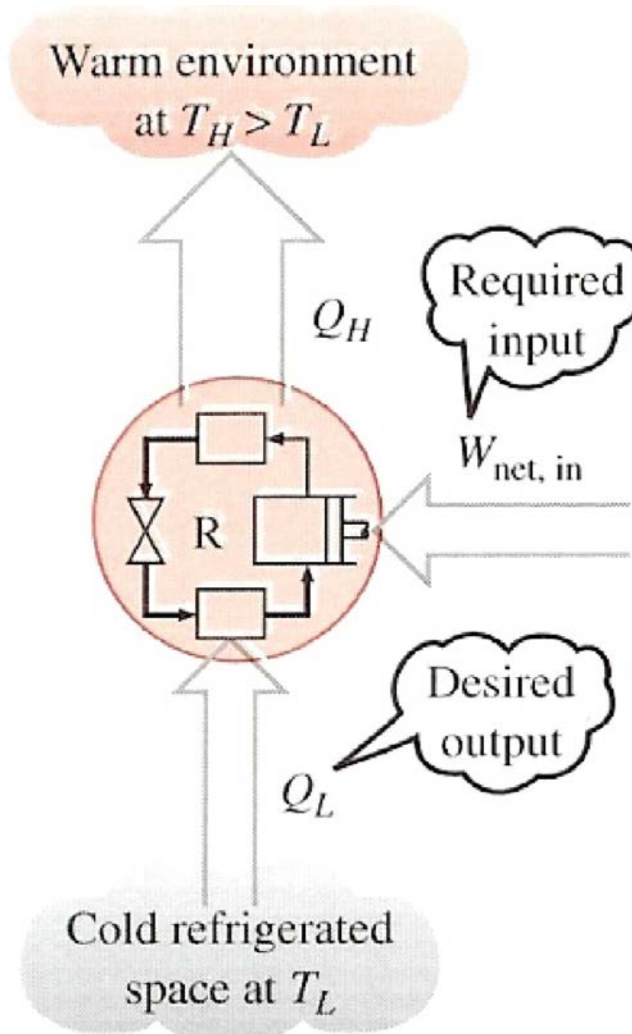
Refrigerators, like heat engines, are cyclic devices. The working fluid used in the refrigeration cycle is called a refrigerant. The most frequently used refrigeration cycle is the *vapor-compression refrigeration cycle* which involves four main components: a compressor, a condenser, an expansion valve, and an evaporator, as shown below



The refrigerant enters the compressor as a vapor and is compressed to the condenser pressure. It leaves the compressor at a relatively high temperature and cools down and condenses as it flows through the coils of the condenser by rejecting heat to the surrounding medium. It then enters a capillary tube where its pressure and temperature drop drastically due to the throttling effect. The low-temperature refrigerant then enters the evaporator, where it evaporates by absorbing heat from the refrigerated space. The cycle is completed as the refrigerant leaves the evaporator and reenters the compressor.

In a household refrigerator, the freezer compartment where heat is picked up by the refrigerant serves as the evaporator, and the coils behind the refrigerator where heat is dissipated to the kitchen air as the condenser.

A refrigerator is shown schematically below. Here Q_L is the magnitude of the heat removed from the refrigerated space at temperature T_L,, Q_H is the magnitude of the heat rejected to the warm environment at temperature T_H' and $W_{net,in}$ is the net work input to the refrigerator. As discussed before, Q_L and Q_H represent magnitudes and so are positive quantities.



Coefficient of Performance

The *efficiency* of a refrigerator is expressed in terms of the coefficient of performance (COP), denoted by COP_R. The objective of a refrigerator is to remove heat (Q_L) from the refrigerated space. To accomplish this objective, it requires a work input of $W_{net,in}$ Then the COP of a refrigerator can be expressed as

$$COP_R = \text{desired output /required input} = Q_L / W_{net,in} \qquad \textit{3-5}$$

or

$$COP_R = \frac{Q_L}{Q_H - Q_L} \qquad 3\text{-}6$$

Note The value of COPR can be *greater than unity.* That is, the amount of heat removed from the refrigerated space can be greater than the amount of work input. This is in contrast to the thermal efficiency, which can never be greater than 1. In fact, one reason for expressing the efficiency of a refrigerator by another term-the coefficient of performance-is the desire to avoid the oddity of having efficiencies greater than unity.

Heat Pumps

Another device that transfers heat from a low-temperature medium to a high-temperature one is the heat pump. Refrigerators and heat pumps operate on the same cycle but differ in their objectives. The objective of a refrigerator is to maintain the refrigerated space at a low temperature by removing heat from it. Discharging this heat to a higher-temperature medium is merely a necessary part of the operation, not the purpose. The objective of a heat pump, however, is to maintain a heated space at a high temperature. This is accomplished by absorbing heat from a low-temperature source, such as well water or cold outside air in winter, and supplying this heat to the high-temperature medium such as a house.

An ordinary refrigerator that is placed in the window of a house with its door open to the cold outside air in winter will function as a heat pump since it will try to cool the outside by absorbing heat from it and rejecting this heat into the house through the coils behind it.

The measure of performance of a heat pump is also expressed in terms of the coefficient of performance COP_{HP}, defined as

$$COP_{HP} = \frac{Q_H}{Q_H - Q_L} \qquad 3\text{-}7$$

$$COP_{HP} = COP_R + 1 \qquad 3\text{-}8$$

The relation implies that the coefficient of performance of a heat pump is always greater than unity since COP_R is a positive quantity. That is, a heat pump will function, at worst, as a resistance heater, supplying as much energy to the house as it consumes. In reality, however, part of Q_H is lost to the outside air through piping and other devices, and COP_{HP} may drop below unity when the outside air temperature is too low. When this happens, the system usually switches to a resistance heating mode. Most heat pumps in operation today have seasonally averaged COP of 2 to 3.

The Second Law of Thermodynamics: Clausius Statement

Clausius statement is related to refrigerators or heat pumps. The Clausius statement is expressed as follows:

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower temperature body to a higher-temperature body.

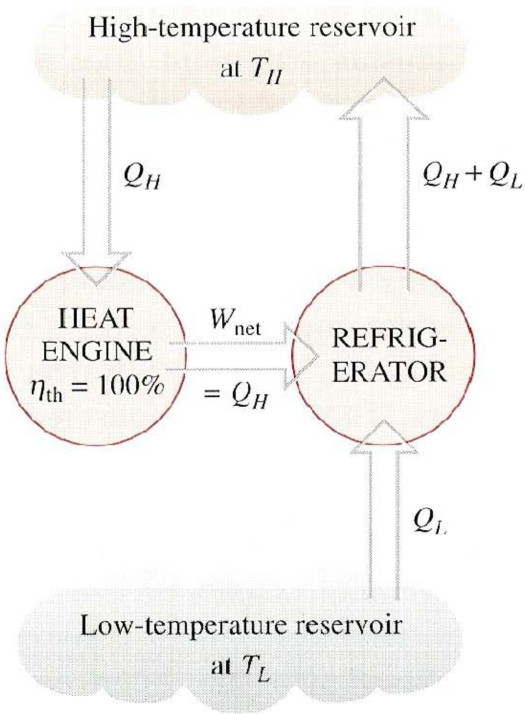
It is common knowledge that heat does not, of its own volition, flow from a cold medium to a warmer one. The Clausius statement does not imply that a cyclic device that transfers heat from a cold medium to a warmer one is impossible to construct. In fact, this is precisely what a common household refrigerator does. It simply states that a refrigerator will not operate unless its compressor is driven by an external power source, such as an electric motor. This way, the net effect on the surroundings involves the consumption of some energy in the form of work, in addition to the transfer of heat from a colder body to a warmer one. That is, it leaves a trace in the surroundings. Therefore, a household refrigerator is in complete compliance with the Clausius statement of the second law.

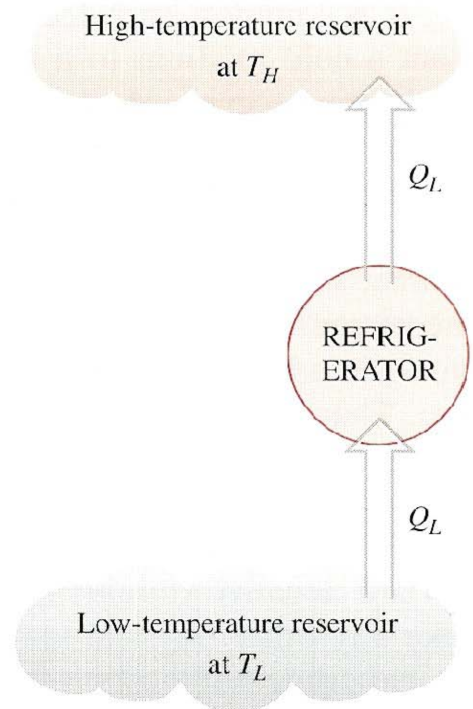
Both the Kelvin-Planck and the Clausius statements of the second law are negative statements, and a negative statement cannot be proved. Like any other physical law, the second law of thermodynamics is based on experimental observations. To date, no experiment has been conducted that contradicts the second law, and this should be taken as sufficient evidence of its validity.

Equivalence of the Two Statements

The Kelvin-Planck and the Clausius statements are equivalent in their consequences, and either statement can be used as the expression of the second law of thermodynamics. Any device that violates the Kelvin-Planck statement also violates the Clausius statement, and vice versa. This can be demonstrated as follows:

Consider the heat-engine-refrigerator combination shown in figure below left, operating between the same two reservoirs.





The heat engine is assumed to have, in violation of the Kelvin-Planck statement, a thermal efficiency of 100 percent, and therefore it converts all the heat Q_H it receives to work W. This work is now supplied to a refrigerator that removes heat in the amount of Q_L from the low-temperature reservoir and rejects heat in the amount of $Q_L + Q_H$ to the high-temperature reservoir. During this process, the high-temperature reservoir receives a net amount of heat Q_L (the difference between $Q_L + Q_H$ and Q_H). Thus the combination of these two devices can be viewed as a refrigerator, as shown in figure at right, that transfers heat in an amount of Q_L from a cooler body to a warmer one without requiring any input from outside. This is clearly a violation of the Clausius statement. Therefore, a violation of the Kelvin-Planck statement results in the violation of the Clausius statement.

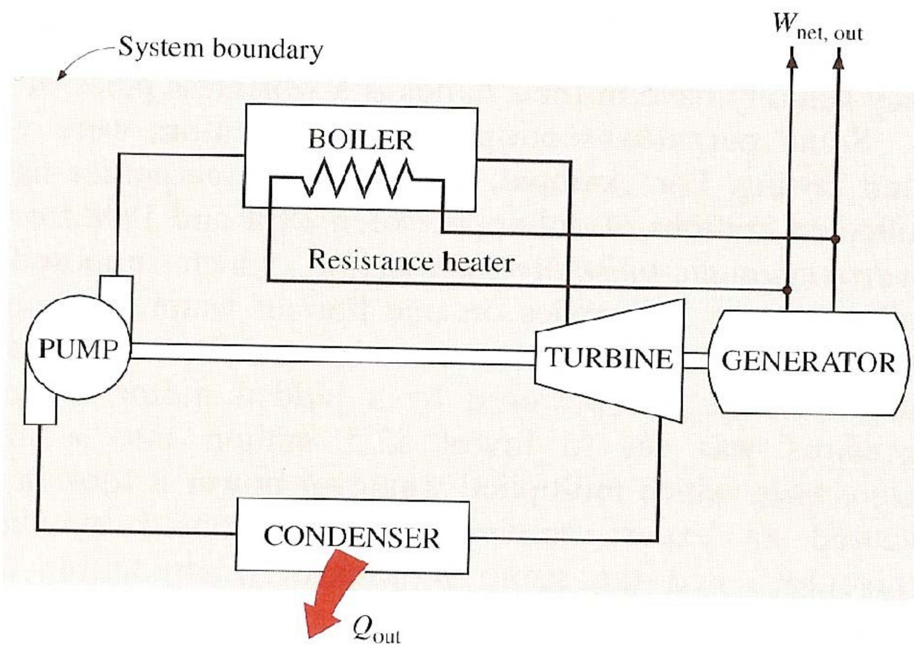
It can also be shown in a similar manner that a violation of the Clausius statement leads to the violation of the Kelvin-Planck statement. Therefore, the Clausius and the Kelvin-Planck statements are two equivalent expressions of the second law of thermodynamics.

PERPETUAL MOTION MACHINES

We have repeatedly stated that a process cannot take place unless it satisfies both the first and second laws of thermodynamics. Any device that violates either law is called a perpetual-motion machine, and despite numerous attempts, no perpetual-motion machine is known to have worked. But this has not stopped inventors from trying to create new ones.

A device that violates the first law of thermodynamics (by *creating* energy) is called a *perpetual-motion machine of the first kind* (PMMI), and a device that violates the second law of thermodynamics is called a *perpetual-motion machine of the second kind* (PMM2).

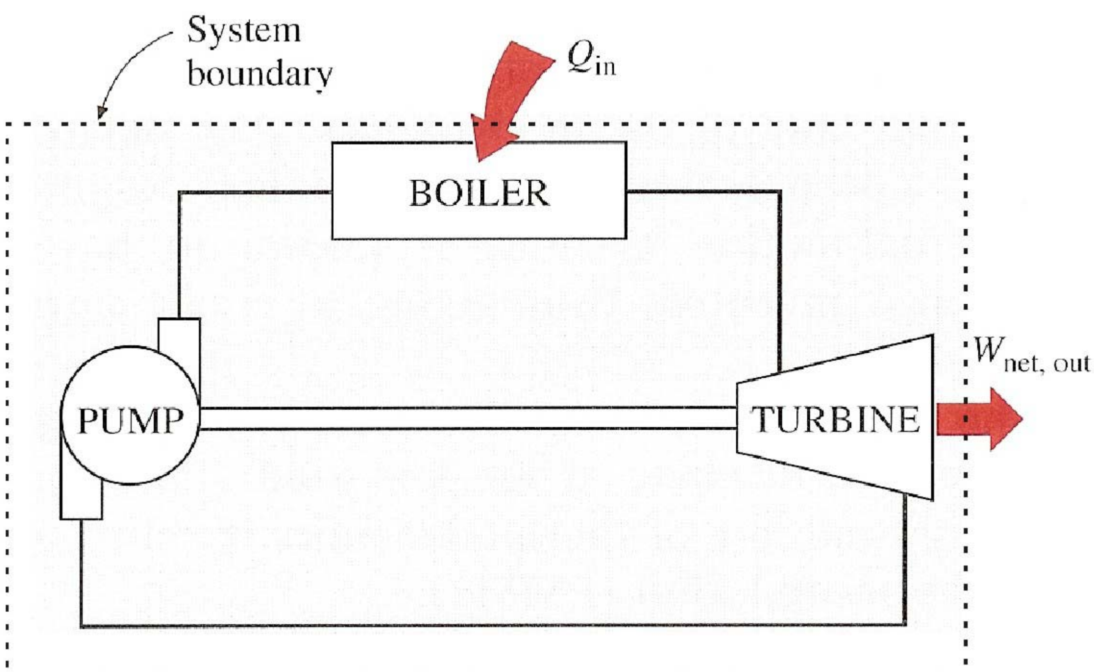
Consider the steam power plant shown below



It is proposed to heat the steam by resistance heaters placed inside the boiler, instead of by the energy supplied from fossil or nuclear fuels. Part of the electricity generated by the plant is to be used to power the resistors as well as the pump. The rest of the electric energy is to be supplied to the electric network as the net work output. The inventor claims that once the system is started, this power plant will produce electricity indefinitely without requiring any energy input from the outside.

Well, here is an invention that could solve the world's energy problem-if it works, of course. A careful examination of this invention reveals that the system enclosed by the shaded area is continuously supplying energy to the outside at a rate of $Q_{out} + W_{net,out}$ every second without receiving any energy. That is, this system is creating energy at a rate of $Q_{out} + W_{net,out}$, which is clearly a violation of the first law. Therefore, this wonderful device is nothing more than a PMM1 and does not warrant any further consideration.

Now let us consider another novel idea by the same inventor. Convinced that energy cannot be created, the inventor suggests the following modification which will greatly improve the thermal efficiency of that power plant without violating the first law. Aware that more than one-half of the heat transferred to the steam in the furnace is discarded in the condenser to the environment, the inventor suggests getting rid of this wasteful component and sending the steam to the pump as soon as it leaves the turbine, as shown below



This way, all the heat transferred to the steam in the boiler will be converted to work, and thus the power plant will have a theoretical efficiency of 100 percent. The inventor realizes that some heat losses and friction between the moving components are unavoidable and that these effects will hurt the efficiency somewhat, but still expects the efficiency to be no less than 80 percent (as opposed to 40 percent in actual power plants) for a carefully designed system.

Well, the possibility of doubling the efficiency would certainly be very tempting to plant managers and, if not properly trained, they would probably give this idea a chance, since intuitively they see nothing wrong with it. A student of thermodynamics, however, will immediately label this device as a PMM2, since it works on a cycle and does a net amount of work while exchanging heat with a single reservoir (the furnace) only. It satisfies the first law but violates the second law, and therefore it will not work.

Note: Countless perpetual-motion machines have been proposed throughout history, and many more are being proposed. Some proposers have even gone so far as patenting their inventions, only to find out that what they actually have in their hands is a worthless piece of paper.

Some perpetual-motion machine inventors were very successful in fund raising. For example, a Philadelphia carpenter named J. W. Kelly collected millions of dollars between 1874 and 1898 from investors in his *hydropneumatic-pulsating-vacu-engine,* which supposedly could push a railroad train 3000 miles on one liter of water. Of course it never did. After his death in 1898, the investigators discovered that the demonstration machine was powered by a hidden motor. Recently a group of investors was set to invest $2.5 million into a mysterious *energy augmentor,* which multiplied whatever power it took in, but their lawyer wanted an expert opinion first. Confronted by the scientists, the "inventor" fled the scene without even attempting to run his demo machine.

Reversible and Irreversible Processes

The second law of thermodynamics states that no heat engine can have an efficiency of 100 percent. Then what is the highest efficiency that a heat engine *can* possibly have? Before we can answer this question, we need to define an idealized process first, which is called the *reversible process.*

The processes that were discussed above occurred in a certain direction. Once having taken place, these processes cannot reverse themselves spontaneously and restore the system to its initial state. For this reason, they are classified as *irreversible processes.* Once a cup of hot coffee cools, it will not heat up retrieving the heat it lost from the surroundings. If it could, the surroundings, as well as the system (coffee), would be restored to their original condition, and this would be a reversible process.

A reversible process is defined as a *process that can be reversed without leaving any trace on the surroundings*. That is, both the system *and* the surroundings are returned to their initial states at the end of the reverse process. This is possible only if the net heat *and* net work exchange between the system and the surroundings is zero for the combined (original and reverse) process. Processes that are not reversible are called irreversible processes.

It should be pointed out that a system can be restored to its initial state following a process, regardless of whether the process is reversible or irreversible. But for reversible processes, this restoration is made without leaving any net change on the surroundings, whereas for irreversible processes, the surroundings usually do some work on the system and therefore will not return to their original state.

Reversible processes actually do not occur in nature. They are merely *idealizations* of actual processes. Reversible processes can be approximated by actual devices, but they can never be achieved. That is, all the processes occurring in nature are irreversible. You may be wondering, then, *why* we are bothering with such fictitious processes. There are two reasons. First, they are easy to analyze, since a system passes through a series of equilibrium states during a reversible process; second, they serve as idealized models to which actual processes can be compared.

Engineers are interested in reversible processes because **work-producing** devices such as car engines and gas or steam turbines *deliver the most work,* and **work-consuming** devices such as compressors, fans, and pumps *require least work* when reversible processes are used instead of irreversible ones.

Reversible processes can be viewed as *theoretical limits* for the corresponding irreversible ones. Some processes are more irreversible than others. We may never be able to have a reversible process, but we may certainly approach it. The more closely we approximate a reversible process, the more work delivered by a work-producing device or the less work required by a work-consuming device.

The concept of reversible processes leads to the definition of *second-law efficiency* for actual processes, which is the degree of approximation to the corresponding reversible processes. This enables us to compare the performance of different devices that are designed to do the same task on the basis of their efficiencies. The better the design, the lower the irreversibilities and the higher the second-law efficiency.

Irreversibilities

The factors that cause a process to be irreversible are called irreversibilities. They include

- friction,
- unrestrained expansion,
- mixing of two gases,
- heat transfer across a finite temperature difference,
- electric resistance,

- inelastic deformation of solids, and
- chemical reactions.

The presence of any of these effects renders a process irreversible. A reversible process involves none of these. Some of the frequently encountered irreversibilities are discussed briefly below.

Friction

Friction is a familiar form of irreversibility associated with bodies in motion. When two bodies in contact are forced to move relative to each, a friction force that opposes the motion develops at the interface of these two bodies, and some work is needed to overcome this friction force. The energy supplied as work is eventually converted to heat during the process and is transferred to the bodies in contact, as evidenced by a temperature rise at the interface. When the direction of the motion is reversed, the bodies will be restored to their original position, but the interface will not cool, and heat will not be converted back to work. Instead, more of the work will be converted to heat while overcoming the friction forces which also oppose the reverse motion. Since the system (the moving bodies) and the surroundings cannot be returned to their original states, this process is irreversible. Therefore, any process that involves friction is irreversible. The larger the friction forces involved, the more irreversible the process is.

Friction does not always involve two solid bodies in contact. It is also encountered between a fluid and solid and even between the layers of a fluid moving at different velocities. A considerable fraction of the power produced by a car engine is used to overcome the friction (the drag force) between the air and the external surfaces of the car, and it eventually becomes part of the internal energy of the air. It is not possible to reverse this process and recover that lost power, even though doing so would not violate the conservation of energy principle.

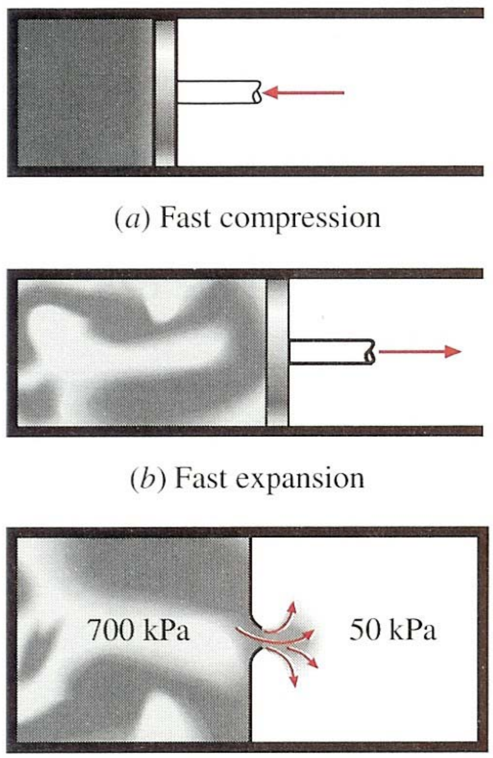
Non-Quasi-Equilibrium Expansion and Compression

In Part 1 we defined a quasi-equilibrium process as one during which the system remains infinitesimally close to a state of equilibrium at all times. Consider a frictionless adiabatic piston-cylinder device that contains a gas. Now the piston is pushed into the cylinder, compressing the gas. If the piston velocity is not very high, the pressure and the temperature will increase uniformly throughout the gas. Since the system is always maintained at a state close to equilibrium, this is a quasi-equilibrium process.

Now the external force on the piston is slightly decreased, allowing the gas to expand.

The expansion process will also be *quasi-equilibrium* if the gas is allowed to expand slowly. When the piston returns to its original position, all the boundary *(P dV)* work done on the gas during compression is returned to the surroundings during expansion. That is, the net work for the combined process is zero. Also, there has been no heat transfer involved during this process, and thus both the system and the surroundings will return to their initial states at the end of the reverse process. Therefore, the slow frictionless adiabatic expansion or compression of a gas is a reversible process.

Now let us repeat this adiabatic process in a *non-quasi-equilibrium* manner, as shown below.



(*a*) Fast compression

(*b*) Fast expansion

(*c*) Unrestrained expansion

If the piston is pushed in very rapidly, the gas molecules near the piston face will not have sufficient time to escape, and they will pile up in front of the piston. This will raise the pressure near the piston face, and as a result, the pressure there will be higher than the pressure in other parts of the cylinder. The non-uniformity of pressure will render this process non-quasi-equilibrium. The actual boundary work is a function of pressure, as measured at the piston face. Because of this higher pressure value at the piston face, a non-quasi-equilibrium compression process will require a larger work input than the corresponding quasi-equilibrium one. When the process is reversed by letting the gas expand rapidly, the gas molecules in the cylinder will not be able to follow the piston as fast, thus creating a low-pressure region before the piston face. Because of this low-pressure value at the piston face, a non-quasi-equilibrium process will deliver less work than a corresponding reversible one. Consequently, the work done by the gas during expansion is less than the work done by the surroundings on the gas during compression, and thus the surroundings have a net work deficit. When the piston returns to its initial position, the gas will have excess internal energy, equal in magnitude to the work deficit of the surroundings.

The system can easily be returned to its initial state by transferring this excess internal energy to the surroundings as heat. But the only way the surroundings can be returned to their initial condition is by completely converting this heat to work, which can only be done by a heat engine that has an efficiency of 100 percent. This, however, is impossible to do, even theoretically, since it would violate the second law of thermodynamics. Since only the system, not both the system and the surroundings, can be returned to its initial state, we conclude that the adiabatic non-quasi-equilibrium expansion or compression of a gas is irreversible.

Another example of non-quasi-equilibrium expansion processes is the unrestrained expansion of a gas separated from a vacuum by a membrane, as shown above. When the membrane is ruptured, the gas fills the entire tank. The only way to restore the system to its original state is to compress it to its initial volume, while transferring heat from the gas until it reaches its initial temperature. From the conservation of energy considerations, it can easily be shown that the amount of heat transferred from the gas equals the amount of work done on the gas by the surroundings. The restoration of the surroundings involves conversion of this heat completely to work, which would violate the second law. Therefore, unrestrained expansion of a gas is an irreversible process.

Heat Transfer

Another form of irreversibility familiar to us all is heat transfer through a finite temperature difference.

Consider a can of cold soda left in a warm room. Heat will flow from the warmer room air to the cooler soda. The only way this process can be reversed and the soda restored to its original temperature is to provide refrigeration, which requires some work input. At the end of the reverse process, the soda will be restored to its initial state, but the surroundings will not be.

The internal energy of the surroundings will increase by an amount equal in magnitude to the work supplied to the refrigerator. The restoration of the surroundings to its initial state can be done only by converting this excess internal energy completely to work, which is impossible to do without violating the second law. Since only the system, not both the system and the surroundings, can be restored to its initial condition, heat transfer through a finite temperature difference is an irreversible process.

Heat transfer can occur only when there is a temperature difference between a system and its surroundings. Therefore, it is physically impossible to have a reversible heat transfer process. But a heat transfer process becomes less and less irreversible as the temperature difference between the two bodies approaches zero. Then heat transfer through a differential temperature difference dT can be considered to be reversible. As dT approaches zero, the process can be reversed in direction (at least theoretically) without requiring any refrigeration. Notice that reversible heat transfer is a conceptual process and cannot be duplicated in the laboratory.

The smaller the temperature difference between two bodies, the smaller the heat transfer rate will be. When the temperature difference is small, any significant heat transfer will require a very large surface area and a very long time. Therefore, even though approaching reversible heat transfer is desirable from a thermodynamic point of view, it is impractical and not economically feasible.

Internally and Externally Reversible Processes

A process is an interaction between a system and its surroundings, and a reversible process involves no irreversibilities associated with either of them.

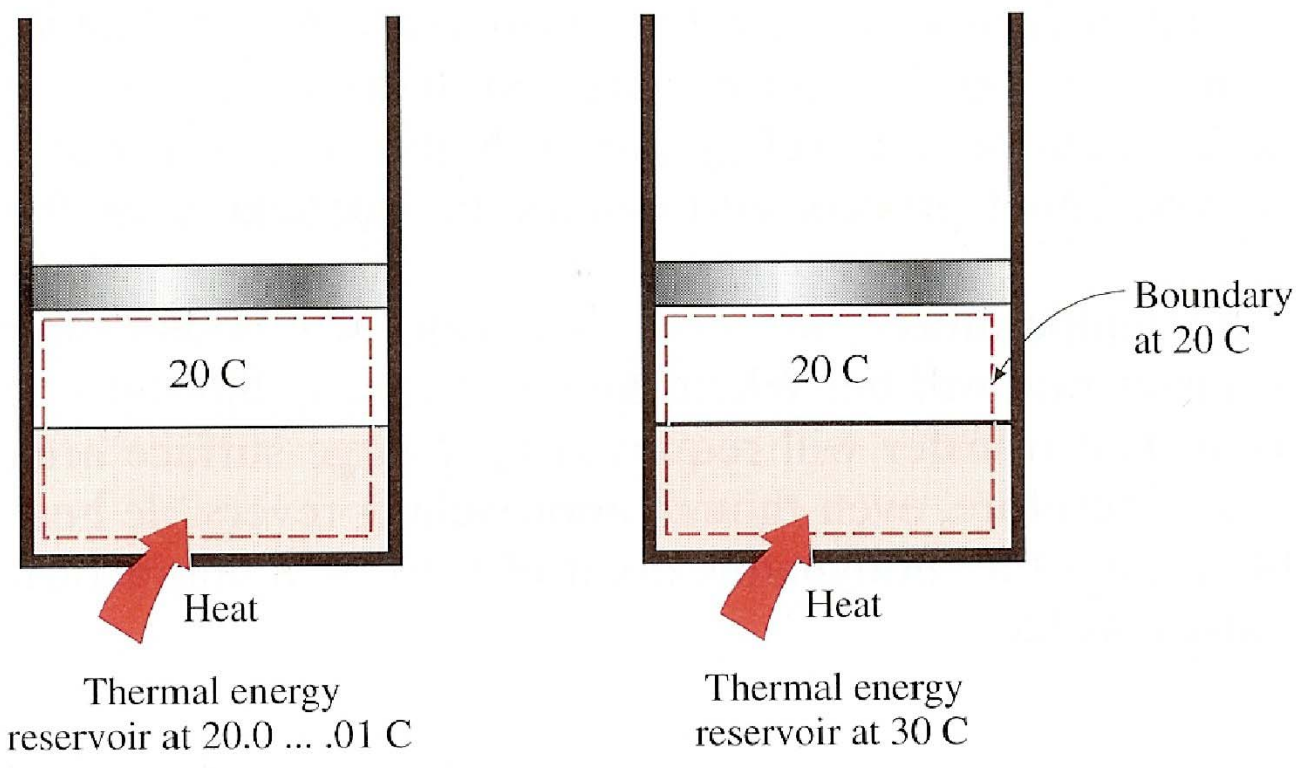
A process is called internally reversible if no irreversibilities occur within the boundaries of the system during the process. During an internally reversible process, a system proceeds through a series of equilibrium states, and when the process is reversed, the system passes through exactly the same equilibrium states while returning to its initial state. <u>That is, the paths of the forward and reverse processes coincide for an internally reversible process</u>. The quasi-equilibrium process discussed earlier is an example of an internally reversible process.

A process is called externally reversible if no irreversibilities occur outside the system boundaries during the process. Heat transfer between a reservoir and a system is an externally reversible process if the surface of contact between the system and the reservoir is at the temperature of the reservoir.

A process is called totally reversible, or simply reversible, if it involves no irreversibilities within the system or its surroundings.

A totally reversible process involves no heat transfer through a finite temperature difference, no non-quasi-equilibrium changes, and no friction or other dissipative effects.

As an example, consider the transfer of heat to two identical systems that are undergoing a constant-pressure (thus constant-temperature) phase-change process, as shown in figure below. Both processes are internally reversible, since both take place isothermally and both pass through exactly the same equilibrium states. The first process shown is externally reversible also, since heat transfer for this process takes place through an infinitesimal temperature difference dT. The second process, however, is externally irreversible, since it involves heat transfer through a finite temperature difference ΔT.



(*a*) Totally reversible (*b*) Internally reversible

THE CARNOT CYCLE

We mentioned earlier that heat engines are cyclic devices and that the working fluid of a heat engine returns to its initial state at the end of each cycle. Work is done by the working fluid during one part of the cycle and on the working fluid during another part. The difference between these two is the net work delivered by the heat engine. The efficiency of a heat-engine cycle greatly depends on how the individual processes that make up the cycle are executed. The net work, thus the cycle efficiency, can be maximized by using processes that require the least amount of work and deliver the most, that is, by using *reversible processes*.

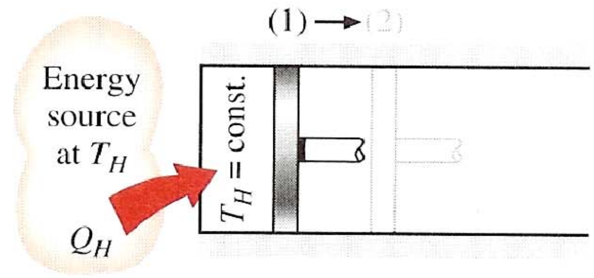
Therefore, it is no surprise that the most efficient cycles are reversible cycles, i.e., cycles that consist entirely of reversible processes.

Reversible cycles cannot be achieved in practice because the irreversibilities associated with each process cannot be eliminated. However, reversible cycles provide upper limits on the performance of real cycles. Heat engines and refrigerators that work on reversible cycles serve as models to which actual heat engines and refrigerators can be compared. Reversible cycles also serve as starting points in the development of actual cycles and are modified as needed to meet certain requirements.

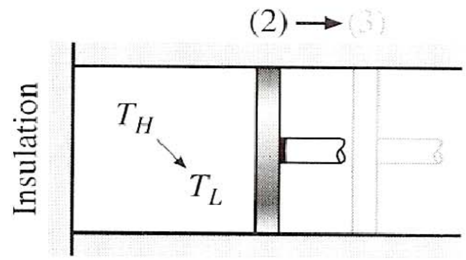
Probably the best known reversible cycle is the Carnot cycle, first proposed in 1824 by a French engineer Sadi Carnot. The theoretical heat engine that operates on the Carnot cycle is called the Carnot heat engine.

The Carnot cycle is composed of four reversible processes-two isothermal and two adiabatic.

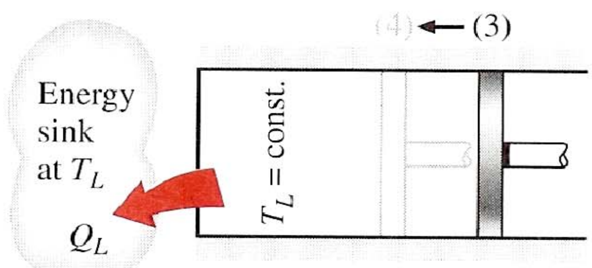
Consider a closed system that consists of a gas contained in an adiabatic piston-cylinder device, as shown in figure below. The insulation of the cylinder head is such that it may be removed to bring the cylinder into contact with reservoirs to provide heat transfer.



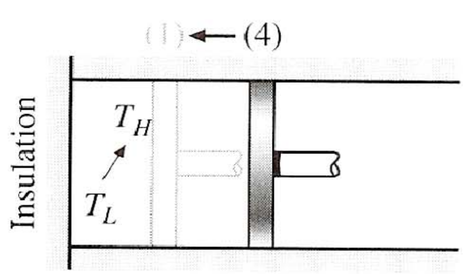
(*a*) Process 1-2



(*b*) Process 2-3



(*c*) Process 3-4



(*d*) Process 4-1

The four reversible processes that make up the Carnot cycle are as follows:

- **Reversible isothermal expansion** (process 1-2, T_H = constant). Initially (state 1) the temperature of the gas is T_H, and the cylinder head is in close contact with a source at temperature T_H. The gas is allowed to expand slowly, doing work on the surroundings. As the gas expands, the temperature of the gas tends to decrease. But as soon as the temperature drops by an infinitesimal amount *dT,* some heat flows from the reservoir into the gas, raising the gas temperature to T_H. Thus, the gas temperature is kept constant at T_H. Since the temperature difference between the gas and the reservoir never exceeds a differential amount *dT,* this is a reversible heat transfer process. It continues until the piston reaches position 2. The amount of total heat transferred to the gas during this process is Q_H.

  For an ideal gas,

$$Q_H = -W_{12} = \int_{V_1}^{V_2} PdV = nRT_H \ln\left(\frac{V_2}{V_1}\right) \qquad 3\text{-}9$$

- **Reversible adiabatic expansion** (process 2-3, temperature drops from T_H to T_L). At state 2, the reservoir that was in contact with the cylinder head is removed and replaced by insulation so that the system becomes adiabatic. The gas continues to expand slowly, doing work on the surroundings until its temperature drops from T_H to T_L (state 3). The piston is assumed to be frictionless and the process to be quasi-equilibrium, so the process is reversible as well as adiabatic.

  Since the gas is ideal and the process is adiabatic, $Q = 0$, So, by the first law

$$W_{23} = \Delta U = n\, C_V\, (T_L - T_H) \qquad 3\text{-}10$$

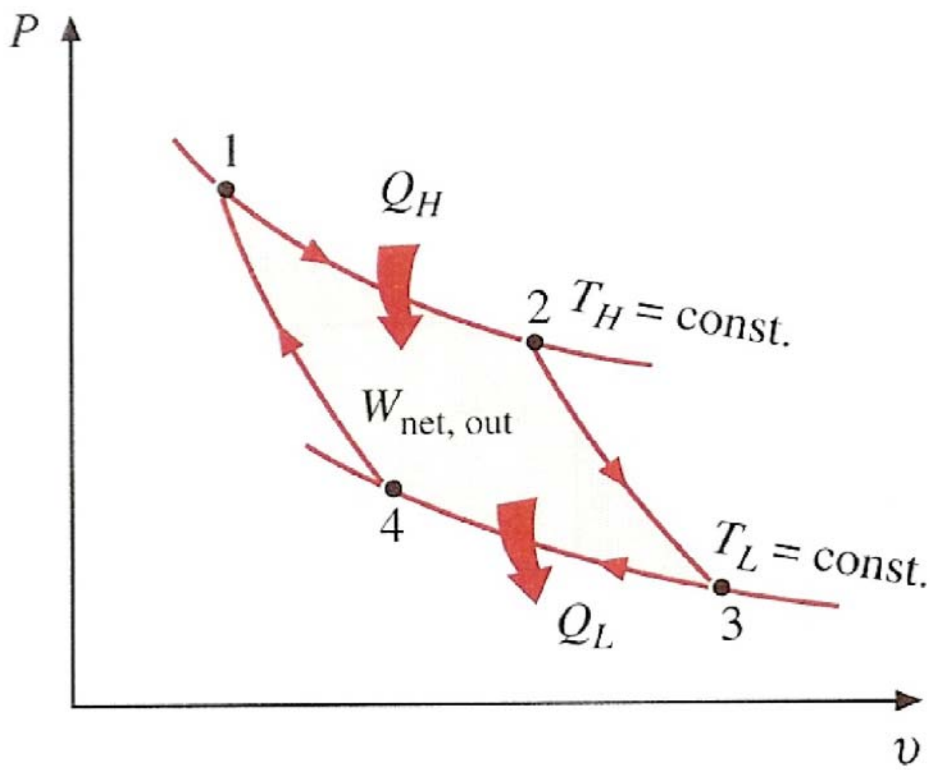
- **Reversible isothermal compression** (process 3-4, T_L = constant). At state 3, the insulation at the cylinder head is removed, and the cylinder is brought into contact with a sink at temperature T_L. Now the piston is pushed inward by an external force, doing work on the gas. As the gas is compressed, its temperature tends to rise. But as soon as it rises by an infinitesimal amount *dT,* heat flows from the gas to the sink, causing the gas temperature to drop to T_L. Thus, the gas temperature is maintained constant at T_L. Since the temperature difference between the gas and the sink never exceeds a differential amount *dT,* this is a reversible heat transfer process. It continues until the piston reaches position 4. The amount of heat rejected from the gas during this process is Q_L.

$$Q_L = -W_{34} = -\int_{V_3}^{V_4} PdV = -nRT_L \ln\left(\frac{V_4}{V_3}\right) \qquad 3\text{-}11$$

- **Reversible adiabatic compression** (process 4-1, temperature rises from T_L to T_H). State 4 is such that when the low-temperature reservoir is removed and the insulation is put back on the cylinder head and the gas is compressed in a reversible manner, the gas returns to its initial state (state 1). The temperature rises from T_L to T_H during this reversible adiabatic compression process, which completes the cycle.

$$W_{41} = \Delta U = n\, C_V\, (T_H - T_L) \qquad 3\text{-}12$$

The *P*-*V* diagram of this cycle is shown below.



Remembering that on a *P*-*V* diagram the area under the process curve represents the boundary work for quasi-equilibrium (internally reversible) processes, we see that the area under curve 1-2-3 is the work done by the gas during the expansion part of the cycle, and the area under curve 3-4-1 is the work done on the gas during the compression part of the cycle. The area enclosed by the path of the cycle (area 1-2-3-4-1) is the difference between these two and represents the net work done during the cycle.

The total work produced during the cycle is the sum of individual for in each cycle. By adding the above four equations we get

$$W_{net,out} = nR\left[T_H \ln\left(\frac{V_1}{V_2}\right) - T_L \ln\left(\frac{V_4}{V_3}\right)\right] \qquad 3\text{-}13$$

From the first law,

$$\Delta U = Q + W = 0$$

or

$$Q = -W,$$

Then

$$Q_H - Q_L = -W_{net,out} = -nR\left[T_H \ln\left(\frac{V_1}{V_2}\right) - T_L \ln\left(\frac{V_4}{V_3}\right)\right] \qquad 3\text{-}14$$

Thus, the work output of the engine is equal to the heat absorbed by the system.

Since V_1 and V_4 lie on one adiabat, and V_2 and V_3 on the other we can write

$$\left(\frac{V_4}{V_1}\right)^{\gamma-1} = \frac{T_L}{T_H}$$

$$\left(\frac{V_3}{V_2}\right)^{\gamma-1} = \frac{T_L}{T_H}$$

which gives

$$\frac{V_4}{V_1} = \frac{V_3}{V_2} \quad \text{or} \quad \frac{V_4}{V_3} = \frac{V_1}{V_2}$$

$$-W_{net,out} = -nR\left[T_H \ln\left(\frac{V_1}{V_2}\right) - T_L \ln\left(\frac{V_1}{V_2}\right)\right] = -nR(T_H - T_L)\ln\left(\frac{V_1}{V_2}\right)$$

3-15

Dividing Eq 3-15 by 3-9 we get

$$\frac{-W_{net,out}}{Q_H} = \frac{T_H - T_L}{T_H} \qquad 3\text{-}16$$

or

$$\frac{Q_H - Q_L}{Q_H} = \frac{T_H - T_L}{T_H} \qquad 3\text{-}17$$

The efficiency of a Carnot engine operating in reversible cycles is therefore

$$\eta = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H} \qquad 3\text{-}18$$

It should be noted that no heat engine is 100% efficient. If the rejected heat were included as part of its output, the efficiency of every engine would be 100%.

The above definition of efficiency applies to every type of heat engine; it is not restricted to the Carnot engine only.

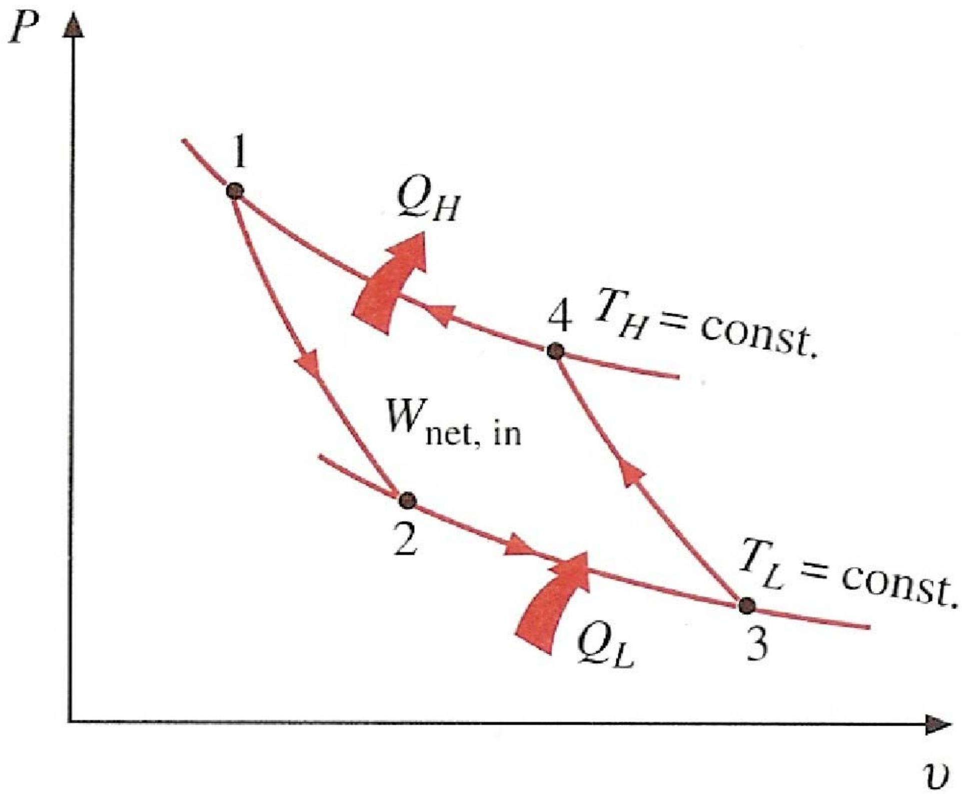
Since every step in this cycle is carried out reversibly, the maximum possible work is obtained for the particular working substance and temperature considered.

It can be shown that no other engine working between the same two temperatures can convert thermal energy to mechanical energy with a greater efficiency than does the Carnot engine. Other reversible engines, in fact, will have the same efficiency as the Carnot engine.

Notice that if we acted stingily and compressed the gas at state 3 adiabatically instead of isothermally in an effort *to save* Q_L, we would end up back at state 2, retracing the process path 3-2. By doing so we would save Q_L, but we would not be able to obtain any net work output from this engine. This illustrates once more the necessity of a heat engine exchanging heat with at least two reservoirs at different temperatures to operate in a cycle and produce a net amount of work.

The Reversed Carnot Cycle

The Carnot heat-engine cycle described above is a totally reversible cycle. Therefore, all the processes that comprise it can be *reversed,* in which case it becomes the Carnot refrigeration cycle. This time, the cycle remains exactly the same, except that the directions of any heat and work interactions are reversed: Heat in the amount of Q_L is absorbed from the low-temperature reservoir, heat in the amount of Q_H is rejected to a high-temperature reservoir, and a work input of $W_{net,in}$ is required to accomplish all this.



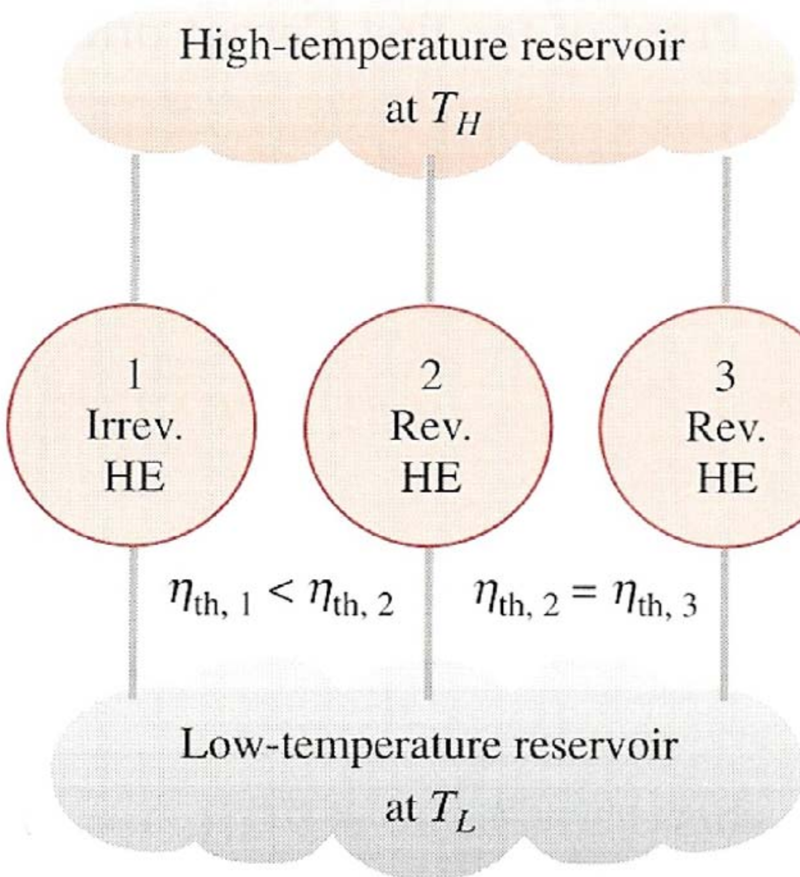
Remember, for a refrigerator, the efficiency is termed Coefficient of Performance (see Eq. 3-6) and can be larger than 100%.

Being a reversible cycle, the Carnot cycle is the most efficient cycle operating between two specified temperature limits. Even though the Carnot cycle cannot be achieved in reality, the efficiency of actual cycles can be improved by attempting to approximate the Carnot cycle more closely.

THE CARNOT PRINCIPLES

The second law of thermodynamics places limitations on the operation of cyclic devices as expressed by the Kelvin-Planck and Clausius statements. A heat engine cannot operate by exchanging heat with a single reservoir, and a refrigerator cannot operate without a net work input from an external source.

We can draw valuable conclusions from these statements. Two conclusions pertain to the thermal efficiency of reversible and irreversible (i.e., actual) heat engines, and they are known as the Carnot principles.



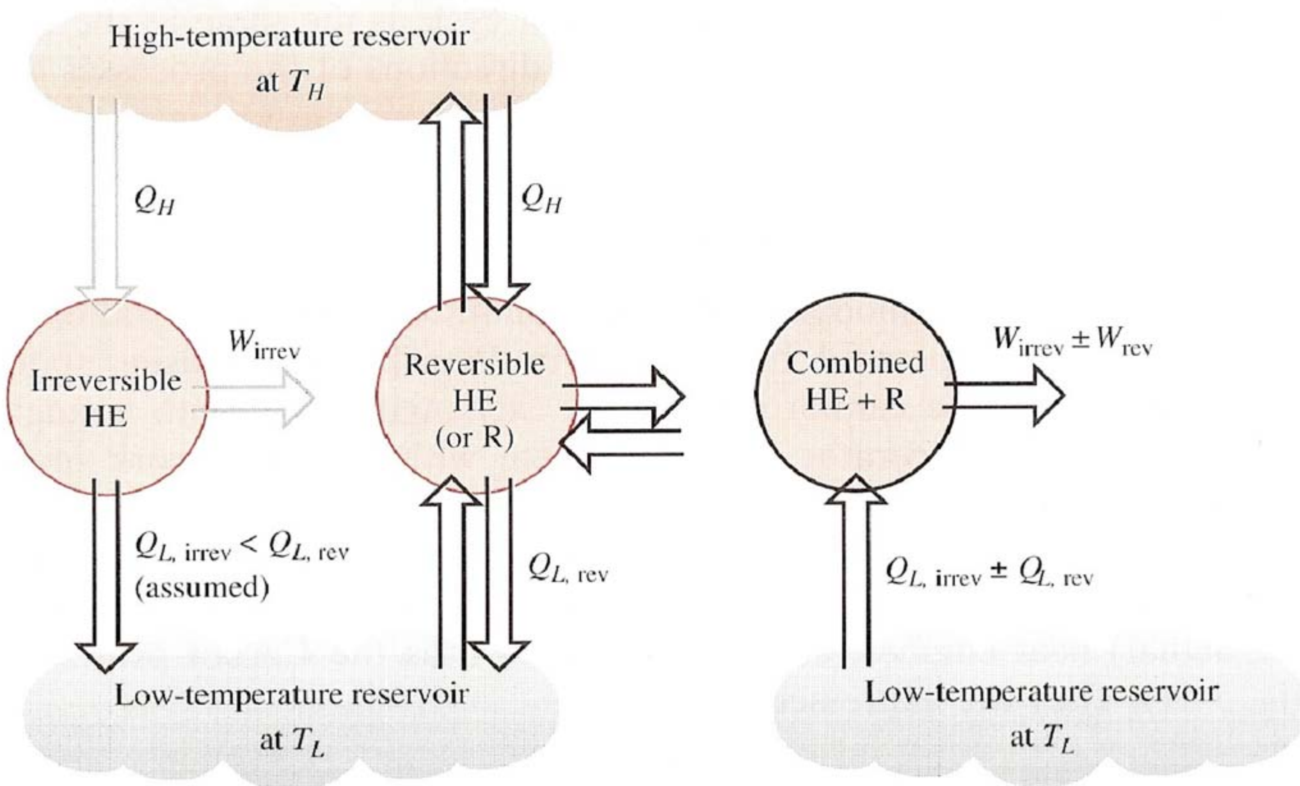
They are expressed as follows:

1 *The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.*

2 *The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.*

These two statements can be proved by demonstrating that the violation of either statement results in the violation of the second law of thermodynamics.

To prove the first statement, consider two heat engines operating between the same reservoirs, as shown below.



(a) A reversible and an irreversible heat engine operating between the same two reservoirs (the reversible heat engine is then reversed to run as a refrigerator)

(b) The equivalent combined system

a. One engine is reversible, and the other is irreversible. Now each engine is supplied with the same amount of heat Q_H. The amount of work produced by the reversible heat engine is W_{rev}, and the amount produced by the irreversible one is $W_{irrev'}$

b. In violation of the first Carnot principle, we assume that the irreversible heat engine is more efficient than the reversible one (that is, $\eta_{irrev} > \eta_{rev}$) and thus delivers more work than the reversible one.

c. Now let the reversible heat engine be reversed and operate as a refrigerator. This refrigerator will receive a work input of W_{rev} and reject heat to the high-temperature reservoir.

d. Since the refrigerator is rejecting heat in the amount of Q_H to the high-temperature reservoir and the irreversible heat engine is receiving the same amount of heat from this reservoir, the net heat exchange for this reservoir is zero. Thus it could be eliminated by having the refrigerator discharge Q_H directly into the irreversible heat engine.

e. Now considering the refrigerator and the irreversible engine together, we have an engine that produces a net work in the amount of $W_{irrev} - W_{rev}$ while exchanging heat with a single reservoir- a violation of the Kelvin-Planck statement of the second law. Therefore, our initial assumption that $\eta_{irrev} > \eta_{rev}$ is incorrect. Then we conclude that no heat engine can be more efficient than a reversible heat engine operating between the same reservoirs.

Note: The second Carnot principle can also be proved in a similar manner. This time, let us replace the irreversible engine by another reversible engine that is more efficient and thus delivers more work than the first reversible engine. By following through the same reasoning as above, we will end up having an engine that produces a new amount of work while exchanging heat with a single reservoir, which is a violation of the second law. Therefore we conclude that no reversible heat engine can be more efficient than another reversible heat engine operating between the same two reservoirs, regardless of how the cycle is completed or the kind of working fluid used.

Example 3.2

1 mol of a perfect gas is subjected to all the steps of a reversible Carnot cycle. Calculate *T, P, V* and *H* at the end of each step. Assume that C_P and C_V are constants.

Solution

See text page 128-129

THERMODYNAMIC EFFICIENCY

We have shown that *all engines operating in a reversible and cyclic manner between the same two temperatures will possess the same thermodynamic efficiency, whatever the working substance.*

Eq. 3-18 gives the efficiency of a reversible engine. The efficiency of a reversible heat engine or any reversible machine is thus determined by the temperature of the heat introduced and the temperature of the heat discharged. It appears that, in order to have an engine of 100% efficiency, either the temperature T_H must be infinite or the temperature T_{L1} must be very small. None of these choices are feasible though.

From Equation 3-18 we have

$$\eta = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H} \tag{3-18}$$

$$1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

or

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0 \tag{3-19}$$

This shows that the absolute magnitudes of the quantities of heat absorbed and rejected are proportional to the temperatures of the heat reservoirs in either cycle. We may generalize Equation 3-19 as

$$\sum_{cycle} \frac{Q}{T} = 0 \tag{3-20}$$

If the ideal gas in the Carnot cycle is considered as being carried through a series of infinitesimally small steps throughout the cycle, then Eq. 3-20 becomes

$$\int \frac{dQ}{T} = 0 \tag{3-21}$$

we will see later that by definition,

$$\frac{dQ}{T} = dS \tag{3-22}$$

is the entropy of the system,

Thus

$$\int dS = 0 \tag{3-23}$$

THE THERMODYNAMIC TEMPERATURE SCALE

A temperature scale that is independent of the properties of the substances that are used to measure temperature is called a thermodynamic temperature scale. Such a temperature scale offers great conveniences in thermodynamic calculations, and its derivation is given below using some reversible heat engine.

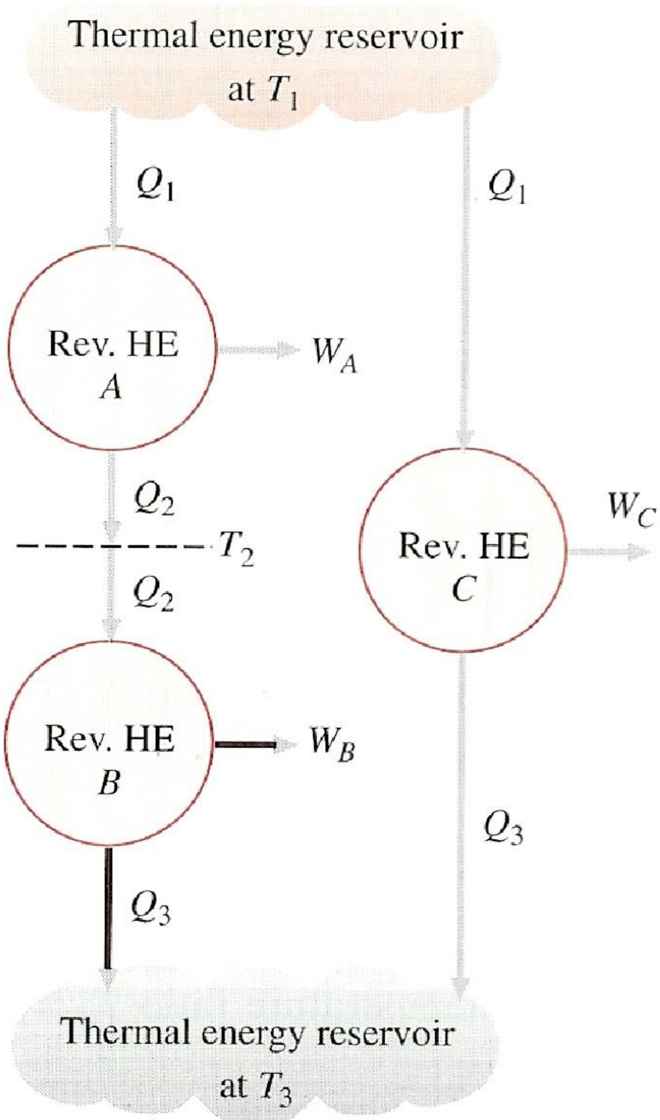
The second Carnot principle states that all reversible heat engines have the same thermal efficiency when operating between the same two reservoirs. That is, the efficiency of a reversible engine is independent of the working fluid employed and its properties, the way the cycle is executed, or the type of reversible engine used. Since energy reservoirs are characterized by their temperatures, the thermal efficiency of reversible heat engines is a function of the reservoir temperatures only. That is,

$$\eta_{rev} = g\,(T_H, T_L)$$

or

$$Q_H \,/\, Q_L = f\,(T_H, T_L) \tag{3-24}$$

The functional form of $f\,(T_H, T_L)$ can be developed with the help of the three reversible heat engines shown in figure below. Engines A and C are supplied with the same amount of heat Q_1 from the high-temperature reservoir at T_1. Engine C rejects Q_3 to the low-temperature reservoir at T_3. Engine B receives the heat Q_2 rejected by engine A at temperature T_2 and rejects heat in the amount of Q_3 to a reservoir at T_3.



The amounts of heat rejected by engines *B* and *C* must be the same since engines *A* and *B* can be combined into one reversible engine operating between the same reservoirs as engine *C* and thus the combined engine will have the same efficiency as engine *C*. Since the heat input to engine *C* is the same as the heat input to the combined engines *A* and *B,* both systems must reject the same amount of heat.

Applying Eq. 3-24 to all three engines separately, we obtain

$$\frac{Q_1}{Q_2} = f(T_1,T_2) \qquad \frac{Q_2}{Q_3} = f(T_2,T_3) \qquad \frac{Q_1}{Q_3} = f(T_1,T_3)$$

But

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2}\frac{Q_2}{Q_3}$$

and from Eq. 3-24

$$f(T_1, T_3) = f(T_1, T_2)\, f(T_2, T_3)$$

A careful examination of this equation reveals that the left-hand side is a function of T_1, T_3 and therefore the right-hand side must also be a function of T_1, T_3 only, and not T_2. That is, the value of the product on the right-hand side of this equation is independent of the value of T_2. This condition will be satisfied only if the function f has the following form:

$$f(T_1, T_2) = \phi(T_1) / \phi(T_2) \qquad f(T_2, T_3) = \phi(T_2) / \phi(T_3)$$

so that $\phi(T_2)$ will cancel from the product of the two f, yielding

$$\frac{Q_1}{Q_3} = f(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_3)} \qquad 3\text{-}25$$

This relation is much more specific than Eq. 3-24 for the functional form of Q_1 / Q_3 in terms of T_1, T_3.

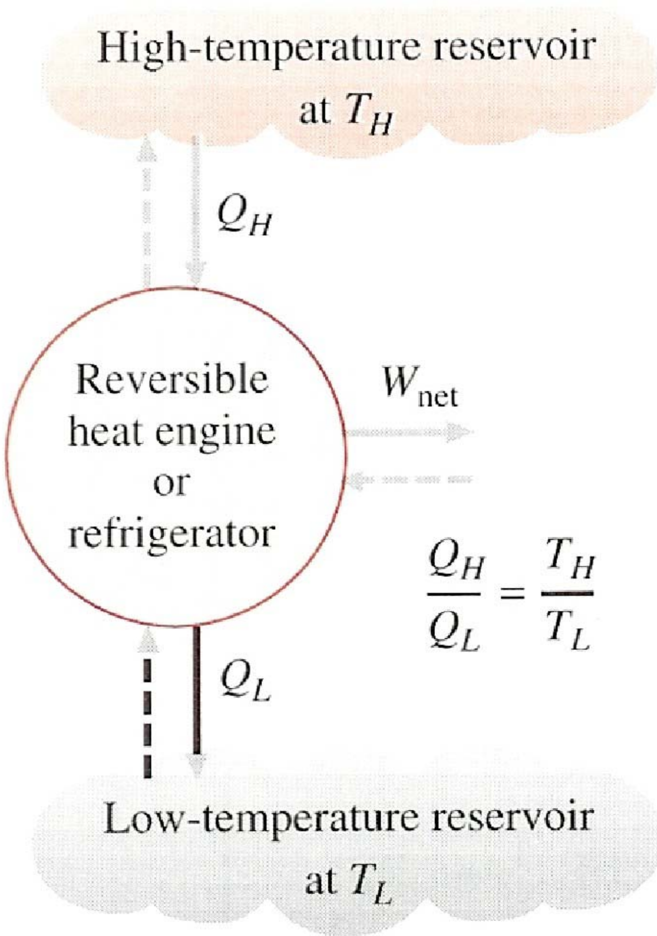
For a reversible heat engine operating between two reservoirs at temperatures T_H and T_L, Eq. 3-25 can be written as

$$\frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)} \qquad 3\text{-}26$$

This is the only requirement that the second law places on the ratio of heat flows to and from the reversible heat engines. Several functions $\phi(T)$ will satisfy this equation, and the choice is completely arbitrary. Lord Kelvin first proposed taking

$$\phi(T) = T$$

to define a thermodynamic temperature scale as (see figure)



$$\left(\frac{Q_H}{Q_L}\right)_{rev} = \frac{T_H}{T_L} \qquad \text{3-27}$$

This temperature scale is called the Kelvin scale, and the temperatures on this scale are called absolute temperatures. *On the Kelvin scale, the temperature ratios depend on the ratios of heat transfer between a reversible heat engine and the reservoirs and are independent of the physical properties of any substance. On this scale, temperatures vary between zero and infinity.*

The thermodynamic temperature scale is not completely defined by Eq. 3-27 since it gives us only a ratio of absolute temperatures. We also need to know the magnitude of a kelvin degree. At the International Conference on Weights and Measures held in 1954, the triple point of water (the state at which all three phases of water exist in equilibrium) was assigned the value 273.16 K. The *magnitude of a kelvin* is defined as 1/273.16 of the temperature interval between absolute zero and the triple-point temperature of water. The magnitudes of temperature units on the kelvin and Celsius scales are identical (1 K == 1°C). The temperatures on these two scales differ by a constant 273.15:

$$T\,(^{0}C) = T(K) - 273.15 \tag{3-28}$$

Even though the thermodynamic temperature scale is defined with the help of the reversible heat engines, it is not possible, nor is it practical, to actually operate such an engine to determine numerical values on the absolute temperature scale. Absolute temperatures can be measured accurately by other means, such as the constant-volume ideal-gas thermometer discussed in Part 1 together with extrapolation techniques. The validity of Eq. 3-28 can be demonstrated from physical considerations for a reversible cycle using an ideal gas as the working fluid.

Example 3.3

A Carnot heat engine receives 500 kJ of heat per cycle from a high-temperature source at 652°C and rejects heat to a low-temperature sink at 30°C. Determine *(a)* the thermal efficiency of this Carnot engine and *(b)* the amount of heat rejected to the sink per cycle.

Solution

(a) The Carnot heat engine is a reversible heat engine, and so its efficiency can be determined from Eq. 3-18:

$$\eta = \mathbf{1} - \frac{T_L}{T_H} = \mathbf{0.672}$$

(b) The amount of heat rejected Q_L by this reversible heat engine is easily determined from Eq. 3-27:

$$\left(\frac{Q_H}{Q_L}\right)_{rev} = \frac{T_H}{T_L}$$

giving Q_L = 163.8 kJ.

GASOLINE ENGINES

Many cyclic processes do not operate on a Carnot cycle. Two common examples of such processes are the Diesel and the Otto cycle of gasoline engines. However, any reversible cyclic process is subjected to the same thermodynamic analysis as a Carnot engine.

In gas power cycles, the working fluid remains a gas throughout the entire cycle. Spark-ignition automobile engines, diesel engines, and conventional gas turbines are familiar examples of devices that operate on gas cycles. In all these engines, energy is provided by burning a fuel within the system boundaries. That is, they are *internal combustion engines.*

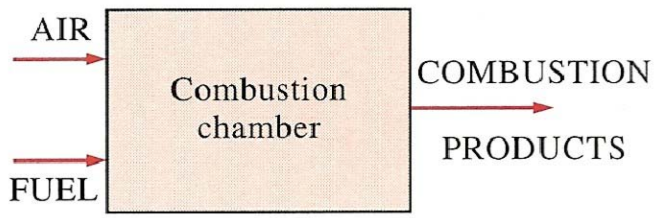
Because of this combustion process, the composition of the working fluid changes from air and fuel to combustion products during the course of the cycle. However, considering that air is predominantly nitrogen, which undergoes hardly any chemical reactions in the combustion chamber, the working fluid closely resembles air at all times.

Even though internal combustion engines operate on a mechanical cycle (the piston returns to its starting position at the end of each revolution), the working fluid does not undergo a complete thermodynamic cycle. It is thrown out of the engine at some point in the cycle (as exhaust gases) instead of being returned to the initial state. Working on an open cycle is the characteristic of all internal combustion engines.

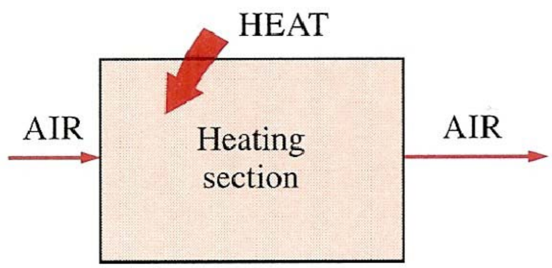
The air-standard assumptions

The actual gas power cycles are rather complex. To reduce the analysis to a manageable level, we utilize the following approximations, commonly known as the air-standard assumptions.

- The working fluid is air that continuously circulates in a closed loop and always behaves as an ideal gas.
- All the processes that make up the cycle are internally reversible.
- The combustion process is replaced by a heat addition process from an external source (see figure)
- The exhaust process is replaced by a heat rejection process that restores the working fluid to its initial state.



(*a*) Actual



(*b*) Ideal

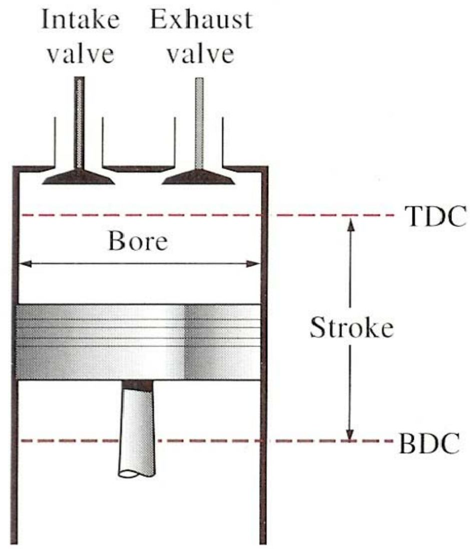
Another assumption that is often utilized to simplify the analysis even more is that the air has constant specific heats whose values are determined at *room temperature* (25°C). When this assumption is utilized, the air-standard assumptions are called the cold-air-standard assumptions. A cycle for which the air-standard assumptions are applicable is frequently referred to as an air-standard cycle.

The air-standard assumptions stated above provide considerable simplification in the analysis without significantly deviating from the actual cycles. This simplified model enables us to study qualitatively the influence of major parameters on the performance of the actual engines.

Brief overview of gasoline (reciprocating) engines

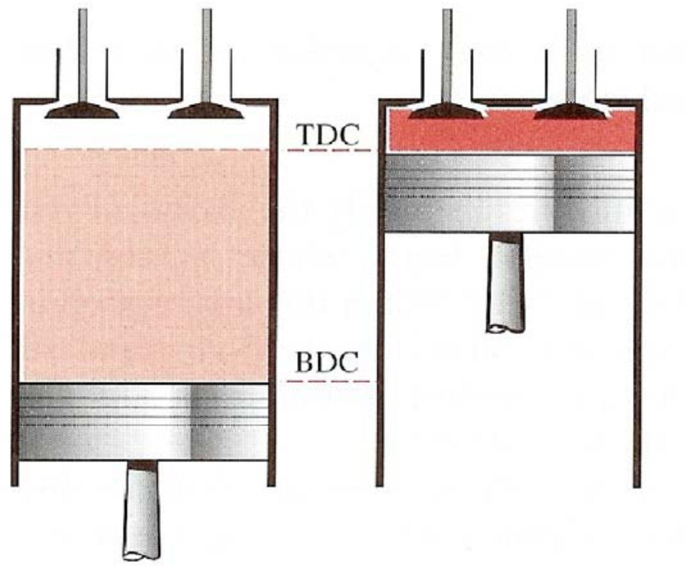
Despite its simplicity, the reciprocating engine (basically a piston-cylinder device) is one of the rare inventions that has proved to be very versatile and to have a wide range of applications. It is the powerhouse of the vast majority of automobiles, trucks, light aircraft, ships, and electric power generators, as well as many other devices.

The basic components of a reciprocating engine are shown in figure below.



- The piston reciprocates in the cylinder between two fixed positions called the top dead center (TDC)-the position of the piston when it forms the smallest volume in the cylinder-and the bottom dead center (BDC)-the position of the piston when it forms the largest volume in the cylinder.
- The distance between the TDC and the BDC is the largest distance that the piston can travel in one direction, and it is called the stroke of the engine.
- The diameter of the piston is called the bore.
- The air or air-fuel mixture is drawn into the cylinder through the intake valve, and the combustion products are expelled from the cylinder through the exhaust valve.

The minimum volume formed in the cylinder when the piston is at TDC is called the clearance volume.



(a) Displacement volume (b) Clearance volume

- The volume displaced by the piston as it moves between TDC and BDC is called the displacement volume.
- The ratio of the maximum volume formed in the cylinder to the minimum (clearance) volume is called the **compression ratio** *r* of the engine:

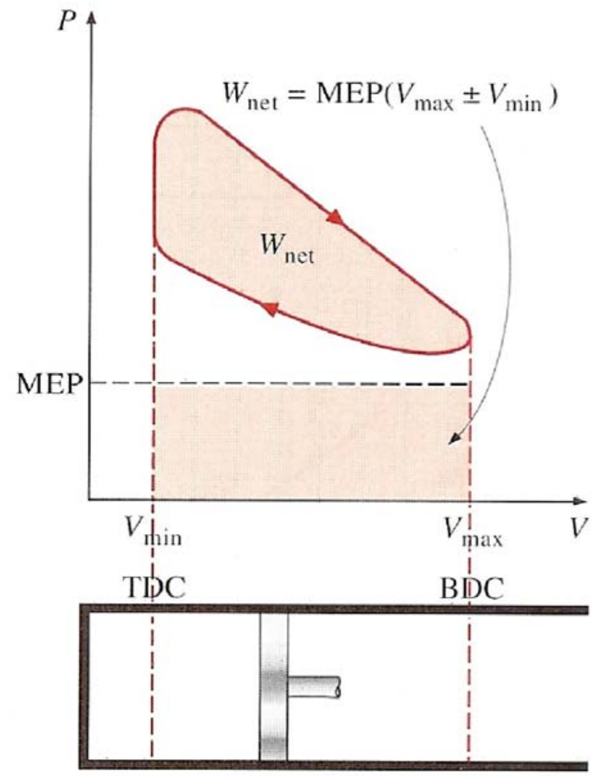
$$r = V_{max} / V_{min} = V_{BDC} / V_{TDC} \qquad 3\text{-}29$$

Note: the compression ratio is a *volume ratio* and should not be confused with the pressure ratio.

- Another term frequently used in conjunction with reciprocating engines is the mean effective pressure (MEP). It is a fictitious pressure which, if it acted on the piston during the entire power stroke, would produce the same amount of net work as that produced during the actual cycle. That is,

$$MEP = \frac{W_{net}}{V_{\max} - V_{\min}} \qquad 3\text{-}30$$

Note: The mean effective pressure can be used as a parameter to compare the performances of reciprocating engines of equal size. The engine that has a larger value of MEP will deliver more net work per cycle and thus will perform better.

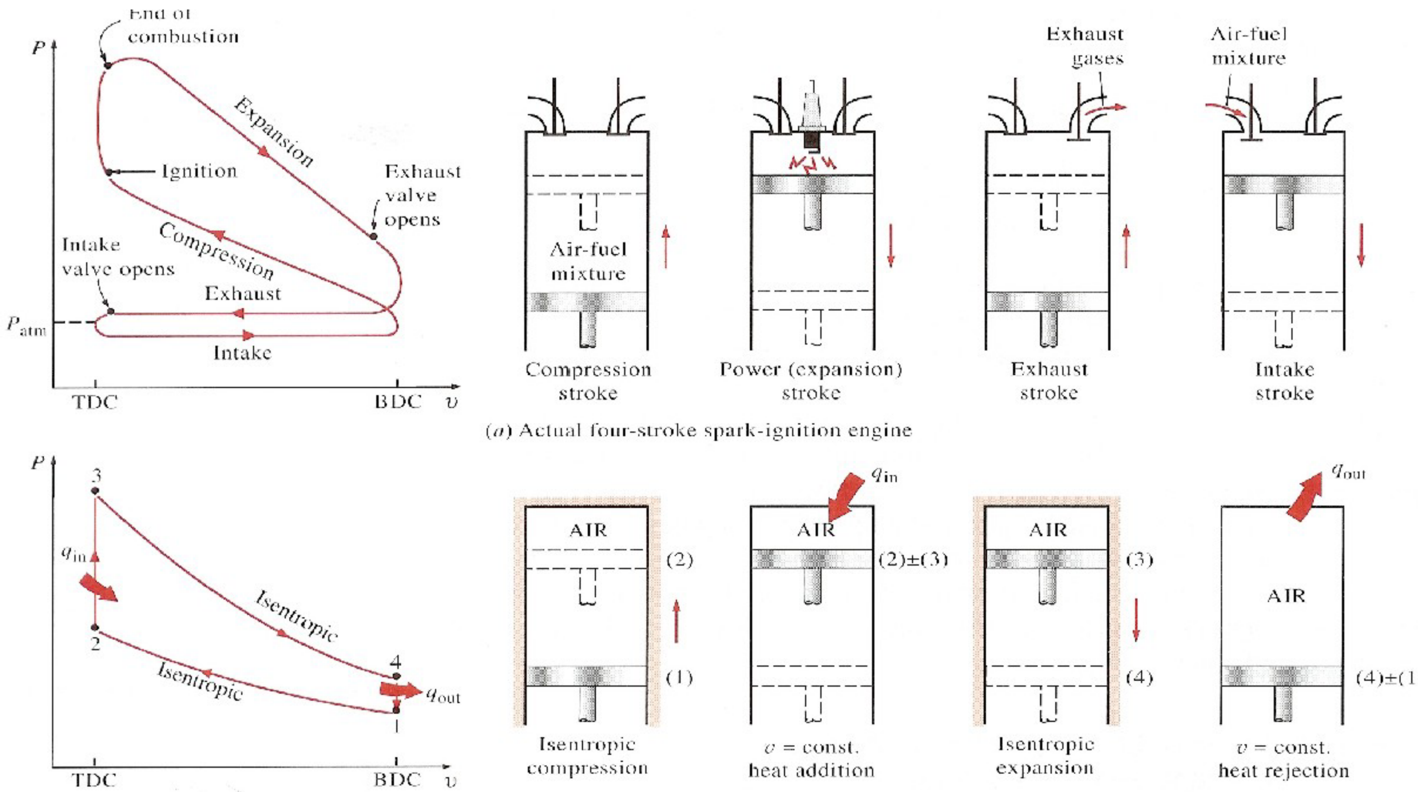


Reciprocating engines are classified as **spark-ignition** (SI) engines or **compression-ignition** (CI) engines, depending on how the combustion process in the cylinder is initiated. In SI engines (such as the **Otto engine**), the combustion of the air-fuel mixture is initiated by a spark plug. In CI engines (such as the Diesel engine), the air-fuel mixture is self-ignited as a result of compressing the mixture above its self-ignition temperature.

OTTO CYCLE THE IDEAL CYCLE FOR SI ENGINES

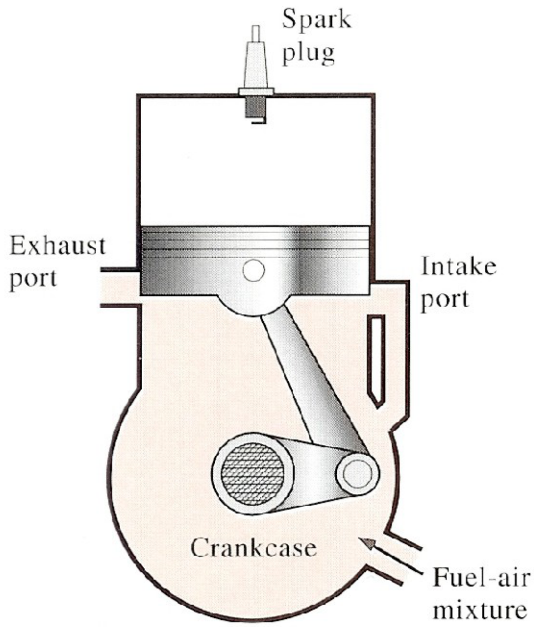
The Otto cycle is the ideal cycle for spark-ignition reciprocating engines. It is named after Nikolaus A. Otto, who built a successful four-stroke engine in 1876 in Germany using the cycle proposed by Frenchman Beau de Rochas in 1862.

In most spark-ignition engines, the piston executes four complete strokes (two mechanical cycles) within the cylinder, and the crankshaft completes 2 revolutions for each thermodynamic cycle. These engines are called **four-stroke internal combustion engines**. A schematic of each stroke as well as a *P*-*V* diagram for an actual four-stroke spark-ignition engine is shown below (part a).



- Initially, both the intake and the exhaust valves are closed, and the piston is at its lowest position (BDC). During the *compression stroke,* the piston moves upward, compressing the air-fuel mixture.
- Shortly before the piston reaches its highest position (TCD), the spark plug fires and the mixture ignites, increasing the pressure and temperature of the system.
- The high-pressure gases force the piston down, which in turn forces the crankshaft to rotate, producing a useful work output during the *expansion* or *power stroke.* At the end of this stroke, the piston is at its lowest position (the completion of the first mechanical cycle), and the cylinder is filled with combustion products.
- Now the piston moves upward one more time, purging the exhaust gases through the exhaust valve (the *exhaust stroke),* and down a second time, drawing in fresh air-fuel mixture through the intake valve (the *intake stroke*). Notice that the pressure in the cylinder is slightly above the atmospheric value during the exhaust stroke and slightly below during the intake stroke.

In **two-stroke engines**, all four functions described above are executed in just two strokes: the power stroke and the compression stroke. In these engines, the crankcase is sealed, and the outward motion of the piston is used to slightly pressurize the air-fuel mixture in the crankcase, as shown below.



Also, the intake and exhaust valves are replaced by openings in the lower portion of the cylinder wall. During the latter part of the power stroke, the piston uncovers first the exhaust port, allowing the exhaust gases to be partially expelled, and then the intake port, allowing the fresh air-fuel mixture to rush in and drive most of the remaining exhaust gases out of the cylinder. This mixture is then compressed as the piston moves upward during the compression stroke and is subsequently ignited by a spark plug.

The two-stroke engines are generally less efficient than their four stroke counterparts because of the incomplete expulsion of the exhaust gases and the partial expulsion of the fresh air-fuel mixture with the exhaust gases. However, they are relatively simple and inexpensive, and they have high power-to-weight and power-to-volume ratios, which make them suitable for applications requiring small size and weight such as for motorcycles, chain saws, and lawn mowers.

Note: Advances in several technologies-such as direct fuel injection, stratified charge combustion, and electronic controls-brought about a renewed interest in two-stroke engines, which can offer high performance and fuel economy while satisfying the future stringent emission requirements. For a given weight and displacement, a well-designed two-stroke engine can provide significantly more power than its four-stroke counterpart because two-stroke engines produce power on every engine revolution instead of every other one. In the new two-stroke engines under development, the highly atomized fuel spray that is injected with compressed air into the combustion chamber towards the end of the compression stroke burns much more completely. The fuel is sprayed after the exhaust valve is closed, which prevents unburned fuel from being ejected into the atmosphere.

With stratified combustion, the flame, which is initiated by igniting a small amount of rich fuel/air mixture near the spark plug, propagates through the combustion chamber filled with much leaner mixture, and this results in much cleaner combustion. Also, the advances in electronics made it possible to ensure the optimum operation under varying engine load and speed conditions. Major car companies have research programs underway on two-stroke engines which are expected to make a comeback in the near future.

The thermodynamic analysis of the actual four-stroke or two-stroke cycles described above is not a simple task. However, the analysis can be simplified significantly if the air-standard assumptions are utilized. The resulting cycle which closely resembles the actual operating conditions is the ideal Otto cycle. It consists of four internally reversible processes:

1-2 adiabatic (isentropic) compression
2-3 V = constant heat addition
3-4 adiabatic (isentropic) expansion
4-1 V = constant heat rejection

Note: As we will see later, the entropy of a fixed mass will not change during an internally reversible, adiabatic process, which is called isentropic (constant entropy) process. An isentropic process appears as a vertical line on a T-S diagram.

The execution of the Otto cycle in a piston-cylinder device together with a *P-V* diagram is illustrated in the figure above (part b).

The Otto cycle is executed in a closed system, and thus the first-law relation for any of the processes is expressed as

$$\Delta U = Q + W \qquad 3\text{-}31$$

No work is involved during the two heat transfer processes since both take place at constant volume. Therefore, heat transfer to and from the working fluid can be expressed, under the cold-air-standard assumptions, as

$$\begin{aligned} Q_{in} &= Q_{23} = U_3 - U_2 = C_V\,(T_3 - T_2) \\ Q_{out} &= -\,Q_{41} = -\,(U_1 - U_4) = C_V\,(T_4 - T_1) \end{aligned} \qquad 3\text{-}32$$

Then the thermal efficiency of the ideal-air-standard Otto cycle becomes

$$\eta_{Otto} = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = \frac{T_1(T_4/T_1 - 1)}{T_2(T_3/T_2 - 1)}$$

Processes 1-2 and 3-4 are adiabatic and $V_2 = V_3$ and $V_4 = V_1$. Thus

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1} = \frac{T_4}{T_3} \qquad 3\text{-}33$$

Substituting these equations into the thermal efficiency relation and simplifying we get

$$\eta_{Otto} = 1 - \frac{1}{r^{\gamma-1}} \qquad 3\text{-}34$$

where r is the compression ratio

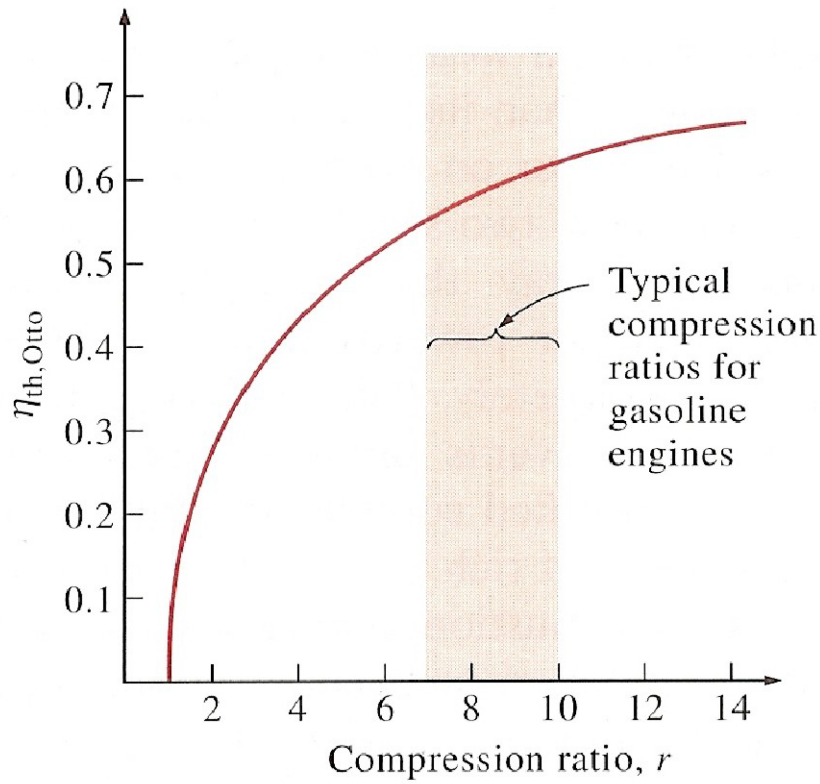
$$r = V_1/V_2$$

Equation 3-34 shows that under the cold-air-standard assumptions,

- the thermal efficiency of an ideal Otto cycle depends on the compression ratio of the engine and the specific heat ratio (γ) of the working fluid (if different from air).

- The thermal efficiency of the ideal Otto cycle increases with both the compression ratio and the specific heat ratio. This is also true for actual spark-ignition internal combustion engines. A plot of thermal efficiency versus the compression ratio is given below for $\gamma = 1.4$, which is the specific-heat-ratio value of air at room temperature.

- For a given compression ratio, the thermal efficiency of an actual spark-ignition engine will be less than that of an ideal Otto cycle because of the irreversibilities, such as friction, and other factors such as incomplete combustion.



We can observe from the graph that the thermal efficiency curve is rather steep at low compression ratios but flattens out starting with a compression ratio value of about 8.

- Therefore, the increase in thermal efficiency with the compression ratio is not that pronounced at high compression ratios. Also,
- when high compression ratios are used, the temperature of the air-fuel mixture rises above the autoignition temperature of the fuel (the temperature at which the fuel ignites without the help of a spark) during the combustion process, causing an early and rapid burn of the fuel at some point or points ahead of the flame front, followed by almost instantaneous inflammation of the end gas. This premature ignition of the fuel, called **autoignition,** produces an audible noise, which is called **engine knock.**

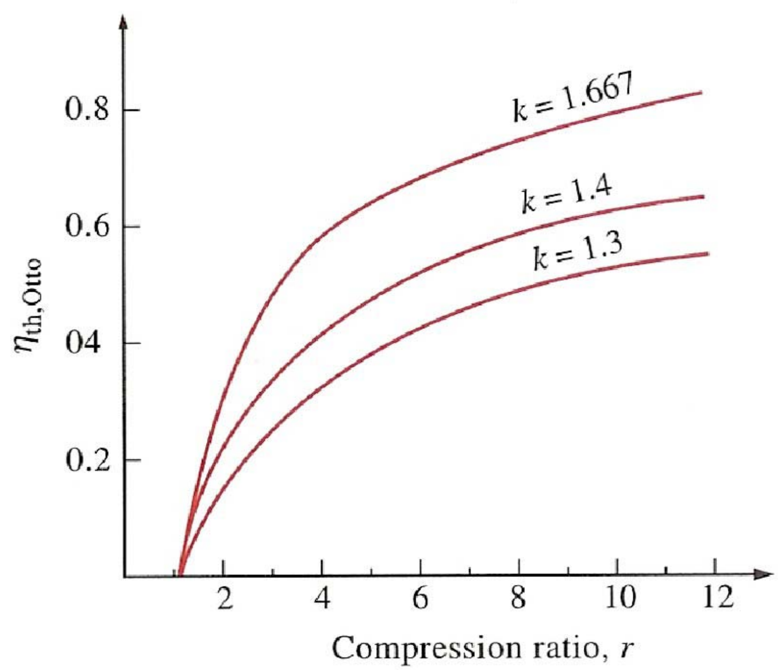
Note (optional): Autoignition in spark- ignition engines cannot be tolerated because it hurts performance and can cause engine damage. The requirement that autoignition not be allowed places an upper limit on the compression ratios that can be used in spark-ignition internal combustion engines.

Improvement of the thermal efficiency of gasoline engines by utilizing higher compression ratios (up to about 12) without facing the autoignition problem has been made possible by using gasoline blends that have good antiknock characteristics, such as gasoline mixed with tetraethyl lead. Tetraethyl lead has been added to gasoline since the

1920s because it is the cheapest method of raising the *octane rating,* which is a measure of the engine knock resistance of a fuel. Leaded gasoline, however, has a very undesirable side effect: it forms compounds during the combustion process that are hazardous to health and pollute the environment. In an effort to combat air pollution, the government adopted a policy in the mid-1970s that resulted in the eventual phase-out of the leaded gasoline. Unable to use lead, the refiners developed other, more elaborate techniques to improve the antiknock characteristics of the gasoline. Most cars made since 1975 have been designed to use unleaded gasoline, and the compression ratios had to be lowered to avoid engine knock.

The thermal efficiency of car engines has decreased somewhat as a result of decreased compression ratios. But, owing to the improvements in other areas (reduction in overall automobile weight, improved aerodynamic design, etc.), today's cars have better fuel economy and consequently get more miles per gallon of fuel. This is an example of how engineering decisions involve compromises, and efficiency is only one of the considerations in reaching a final decision.

The second parameter affecting the thermal efficiency of an ideal Otto cycle is the specific heat ratio γ. For a given compression ratio, an ideal Otto cycle using a monatomic gas (such as argon or helium, $\gamma = 1.667$) as the working fluid will have the highest thermal efficiency. The specific heat ratio γ, and thus the thermal efficiency of the ideal Otto cycle, decreases as the molecules of the working fluid get larger .



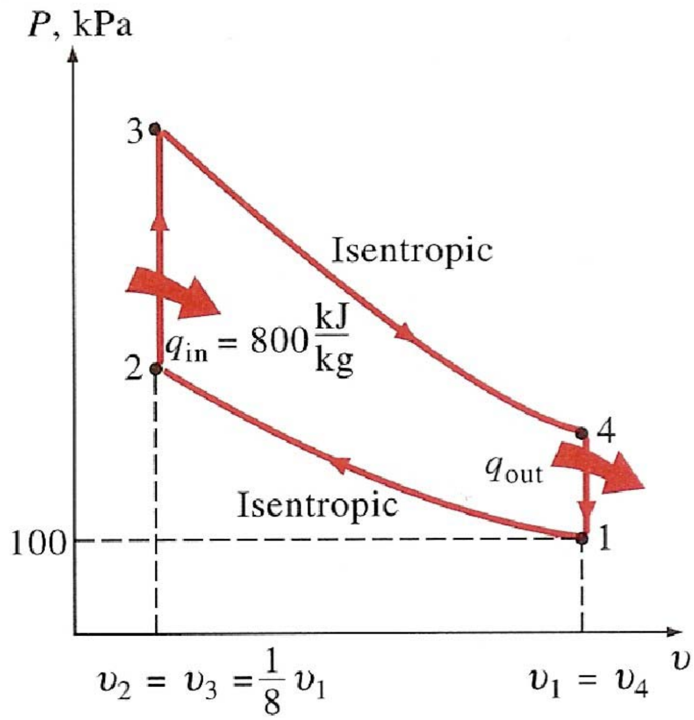
At room temperature it is 1.4 for air, 1.3 for carbon dioxide, and 1.2 for ethane. The working fluid in actual engines contains larger molecules such as carbon dioxide, and the specific heat ratio decreases with temperature, which is one of the reasons that the actual cycles have lower thermal efficiencies than the ideal Otto cycle. The thermal efficiencies of actual spark-ignition engines range from about 25 to 30 percent.

Example 3.3

An ideal Otto cycle has a compression ratio of 8. At the beginning of the compression process, the air is at 100 kPa and 17°C, and 800 kJ/kg of heat is transferred to air during the constant-volume heat addition process. Determine *(a)* the maximum temperature and pressure that occur during the cycle, *(b)* the net work output, *(c)* the thermal efficiency, and *(d)* the mean effective pressure for the cycle.

Solution

The Otto cycle described is shown on a *P-V* diagram below, where the heat is shown per unit mass.



The air contained in the cylinder forms a closed system. We assume constant specific heat for air at room temperature and thus take Cp = 1.005 kJ/(kg. K), C_V = 0.718 kJ/kg. K), and γ = 1.4.

(a) The maximum temperature and pressure in an Otto cycle occur at the end of the constant-volume heat addition process (state 3). But first we need to determine the temperature and pressure of air at the end of the isentropic compression process

(state 2). From Eq. 3-33 we find $T_2 = 666.2$ K
From the law of ideal gases we find $P_2 = 1837.8$ kPa

Process 2-3 (V = constant heat addition) from Eq. 3-32 we get **T3 = 1780.4 K**

And from the law of ideal gases P_3 = **4911.5 kPa**

(b) The net work output for the cycle is determined either by finding the boundary (P *dV)* work involved in each process by integration and adding them or by finding the net heat transfer which is equivalent to the net work done during the cycle. We take the latter approach. But first we need to find the internal energy of the air at state 4:

Process 3-4 (adiabatic expansion of an ideal gas): From Eq. 3-33 we find $T_4 = 775.0$ K

Process 4-1 *(V* = constant heat rejection): From Eq. 3-32 we find $Q_{out} = 348.2$ kJ/kg.

Thus $W_{net} = Q_{net} = Q_{in} - Q_{out} =$ **451.8 kJ/kg**

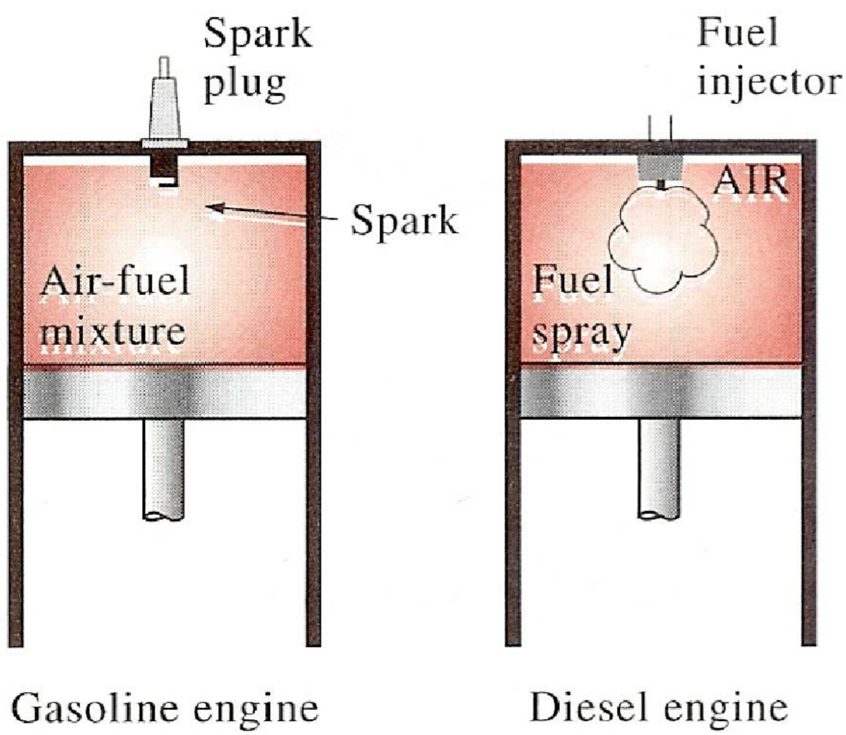
(c) The thermal efficiency of the cycle is determined from its definitions (Eq. 3-6 or 3-34): η **= 0.565**

(d) The mean effective pressure is determined from its definition (Eq. 3-30) where we use the specific volumes **MEP = 620.6 kPa**.

Therefore, a constant pressure of 620.6 kPa during the power stroke would produce the same net work output as the entire cycle.

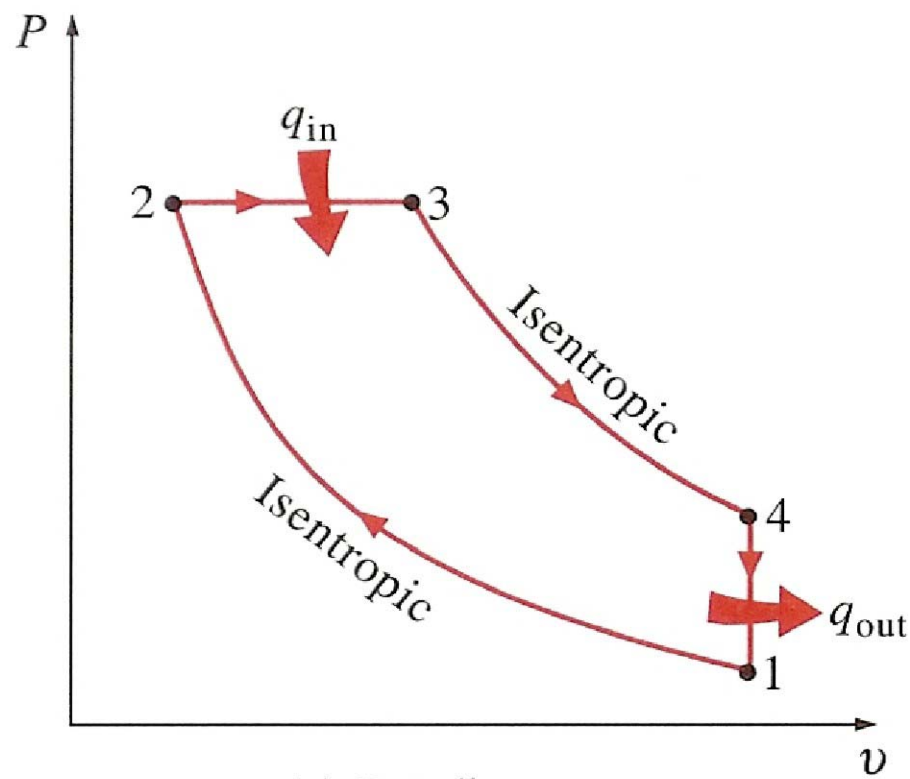
DIESEL CYCLE - THE IDEAL CYCLE FOR CI ENGINES

The Diesel cycle is the ideal cycle for CI reciprocating engines. The CI engine, first proposed by Rudolph Diesel in the 1890s, is very similar to the SI engine discussed in the last section, differing mainly in the method of initiating combustion. In spark-ignition engines (also known as *gasoline engines),* the air-fuel mixture is compressed to a temperature that is below the autoignition temperature of the fuel, and the combustion process is initiated by firing a spark plug. In CI engines (also known as *diesel engines),* the air is compressed to a temperature which is above the autoignition temperature of the fuel, and combustion starts on contact as the fuel is injected into this hot air. Therefore, the spark plug and carburetor are replaced by a fuel injector in diesel engines.



In gasoline engines, a mixture of air and fuel is compressed during the compression stroke, and the compression ratios are limited by the onset of autoignition or engine knock. In diesel engines, only air is compressed during the compression stroke, eliminating the possibility of autoignition. Therefore, diesel engines can be designed to operate at much higher compression ratios, typically between 12 and 24. Not having to deal with the problem of autoignition has another benefit: many of the stringent requirements placed on the gasoline can now be removed, and fuels that are less refined (thus less expensive) can be used in diesel engines.

The fuel injection process in diesel engines starts when the piston approaches TDC and continues during the first part of the power stroke. Therefore, the combustion process in these engines takes place over a longer interval. Because of this longer duration, the combustion process is approximated as a constant-pressure heat addition process. In fact this is the only process where the Otto and the Diesel cycles differ. The remaining three processes are the same for both ideal cycles. That is, process 1-2 is isentropic compression, 3-4 is isentropic expansion, and 4-1 is constant-volume heat rejection. The similarity between the two cycles is also apparent from the *P-V* diagram of the Diesel cycle, shown below.



(a) *P*-*υ* diagrar

A measure of performance for any power cycle is its thermal efficiency. Below we develop a relation for the thermal efficiency of a Diesel cycle, utilizing the cold-air-standard assumptions. Such a relation will enable us to examine the effects of major parameters on the performance of diesel engines.

The Diesel style cycle, like the Otto cycle, is executed in a piston-cylinder device, which forms a closed system. Therefore, equations developed for closed systems should be used in the analysis of individual processes. Under the cold-air-standard assumptions, the amount of heat added to the working fluid at constant pressure and rejected from it at constant volume can be expressed as

$$Q_{in} = Q_{23} = W_{23} + (\Delta U)_{23} = P_2 (V_3 - V_2) + (U_3 - U_2) = H_3 - H_2 = C_P (T_3 - T_2)$$

and 3-35

$$Q_{out} = - Q_{41} = W_{41} - (\Delta U)_{41} = U_4 - U_1 = C_V (T_4 - T_1)$$

Then the thermal efficiency of the ideal Diesel cycle under the cold-air standard assumptions becomes

$$\eta_{Diesel} = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_4 - T_1}{\gamma(T_3 - T_2)} = 1 - \frac{T_1(T_4/T_1 - 1)}{\gamma T_2(T_3/T_2 - 1)}$$

We now define a new quantity, the **cutoff ratio** r_c as the ratio of the cylinder volumes after and before the combustion process:

$$r_c = V_3 / V_2$$

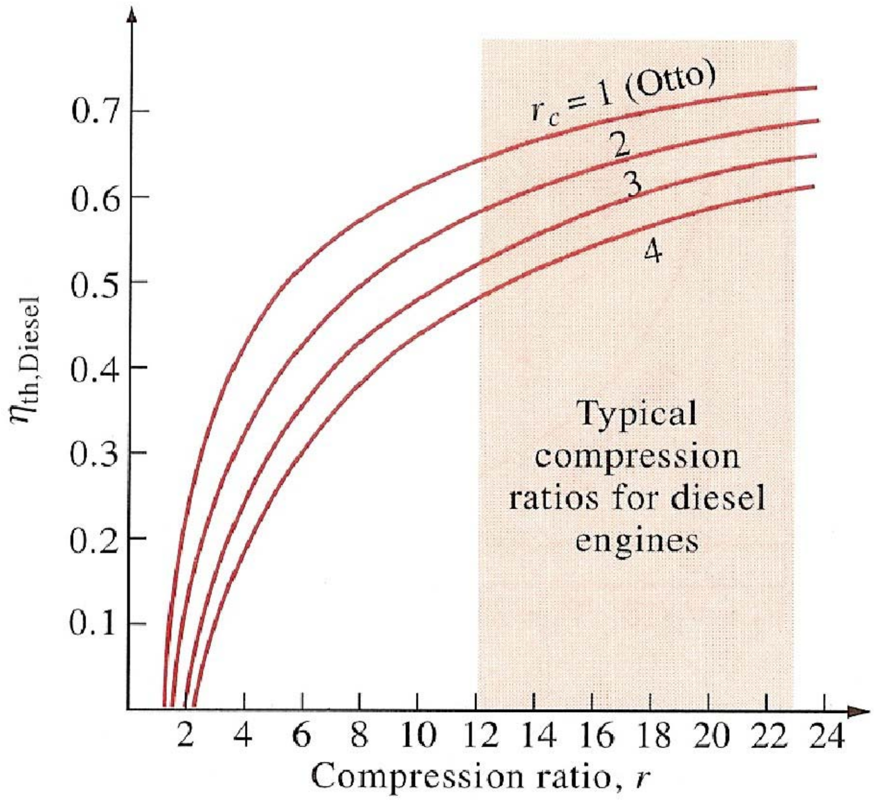
Utilizing this definition and the isentropic ideal-gas relations for processes 1-2 and 3-4, we see that the thermal efficiency relation reduces to

$$\eta_{Diesel} = 1 - \frac{1}{r^{\gamma-1}} = \left[\frac{r_c^{\gamma} - 1}{\gamma(r_c - 1)}\right] \qquad 3\text{-}36$$

where r is the compression ratio defined by Eq. 3-29. Looking at Eq. 3-36 carefully, one would notice that under the cold-air-standard assumptions, the efficiency of a Diesel cycle differs from the efficiency of an Otto cycle by the quantity in the brackets. This quantity is always greater than 1. Therefore,

$$\eta_{Otto} > \eta_{Diesel} \qquad 3\text{-}37$$

when both cycles operate on the same compression ratio. Also as the cutoff ratio decreases, the efficiency of the Diesel cycle increases (the graph takes $\gamma = 1.4$).



- For the limiting case of $r_c = 1$, the quantity in the brackets becomes unity, and the efficiencies of the Otto and Diesel cycles become identical. Remember, though, that diesel engines operate at much higher compression ratios and thus are usually more efficient than the spark-ignition (gasoline) engines. The diesel engines also burn the fuel more completely since they usually operate at lower revolutions per minute than spark-ignition engines.

- Thermal efficiencies of diesel engines range from about 35 to 40 percent.

- The higher efficiency and lower fuel costs of diesel engines make them the clear choice in applications, requiring relatively large amounts of power, such as in locomotive engines, emergency power generation units, large ships, and heavy trucks.

- Approximating the combustion process in internal combustion engines as a constant-volume or a constant-pressure heat addition process is overly simplistic and not quite realistic. Probably a better (but slightly more complex) approach would be to model the combustion process in both gasoline and diesel engines as a combination of two heat transfer processes, one occurring at constant volume and the other at constant pressure. The ideal cycle based on this concept is called the

dual cycle, and a *P-V* diagram for it is given below. The relative amounts of heat added during each process can be adjusted to approximate the actual cycle more closely. Note that both the Otto and the Diesel cycles can be obtained as special cases of the dual cycle.