

CHAPTER FIVE

THE SECOND LAW OF THERMODYNAMICS

Introduction

In previous chapter, we learn about first law of thermodynamics or conservation of energy principles.

under this, we see processes involve closed or open system.

Also we see that, 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 here, satisfying the first law alone does not ensure that the process will actually take place.

Example

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

Conti.



Fig. cup of hot coffee does not get hotter in a cooler room.

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 take 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.

Another example

The heating of a room by the passage of electric current through a resistor. Again, the first law dictates that the amount of electric energy supplied to the resistance wires be equal to the amount of energy transferred to the room air as heat.

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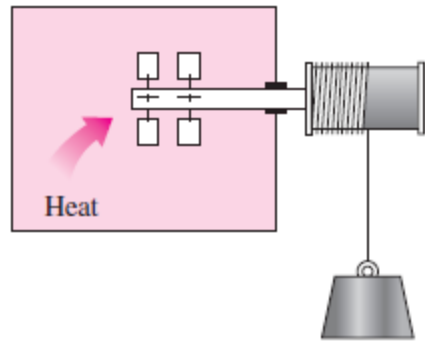
Transferring heat to a wire will not generate electricity.

let us attempt to reverse this process. It will come as no surprise that transferring some heat to the wires does not cause an equivalent amount of electric energy to be generated in the wires.

Another example,

A paddle-wheel mechanism that is operated by the fall of a mass . The paddle wheel rotates as the mass falls and stirs a fluid within an insulated container. As a result, the potential energy of the mass decreases, and the internal energy of the fluid increases in accordance with the conservation of energy principle.

Conti.



Transferring heat to a paddle wheel will not cause it to rotate.

However, the reverse process, raising the mass by transferring heat from the fluid to the paddle wheel, does not occur in nature, although doing so would not violate the first law of thermodynamics.

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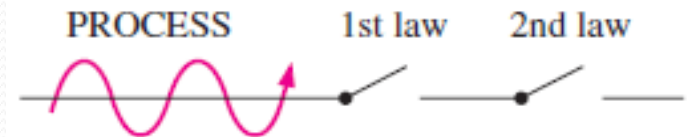
It is clear from the previous examples that,
Processes proceed in certain direction and not in the reverse
direction.



The first law places no restriction on the direction of a process.
but satisfying the first law does not ensure that the process
can actually occur.

Therefore we need another law (the second law of
thermodynamics) to determine the direction of a process.

A process cannot occur unless it satisfies both the first and the
second laws of thermodynamics



A process must satisfy both the first and second laws of
thermodynamics to proceed.

Conti.

Use of second law of thermodynamics

- ✓ to identify the direction of processes
- ✓ also asserts that energy has quality as well as quantity
- ✓ 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.

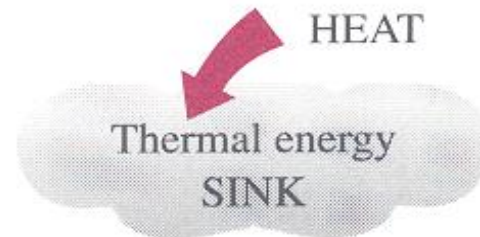
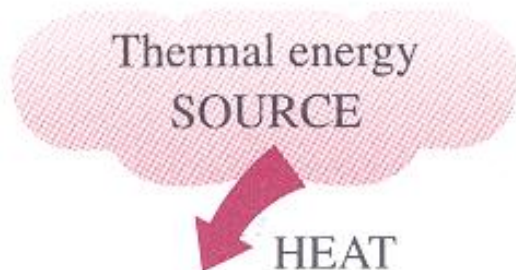
THERMAL ENERGY RESERVOIRS

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 ($\text{mass} \times \text{specific heat}$) 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**.

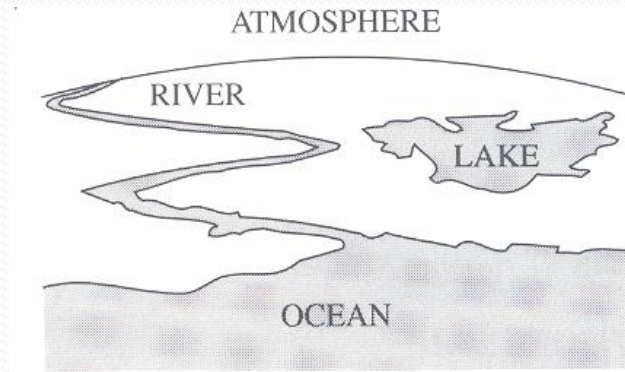
A reservoir that supplies energy in the form of heat is called a source

one that absorbs energy in the form of heat is called a sink

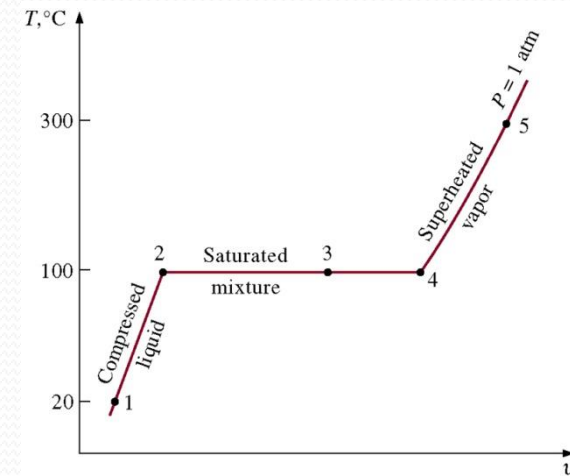
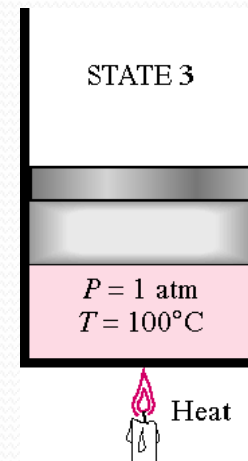


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Some obvious examples are solar energy, oil furnace, atmosphere, lakes, and oceans



Another example is two-phase systems

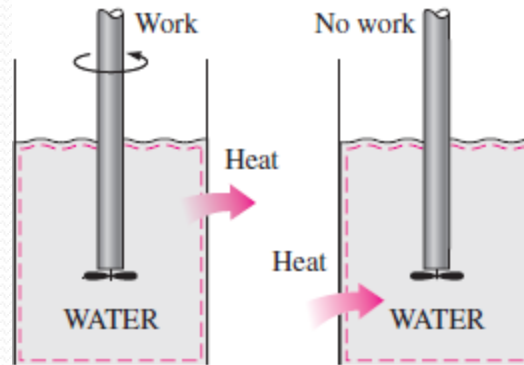


and even the air in a room if the heat added or absorbed is small compared to the air thermal capacity (e.g. TV heat in a room)



HEAT ENGINES

Work can easily be converted to other forms of energy, but converting other forms of energy to work is not that easy.



Work can always be converted to heat directly and completely, but the reverse is not true.

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**.

Characteristics of heat engines

1. They receive heat from a high-temperature source(solar-energy , oil furnace, nuclear reactor,etc..)
2. They convert part of this heat to work (usually in the form of a rotating shaft).

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3. They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).
4. They operate on a cycle.

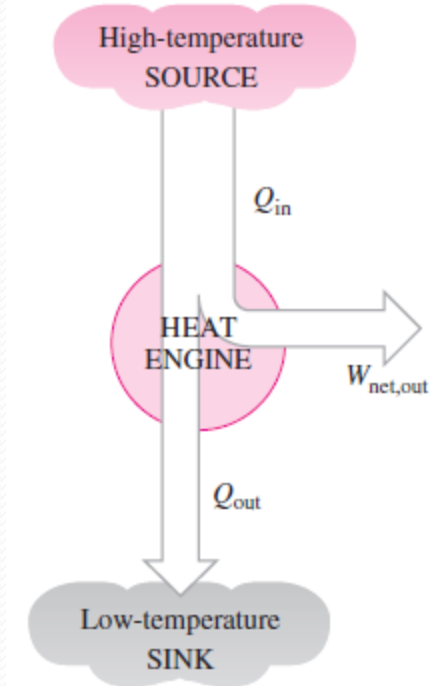


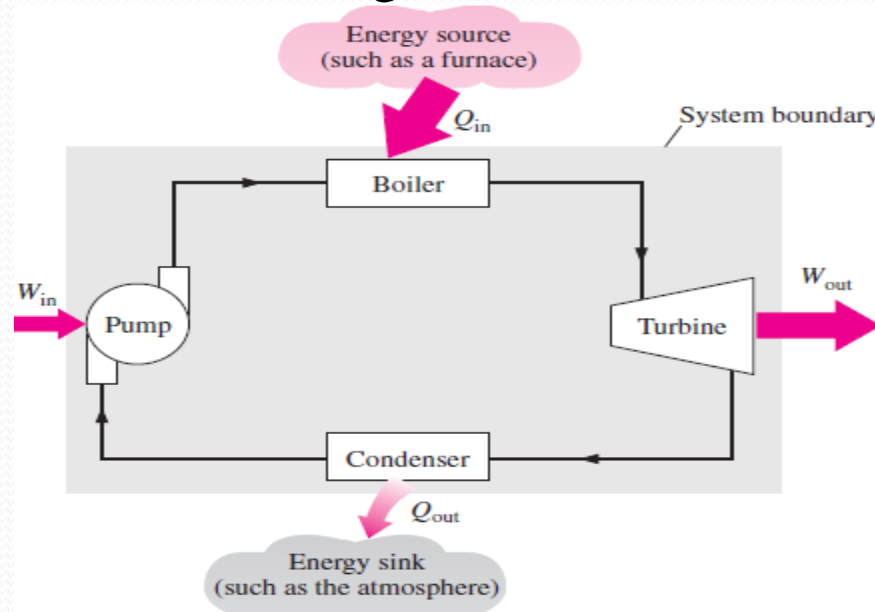
Fig. Part of the heat received by a heat engine is converted to work, while the rest is rejected to a sink.

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**.

Conti.

Heat engine is often use for work producing devices, such as, gas turbines, car engines etc.

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, combustion 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 in Fig. below.



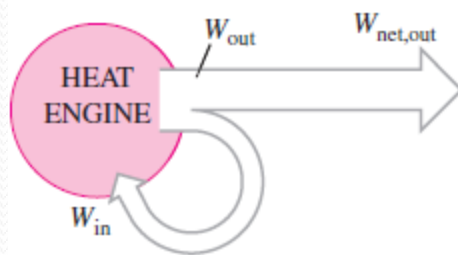
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The various quantities shown on this figure are as follows:

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

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

$$W_{net,out} = W_{out} - W_{in} \quad (\text{kJ})$$



A portion of the work output of a heat engine is consumed internally to maintain continuous operation.

Conti.

For the above steam power plant where no mass enters or leave this combination system which is indicated by dash by shaded area as shown in the fig. above.

this system can be analyzed as a closed system. Recall that 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:

$$W_{\text{net,out}} = Q_{\text{in}} - Q_{\text{out}} \quad (\text{kJ})$$

Thermal efficiency

In the above equation, 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**.

For heat engines, the desired output is the net work output, and the required input is the amount of heat supplied to the working fluid. Then the thermal efficiency of a heat engine can be expressed as

$$\text{Thermal efficiency} = \frac{\text{Net work output}}{\text{Total heat input}}$$

Conti.

Or

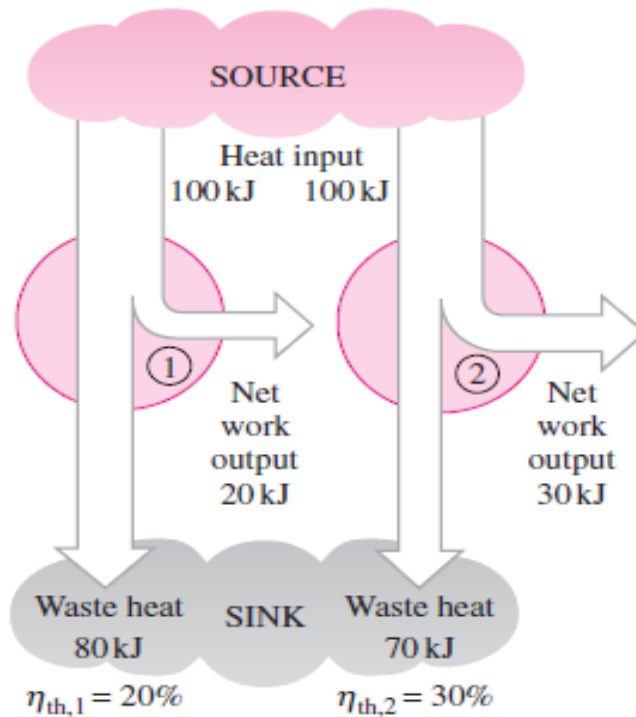
$$\eta_{th} = \frac{W_{net,out}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}}$$
$$= 1 - \frac{Q_{out}}{Q_{in}}$$

since

$$W_{net,out} = Q_{in} - Q_{out}$$

$< 100\%$

Conti.



Some heat engines perform better than others (convert more of the heat they receive to work).

Cyclic devices of practical interest 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 these two quantities:

Conti.

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

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

Then the net work output and thermal efficiency relations for any heat engine can also be expressed as

$$\eta_{th} = \frac{W_{net,out}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

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

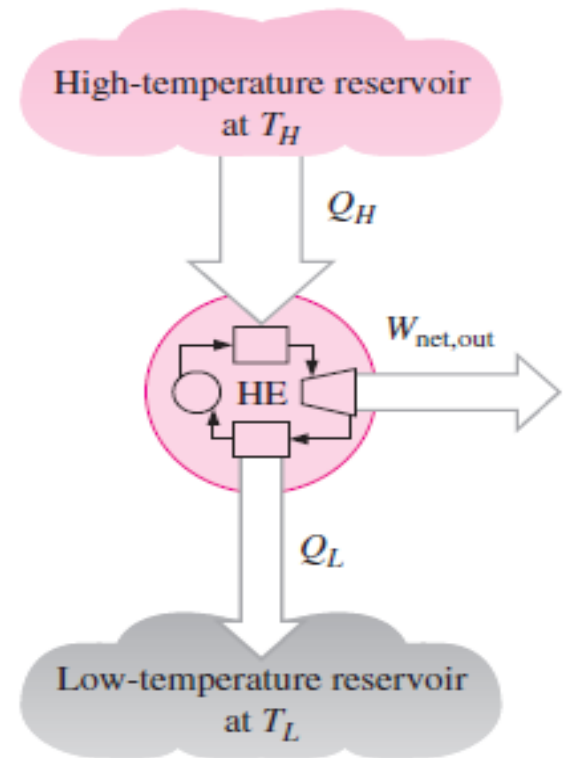


Fig.Schematic of a heat engine.

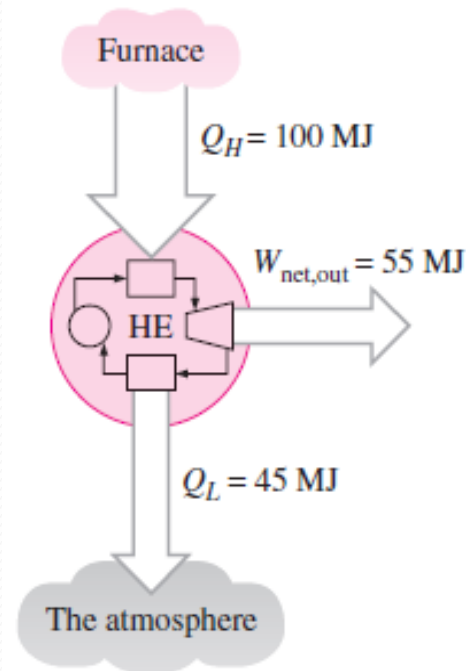
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Thermal efficiency is a measure of how efficiently a heat engine converts

the heat that it receives to work. Heat engines are built for the purpose of converting heat to work.

The thermal efficiencies of work-producing devices are relatively low.

- ✓ Automobile Engine 20%
- ✓ Diesel Engine 30%
- ✓ Gas Turbine 30%
- ✓ Steam Power Plant 40%



It's thermal efficiency is 4

Fig. most efficient heat engines reject almost one-half of the energy they receive as waste heat.

Example

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.

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

The net power output of this heat engine is

$$\dot{W}_{\text{net,out}} = \dot{Q}_H - \dot{Q}_L = (80 - 50) \text{ MW} = \mathbf{30 \text{ MW}}$$

Then the thermal efficiency is easily determined to be

$$\eta_{\text{th}} = \frac{\dot{W}_{\text{net,out}}}{\dot{Q}_H} = \frac{30 \text{ MW}}{80 \text{ MW}} = \mathbf{0.375} \text{ (or } 37.5\%)$$

Conti.

The Second Law of Thermodynamics: Kelvin-Planck Statement

A heat engine must reject some heat to a low-temperature reservoir in order to complete the cycle. That is, 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.

That is, a heat engine must exchange heat with a low-temperature sink as well as a high-temperature source to keep operating.

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

Conti.

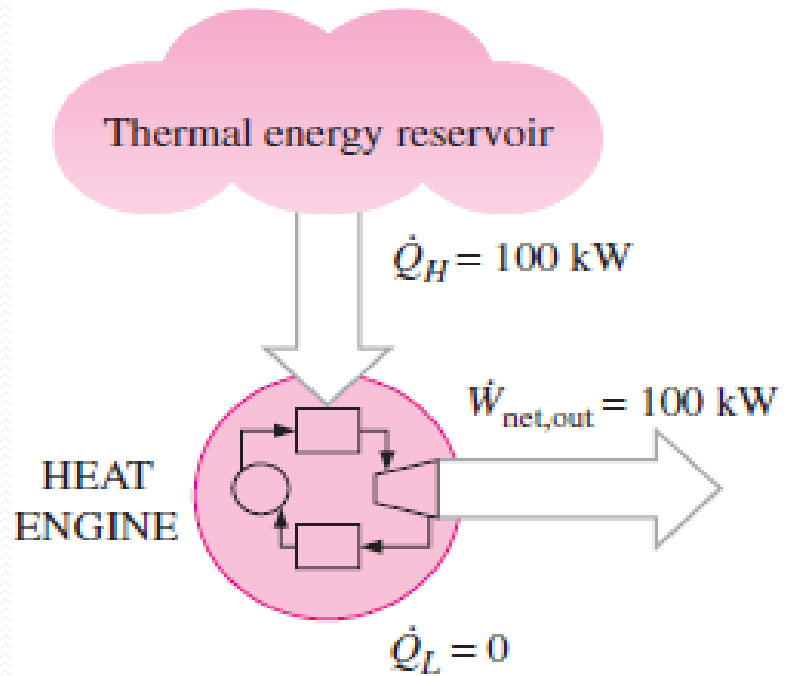


fig. A heat engine that violates the Kelvin–Planck statement of the second law.

REFRIGERATORS AND HEAT PUMPS

We all know from experience that heat is transferred in the direction of decreasing temperature, that is, 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 medium require special devices. This devices are called **refrigerators** and **heat pumps**.

Both these devices differ in their intended use.

Refrigerators

are cyclic devices. working fluid used is called a refrigerant
most frequently used refrigeration cycle is the Vapor-compression refrigeration cycle which involves four main components; a compressor, a condenser, an expansion and an evaporator.

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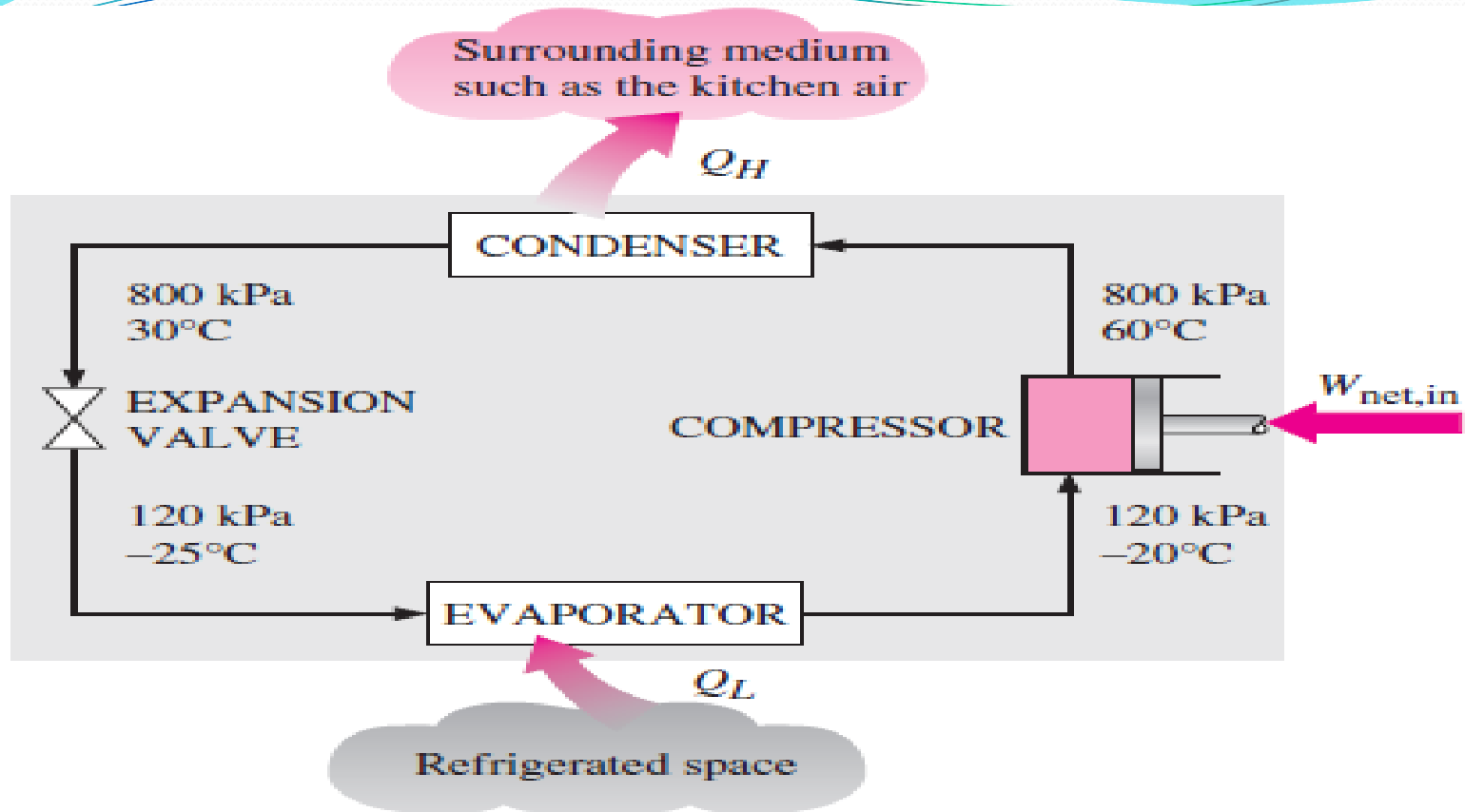


Fig. Basic components of a refrigeration system and typical operating conditions.

Conti.

Working principle of refrigerator

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.

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 $W_{\text{net,in}}$.

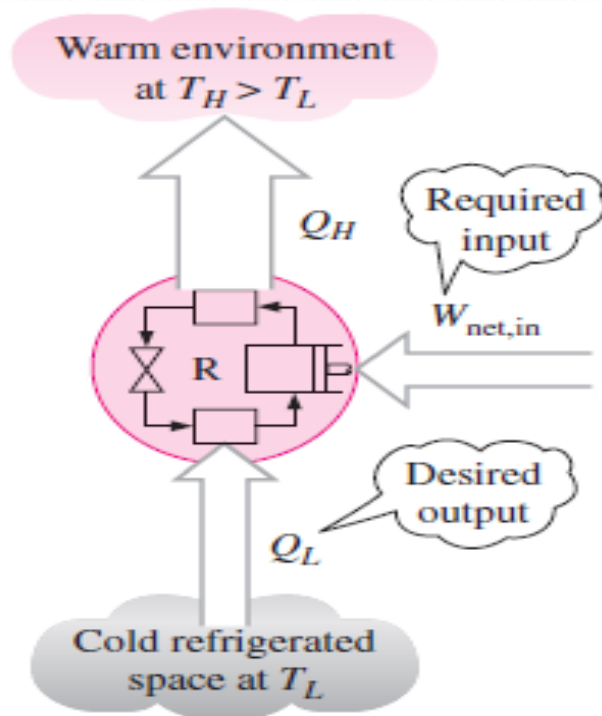


Fig. The objective of a refrigerator is to remove Q_L from the cooled space.

Conti.

Then the COP of a refrigerator can be expressed as

$$\begin{aligned} COP_R &= \frac{\text{Desired output}}{\text{Required input}} \\ &= \frac{Q_L}{W_{net,in}} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1} \end{aligned}$$

Notice that the value of COP_R 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**.

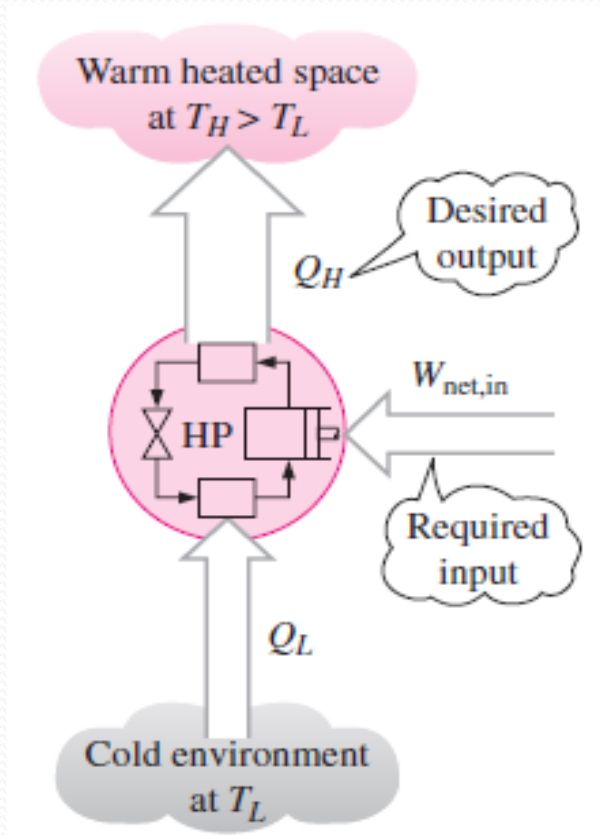


Fig. The objective of a heat pump is to Maintain heated space at high temperature i.e to supply heat Q_H into the warmer space.

Conti.

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

$$COP_{HP} = \frac{\text{Desired output}}{\text{Required input}}$$

$$= \frac{Q_H}{W_{net, in}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}}$$

Conti.

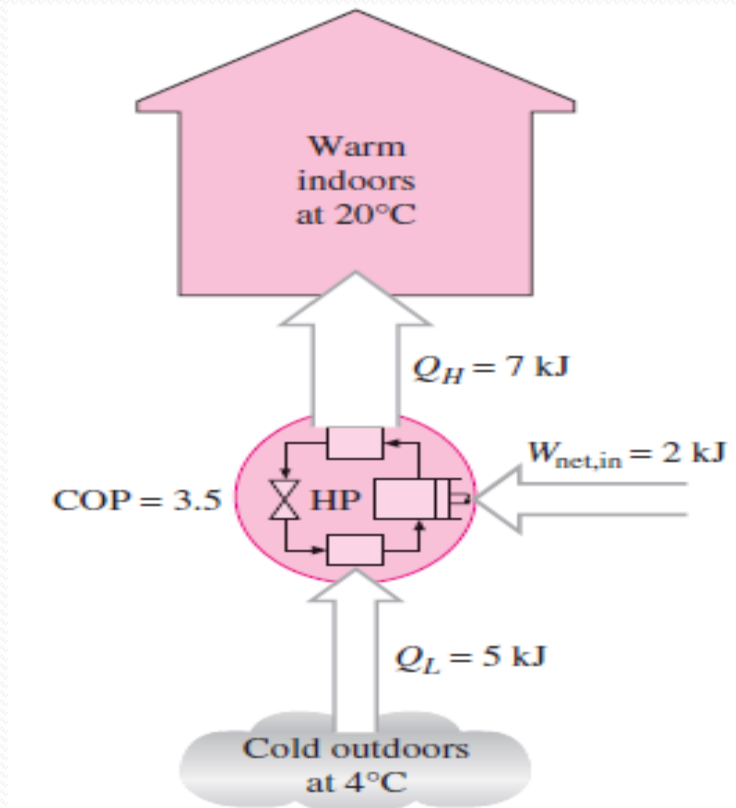
Relationship between Coefficient of Performance of a Refrigerator (COP_R) and a Heat Pump (COP_{HP}).

$$COP_{HP} = \frac{Q_H}{W_{net,in}} = \frac{Q_H}{Q_H - Q_L} = \frac{W_{net,in} + Q_L}{Q_H - Q_L}$$

$$COP_{HP} = \frac{W_{net,in}}{Q_H - Q_L} + \frac{Q_L}{Q_H - Q_L} = 1 + COP_R$$

$$COP_{HP} = 1 + COP_R$$

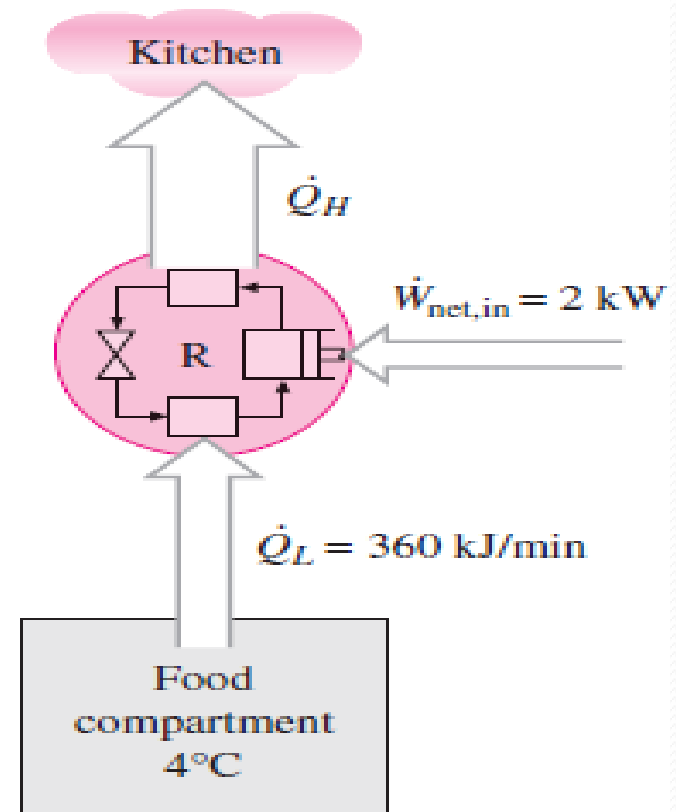
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The work supplied to a heat pump is used to extract energy from the cold outdoors and carry it into the warm indoors.

Example 1

The food compartment of a refrigerator, shown in fig., is maintained at 4°C by removing heat from it at a rate of 360 kJ/min . If the required power input to the refrigerator is 2 kW , determine (a) the coefficient of performance of the refrigerator and (b) the rate of heat rejection to the room that houses the refrigerator.



Solution

Solution The power consumption of a refrigerator is given. The COP and the rate of heat rejection are to be determined.

Assumptions Steady operating conditions exist.

Analysis (a) The coefficient of performance of the refrigerator is

$$\text{COP}_R = \frac{\dot{Q}_L}{\dot{W}_{\text{net,in}}} = \frac{360 \text{ kJ/min}}{2 \text{ kW}} \left(\frac{1 \text{ kW}}{60 \text{ kJ/min}} \right) = 3$$

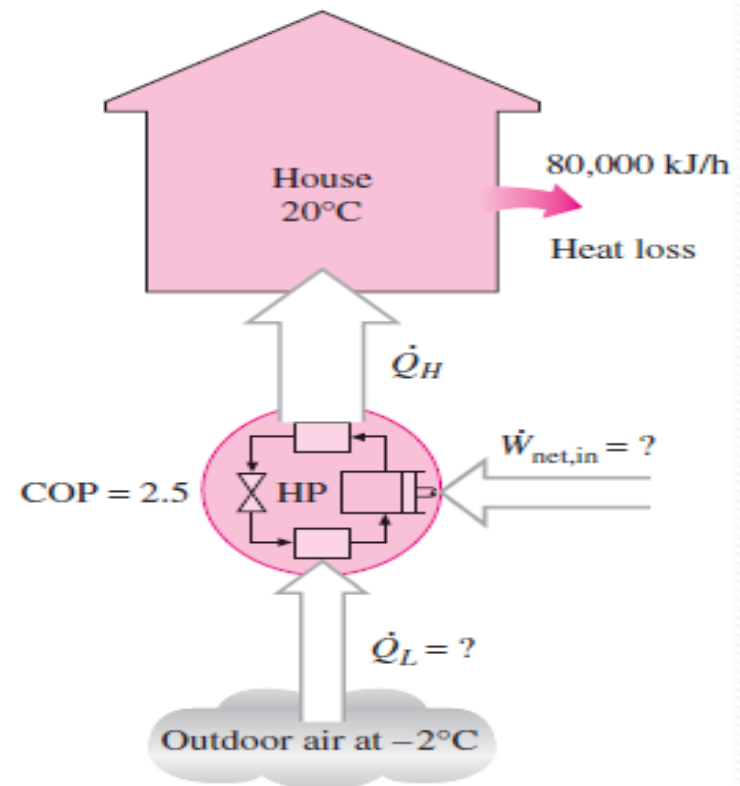
That is, 3 kJ of heat is removed from the refrigerated space for each kJ of work supplied.

(b) The rate at which heat is rejected to the room that houses the refrigerator is determined from the conservation of energy relation for cyclic devices,

$$\dot{Q}_H = \dot{Q}_L + \dot{W}_{\text{net,in}} = 360 \text{ kJ/min} + (2 \text{ kW}) \left(\frac{60 \text{ kJ/min}}{1 \text{ kW}} \right) = 480 \text{ kJ/min}$$

Example 2

A heat pump is used to meet the heating requirements of a house and maintain it at 20°C . On a day when the outdoor air temperature drops to 2°C , the house is estimated to lose heat at a rate of $80,000 \text{ kJ/h}$. If the heat pump under these conditions has a COP of 2.5, determine (a) the power consumed by the heat pump and (b) the rate at which heat is absorbed from the cold outdoor air.



(a) *The power consumed by this heat pump is determined from the definition of the coefficient of performance to be*

$$\dot{W}_{\text{net,in}} = \frac{\dot{Q}_H}{\text{COP}_{\text{HP}}} = \frac{80,000 \text{ kJ/h}}{2.5} = \mathbf{32,000 \text{ kJ/h}} \text{ (or 8.9 kW)}$$

(b) The house is losing heat at a rate of 80,000 kJ/h. If the house is to be maintained at a constant temperature of 20°C, the heat pump must deliver

heat to the house at the same rate, that is, at a rate of 80,000 kJ/h. The rate of heat transfer from the outdoor becomes

$$\dot{Q}_L = \dot{Q}_H - \dot{W}_{\text{net,in}} = (80,000 - 32,000) \text{ kJ/h} = \mathbf{48,000 \text{ kJ/h}}$$

Conti.

The second Law of Thermodynamics:

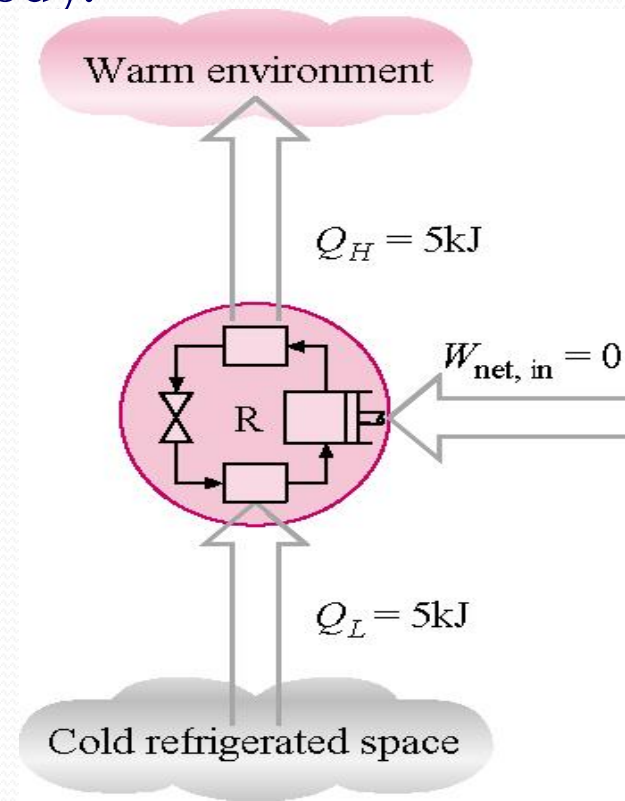
Clausius Statement

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 simply states that a refrigerator cannot 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.

A refrigerator that violates the Clausius statement of the second law.

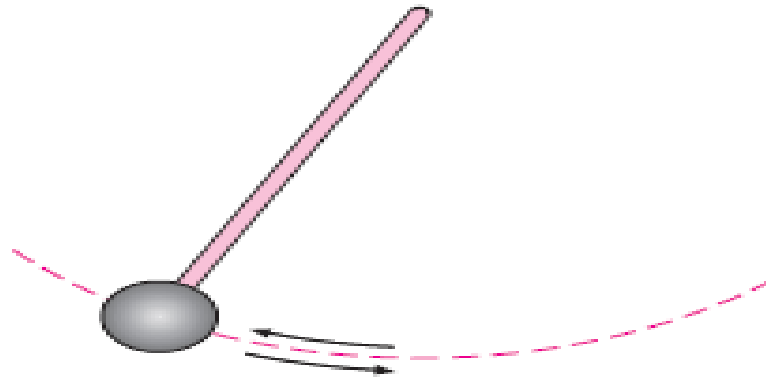


REVERSIBLE AND IRREVERSIBLE PROCESSES

The second law of thermodynamics states that no heat engine can have an efficiency of 100 percent. Then one may ask, 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*.

A **reversible process** is defined as a process that can be reversed without leaving any trace on the surroundings (Fig. below). 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**.

Conti.



(a) Frictionless pendulum



(b) Quasi-equilibrium expansion and compression of a gas

Fig. Two familiar reversible processes.

Conti.

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 does not return to their original state.

Conti.

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.

Conti.

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 can 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.

Conti.

The concept of reversible processes leads to the definition of the 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.

The factors that cause a process to be irreversible are called **irreversibilities**. They include friction, unrestrained expansion, mixing of two fluids, 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.

Internally and Externally Reversible Processes

A typical process involves interactions 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.

A process is called **externally reversible** if **no irreversibilities occur outside** the system boundaries during the process.

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

Conti.

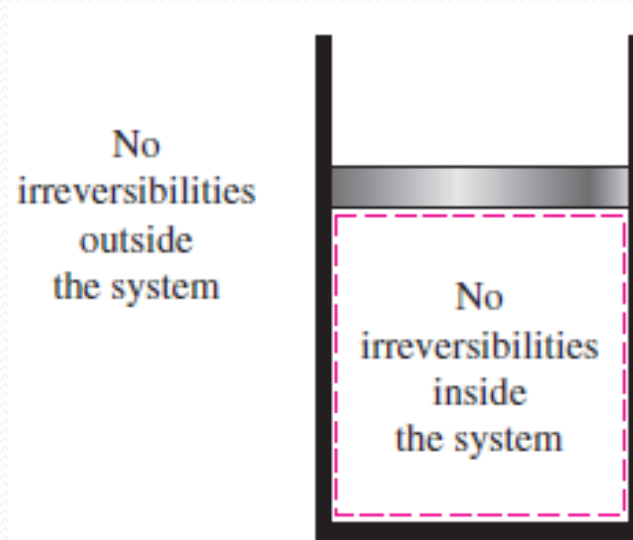


Fig. A reversible process involves no internal and external irreversibilities

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, that is, 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 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—and it can be executed either in a closed or a steady-flow system.

Conti.

Consider a closed system that consists of a gas contained in an adiabatic piston–cylinder device, as shown in Fig. 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. The four reversible processes that make up the Carnot cycle are as follows:

Conti.

Reversible Isothermal Expansion (process 1-2, $T_H = \text{constant}$). 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 is transferred 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 .

Conti.

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.

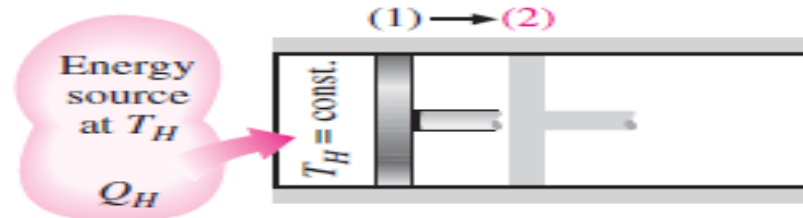
Reversible Isothermal Compression (process 3-4, $T_L = \text{constant}$). At state 3, the insulation at the cylinder head is removed, and the cylinder is brought into contact with a sink at temperature T_L . Now the piston is pushed inward by an external force, doing work on the gas. As the gas is compressed, its temperature tends to rise. But as soon as it rises by an infinitesimal amount dT , heat is transferred from the gas to the sink, causing the gas temperature to drop to T_L . Thus, the gas temperature remains constant at T_L . Since the temperature difference between the gas and the sink never exceeds a differential amount dT , this is a reversible

Conti.

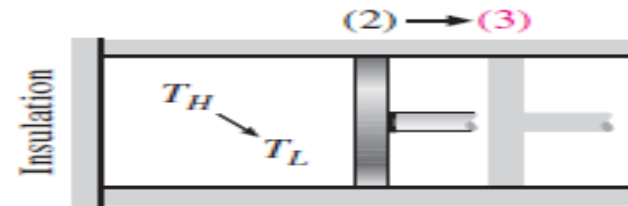
heat transfer process. It continues until the piston reaches state 4. The amount of heat rejected from the gas during this process is Q_L .

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, 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.

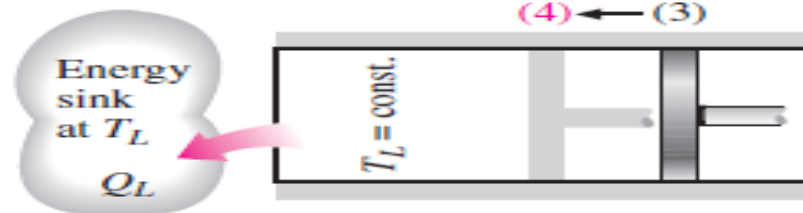
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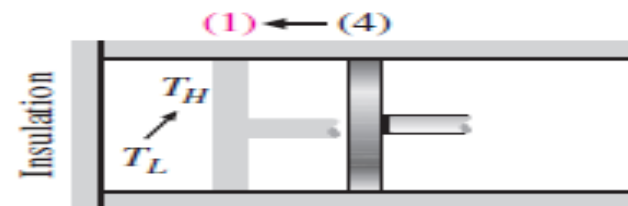
(a) Process 1-2



(b) Process 2-3



(c) Process 3-4



(d) Process 4-1

Execution of the Carnot cycle in a closed system.

Conti.

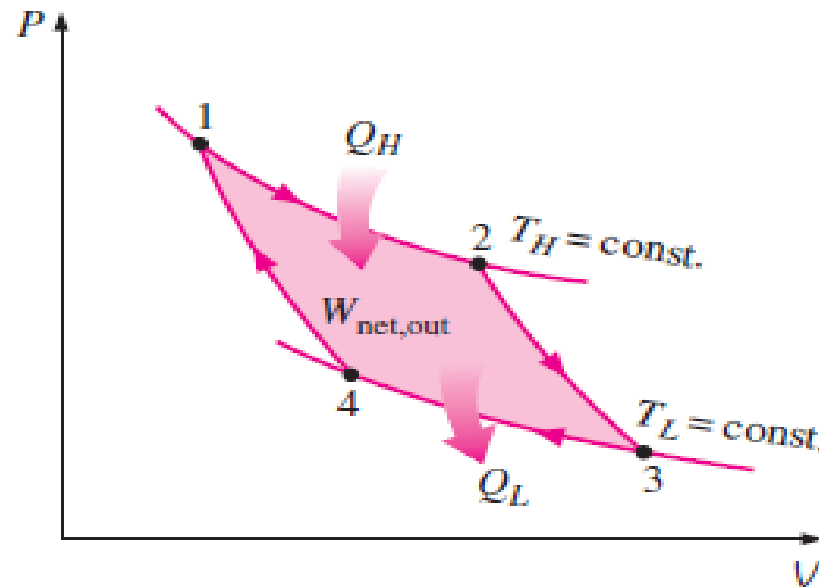


Fig. P-V diagram of the Carnot cycle

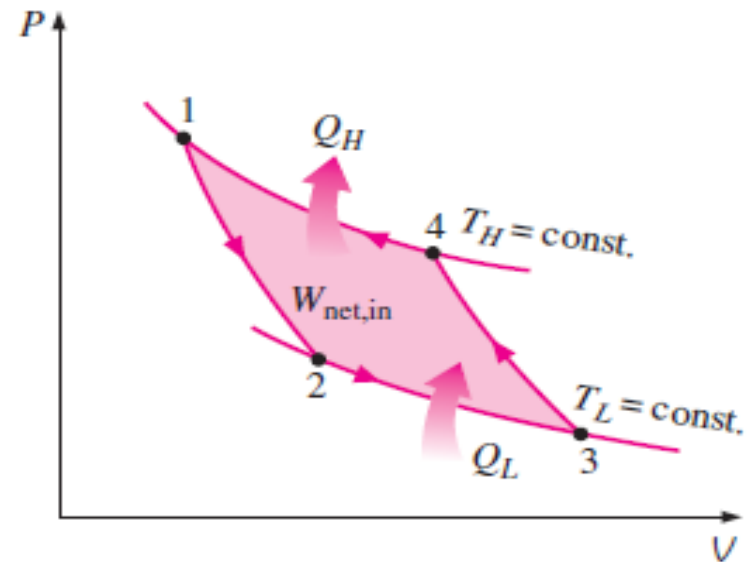


Fig. P-V diagram of the reversed Carnot cycle.

THE CARNOT PRINCIPLES

The second law of thermodynamics puts limits 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 heat reservoir, and a refrigerator cannot operate without net work input from an external source.

Consider heat engines operating between two fixed temperature reservoirs at $T_H > T_L$. We draw two conclusions about the thermal efficiency of reversible and irreversible heat engines, known as the Carnot principles and are expressed as follow;

Conti.

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.

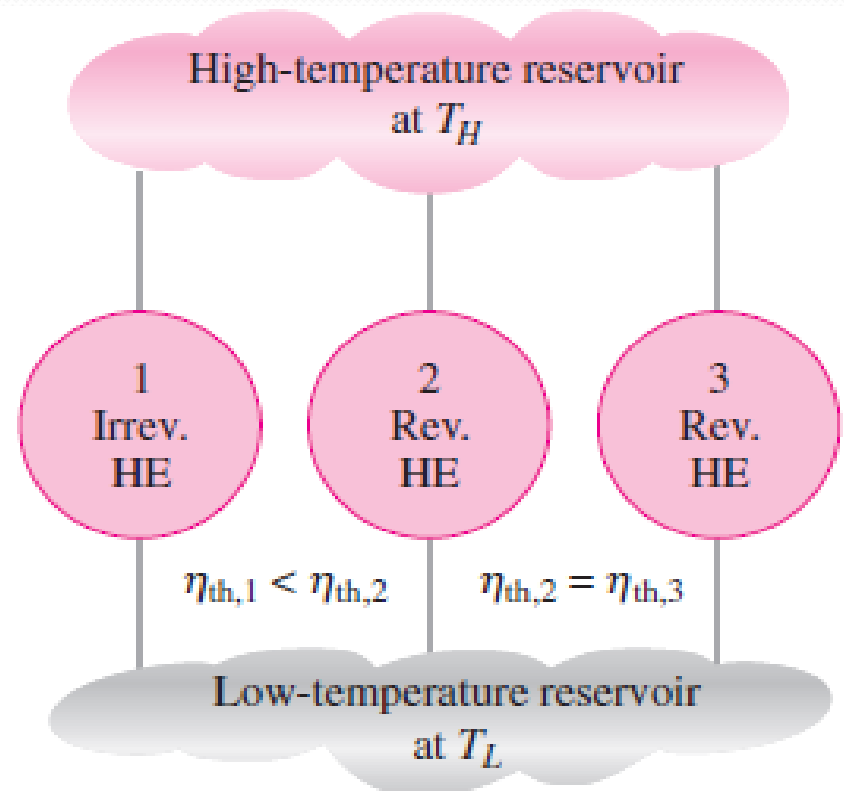


Fig. The Carnot principles.

Conti.

As the result of the above, Lord Kelvin in 1848 used energy as a thermodynamic property to define temperature and devised a temperature scale that is independent of the properties of thermodynamic substance is called thermodynamic temperature scale.

The arrangement of heat engines used to develop the thermodynamic temperature scale

Conti.

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,

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

$$\frac{Q_H}{Q_L} = f(T_H, T_L)$$

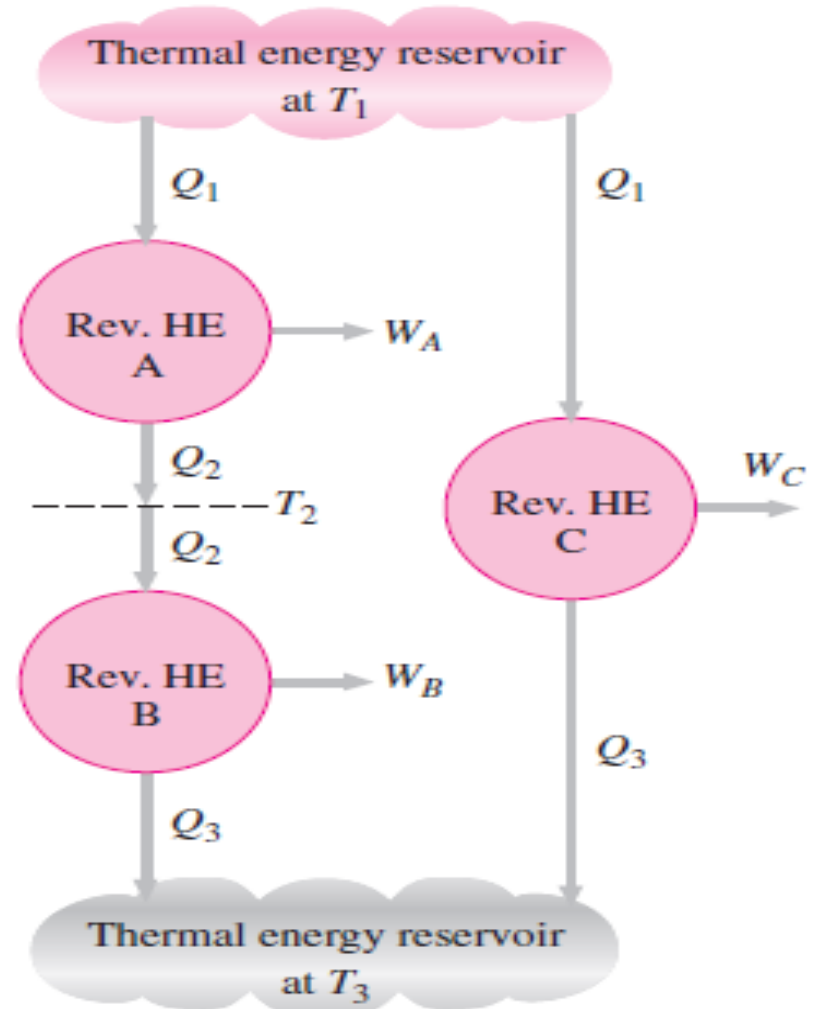


Fig. The arrangement of heat engines used to develop the thermodynamic temperature scale.

Conti.

since $\eta_{\text{th}} = 1 - Q_L/Q_H$. In these relations T_H and T_L are the temperatures of the high- and low-temperature reservoirs, respectively.

The functional form of $f(T_H, T_L)$ can be developed with the help of the three reversible heat engines shown in Fig. . . . 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

Conti.

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. 4.60 to all three engines separately, we obtain

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

Now consider the identity

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

which corresponds to

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

Conti.

A careful examination of this equation reveals that the left-hand side is a function of T_1 and T_3 , and therefore the right-hand side must also be a function of T_1 and 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:

$$f(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)} \quad \text{and} \quad f(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$$

so that $\phi(T_2)$ will cancel from the product of $f(T_1, T_2)$ and $f(T_2, T_3)$, yielding

$$\frac{Q_1}{Q_3} = f(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_3)}$$

Conti.

For a reversible heat engine operating between two reservoirs at temperatures T_H and T_L , can be written as

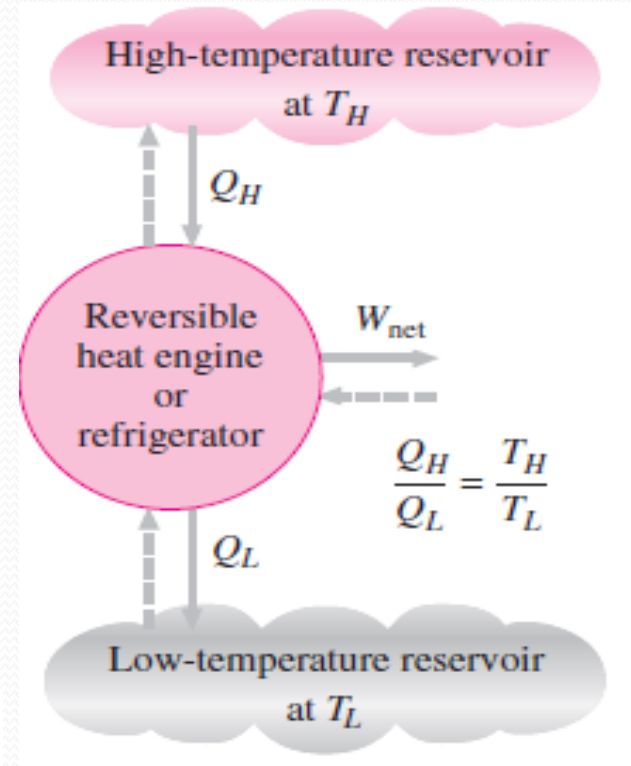
$$\frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)}$$

This is the only requirement that the second law places on the ratio of heat transfers to and from the reversible heat engines. Several functions $\phi(T)$ satisfy this equation, and the choice is completely arbitrary. Lord Kelvin first proposed taking $\phi(T) = T$ to define a thermodynamic temperature scale as

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

Conti.

For reversible cycles, the heat transfer ratio Q_H/Q_L can be replaced by the absolute temperature ratio T_H/T_L .





Perpetual Motion Machines

- Any device that violates the first or second law is called a perpetual motion machine
- If it violates the first law, it is a perpetual motion machine of the first type (PMM₁)
- If it violates the second law, it is a perpetual motion machine of the second type (PMM₂)
- Perpetual Motion Machines are not possible

Conti.

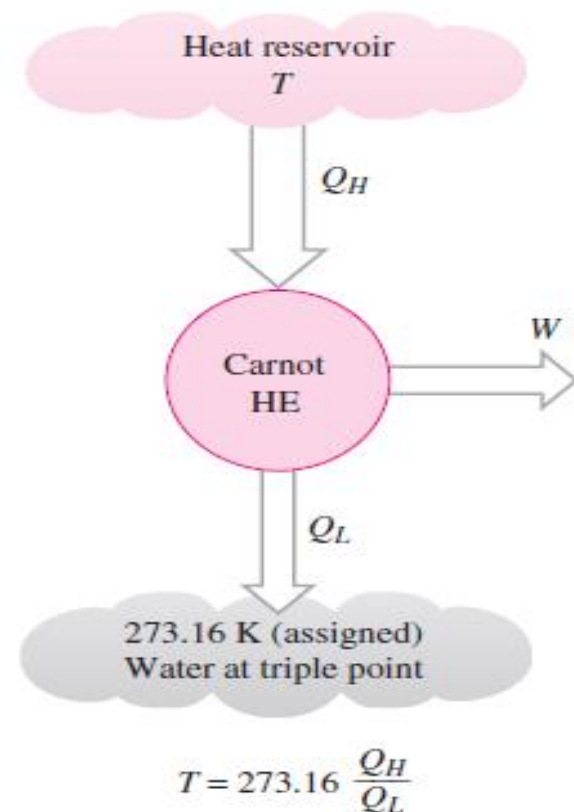
This temperature scale is called the Kelvin scale, and the temperatures on this scale are called absolute temperatures. On the Kelvin scale, the temperature ratios depend on the ratios of heat transfer between a reversible heat engine and the reservoirs and are independent of the physical properties of any substance. On this scale, temperatures vary between zero and infinity. The thermodynamic temperature scale is not completely defined by Eq. above, since it gives us only a ratio of absolute temperatures. We also need to know the magnitude of a kelvin. 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 (Fig. below).

Conti.

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 ($1 \text{ K} \equiv 1^\circ\text{C}$). The temperatures on these two scales differ by a constant 273.15:

$$T(^{\circ}\text{C}) = T(\text{K}) - 273.15$$

A conceptual experimental setup to determine thermodynamic temperatures on the Kelvin scale by measuring heat transfers Q_H and Q_L .



THE CARNOT HEAT ENGINE

The hypothetical heat engine that operates on the reversible Carnot cycle is called the **Carnot heat engine**. The thermal efficiency of any heat engine, reversible or irreversible, is given by

$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

For reversible heat engines, the heat transfer ratio in the above relation can be replaced by the ratio of the absolute temperatures of the two reservoirs, as given by previous equation. Then the efficiency of a Carnot engine, or any reversible heat engine, becomes

$$\eta_{th,rev} = 1 - \frac{T_L}{T_H}$$

(this equation often referred as Carnot efficiency)

This relation is often referred to as the **Carnot efficiency**, since the Carnot heat engine is the best known reversible engine. This is the highest efficiency a heat engine operating between the two thermal energy reservoirs at temperatures T_L and T_H can have. All irreversible (i.e., actual) heat engines operating between these temperature limits (T_L and T_H) have lower efficiencies.

An actual heat engine cannot reach this maximum theoretical efficiency value because it is impossible to completely eliminate all the irreversibilities associated with the actual cycle.

Here T_L and T_H are in absolute temperatures.

Conti.

The thermal efficiencies of actual and reversible heat engines operating between the same temperature limits compare as follows

$$\eta_{th} \begin{cases} < \eta_{th,rev} & \text{irreversible heat engine} \\ = \eta_{th,rev} & \text{reversible heat engine} \\ > \eta_{th,rev} & \text{impossible heat engine} \end{cases}$$

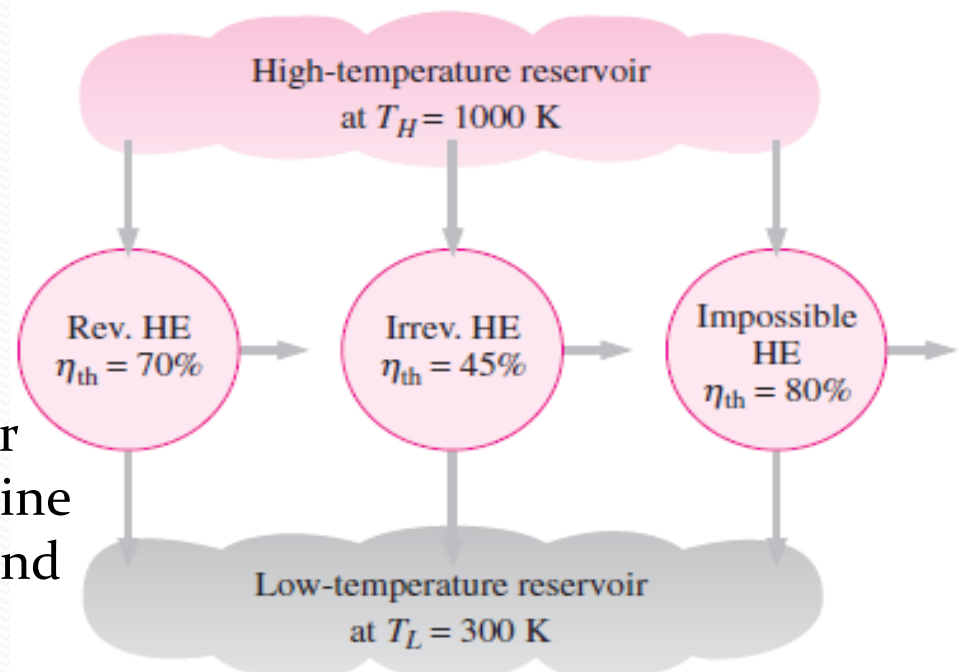
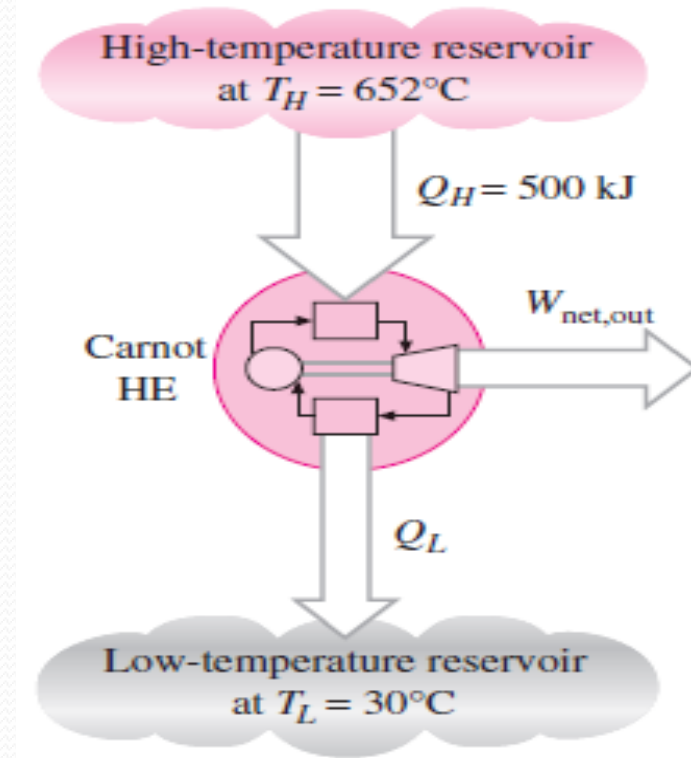


Fig. No heat engine can have a higher efficiency than a reversible heat engine operating between the same high- and low-temperature reservoirs.

example

A Carnot heat engine, shown in Fig. below, 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.



THE CARNOT REFRIGERATOR AND HEAT PUMP

A refrigerator or a heat pump that operates on the reversed Carnot cycle is called a **Carnot refrigerator**, or a **Carnot heat pump**. The coefficient of performance of any refrigerator or heat pump, reversible or irreversible, is given by

$$\text{COP}_R = \frac{1}{Q_H/Q_L - 1} \quad \text{and} \quad \text{COP}_{HP} = \frac{1}{1 - Q_L/Q_H}$$

The COPs of all reversible refrigerators or heat pumps can be determined by replacing the heat transfer ratios in the above relations by the ratios of the absolute temperatures of the high- and low-temperature reservoirs. Then the COP relations for reversible refrigerators and heat pumps become

$$\text{COP}_{R,\text{rev}} = \frac{1}{T_H/T_L - 1}$$

$$\text{COP}_{HP,\text{rev}} = \frac{1}{1 - T_L/T_H}$$

Conti.

These are the highest coefficients of performance that a refrigerator or a heat pump operating between the temperature limits of T_L and T_H can have. All actual refrigerators or heat pumps operating between these temperature limits (T_L and T_H) have lower coefficients of performance (Fig. below).

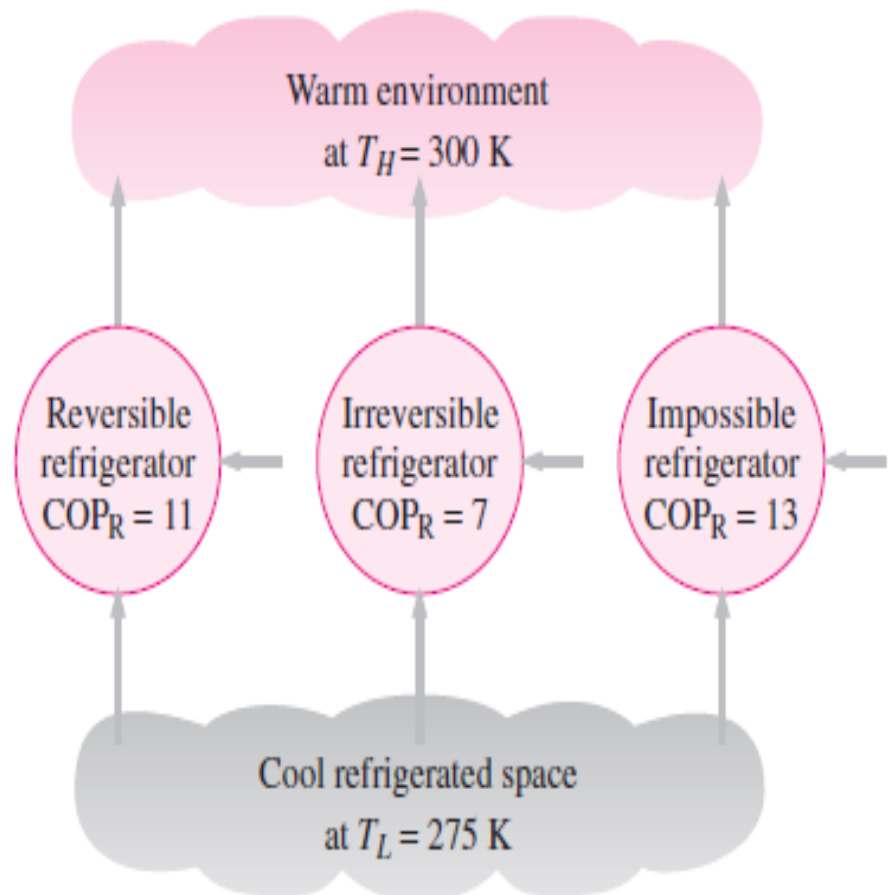


Fig. No refrigerator can have a higher COP than a reversible refrigerator operating between the same temperature limits.

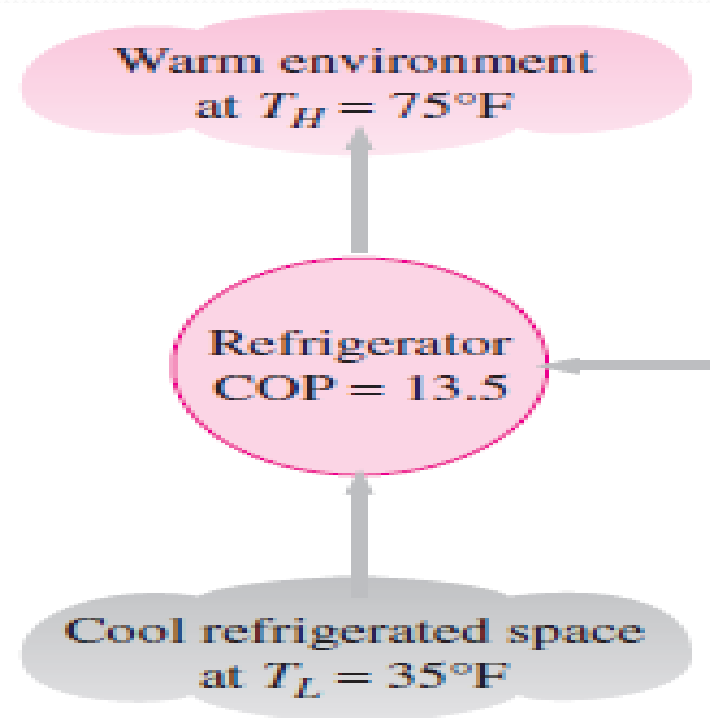
Conti.

The coefficients of performance of actual and reversible refrigerators operating between the same temperature limits can be compared as follows:

$$\text{COP}_R \begin{cases} < \text{COP}_{R,\text{rev}} & \text{irreversible refrigerator} \\ = \text{COP}_{R,\text{rev}} & \text{reversible refrigerator} \\ > \text{COP}_{R,\text{rev}} & \text{impossible refrigerator} \end{cases} \quad (6-22)$$

example

An inventor claims to have developed a refrigerator that maintains the refrigerated space at 35°F while operating in a room where the temperature is 75°F and that has a COP of 13.5. Is this claim reasonable?



Conti.

A heat pump is to be used to heat a house during the winter, as shown in Fig. 6–53. The house is to be maintained at 21°C at all times. The house is estimated to be losing heat at a rate of $135,000\text{ kJ/h}$ when the outside temperature drops to -5°C . Determine the minimum power required to drive this heat pump.

