Thermodynamics: An Engineering Approach, 5^{th} Edition
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McGraw-Hill, 2008

Chapter 6

The SECOND LAW OF THERMODYNAMICS

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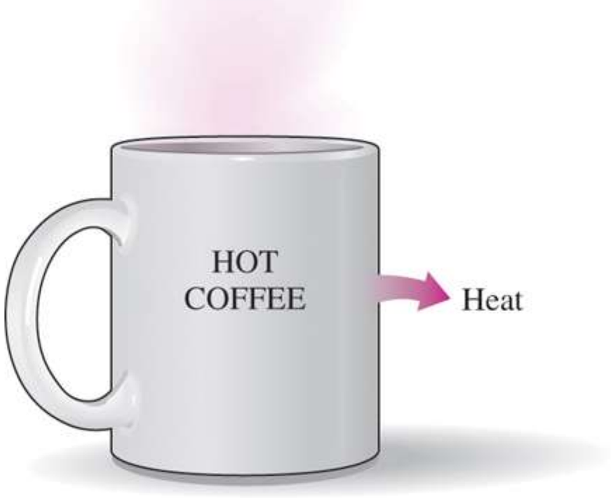
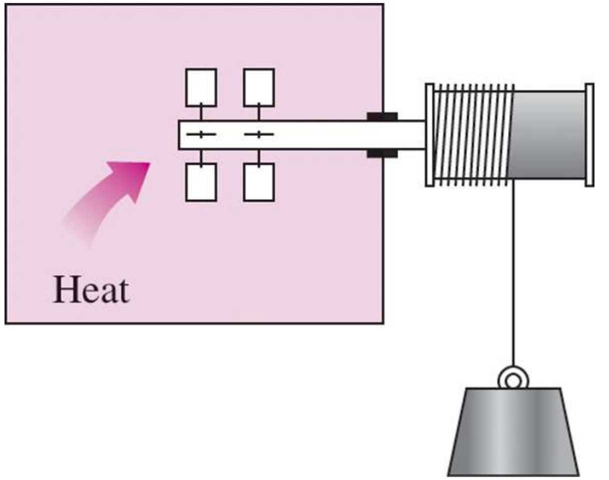
Objectives

- Introduce the second law of thermodynamics.
- Identify valid processes as those that satisfy both the first and second laws of thermodynamics.
- Discuss thermal energy reservoirs, reversible and irreversible processes, heat engines, refrigerators, and heat pumps.
- Describe the Kelvin–Planck and Clausius statements of the second law of thermodynamics.
- Apply the second law of thermodynamics to cycles and cyclic devices.
- Apply the second law to develop the absolute thermodynamic temperature scale.
- Describe the Carnot cycle.
- Examine the Carnot principles, idealized Carnot heat engines, refrigerators, and heat pumps.
- Determine the expressions for the thermal efficiencies and coefficients of performance for reversible heat engines, heat pumps, and refrigerators.

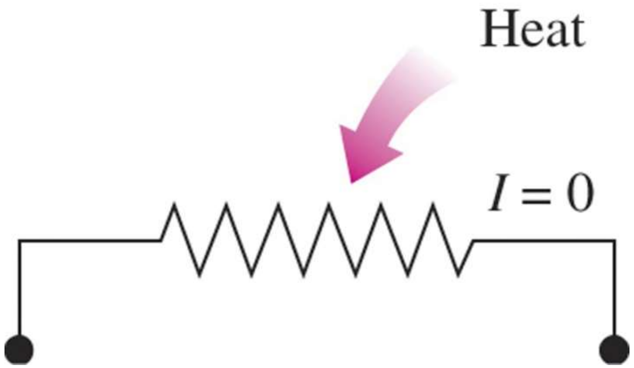
INTRODUCTION TO THE SECOND LAW

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





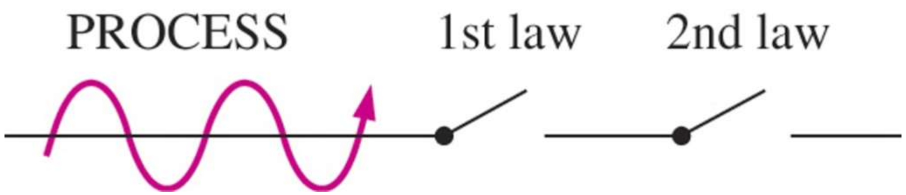
Transferring heat to a paddle wheel will not cause it to rotate.



Transferring heat to a wire will not generate electricity.

These processes cannot occur even though they are not in violation of the first law.

Processes occur in a certain direction, and not in the reverse direction.

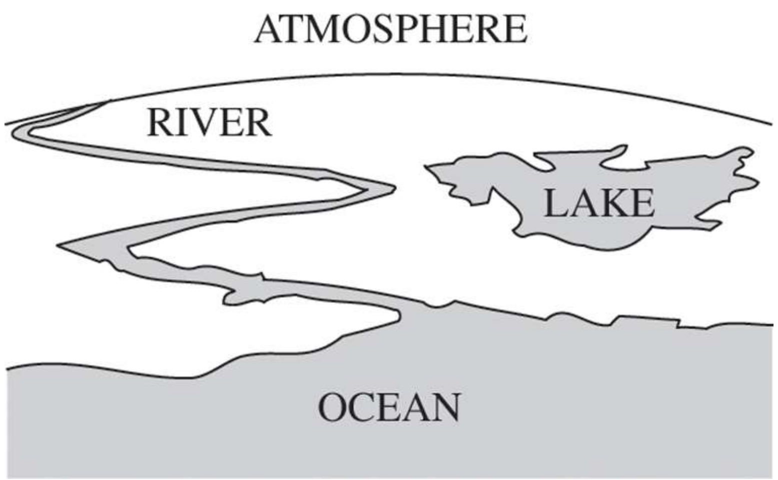


A process must satisfy both the first and second laws of thermodynamics to proceed.

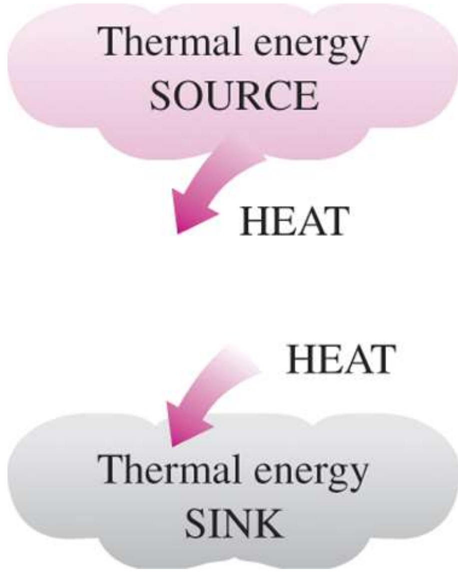
MAJOR USES OF THE SECOND LAW

1. The second law may be used to identify the direction of processes.
2. The second law also asserts that energy has *quality* as well as quantity. The first law is concerned with the quantity of energy and the transformations of energy from one form to another with no regard to its quality. The second law provides the necessary means to determine the quality as well as the degree of degradation of energy during a process.
3. 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.

THERMAL ENERGY RESERVOIRS



Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.



A source supplies energy in the form of heat, and a sink absorbs it.

- 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 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.

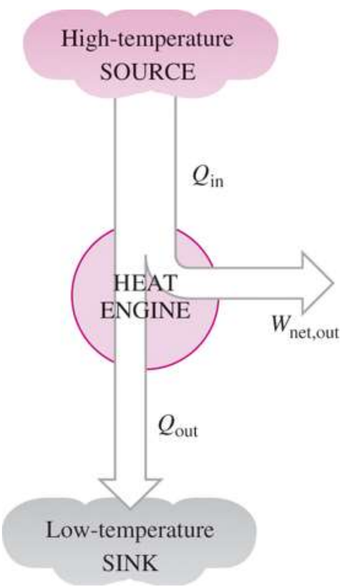
HEAT ENGINES

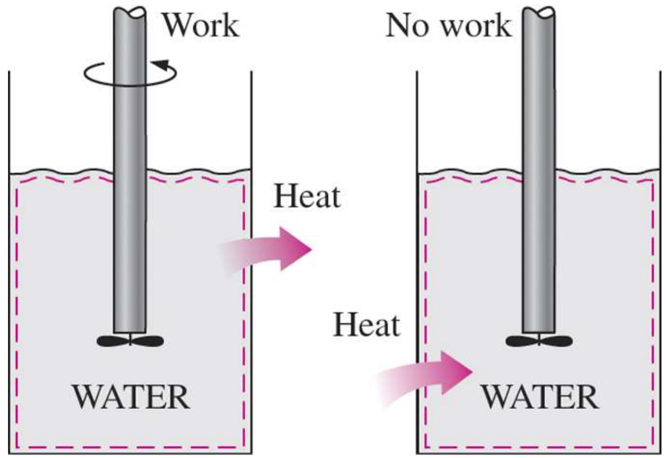
The devices that convert heat to work.

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

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

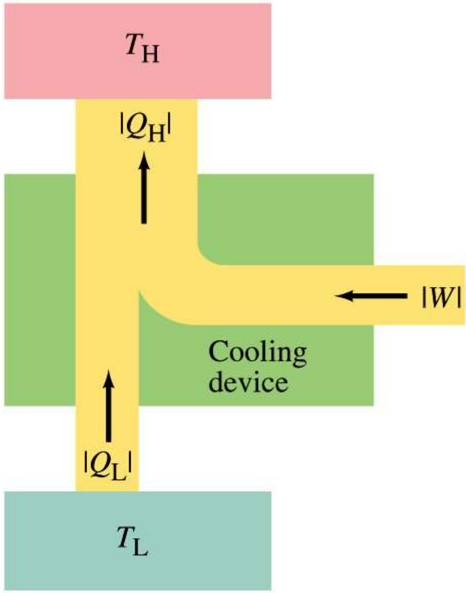




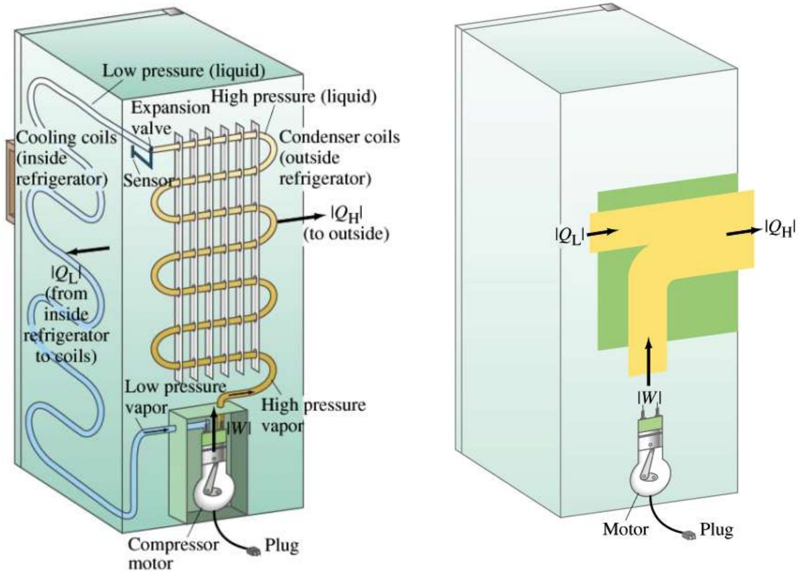
Work can always be converted to heat directly and completely, but the reverse is not true.

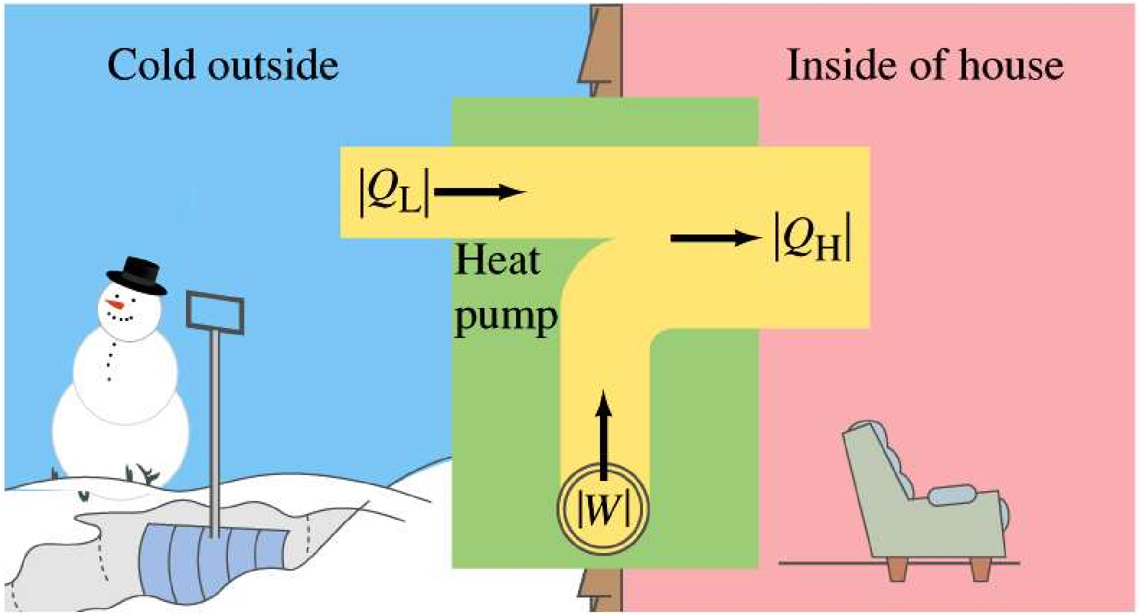
Heat Pump

You cannot get cool the home opening the refrigarator door.

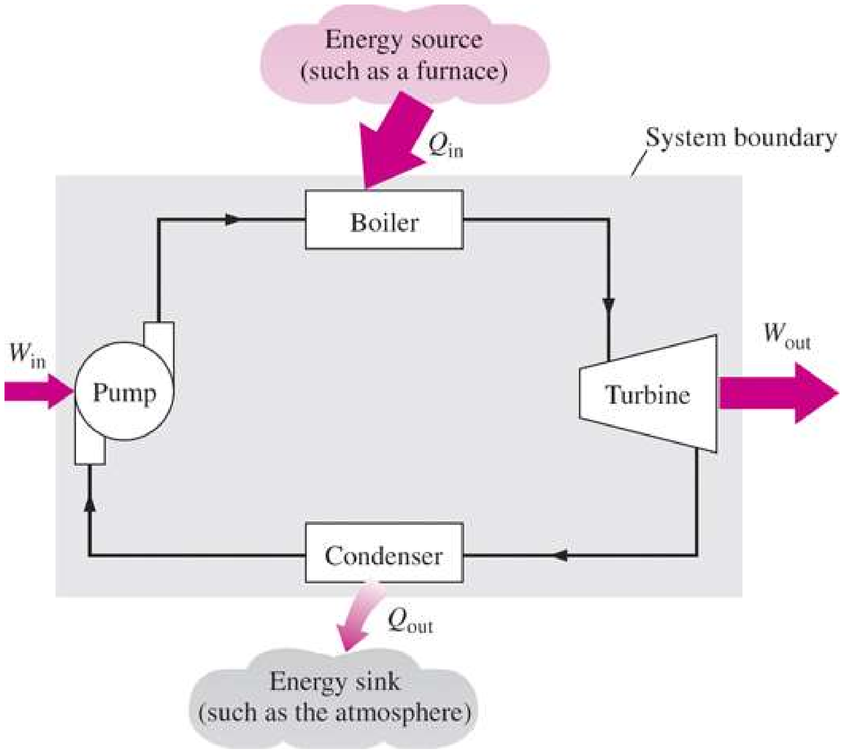


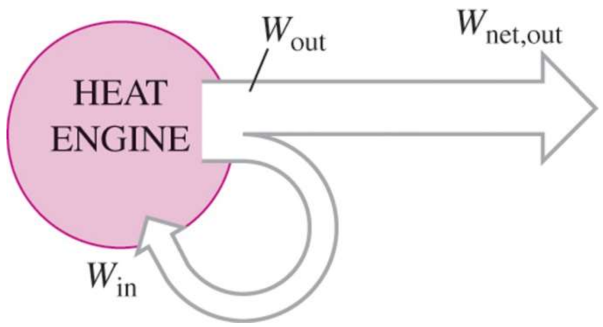
We just pay for the work not the heat absorbing.





A steam power plant





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

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

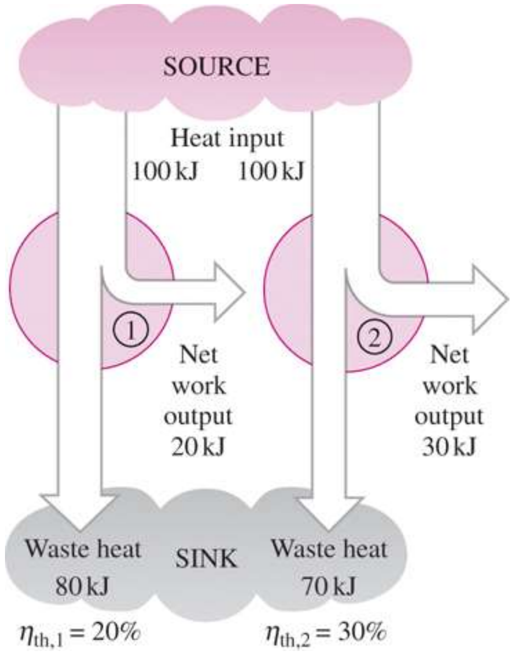
$$W_{net,\,out} = Q_{in} - Q_{out} \qquad (kJ)$$

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

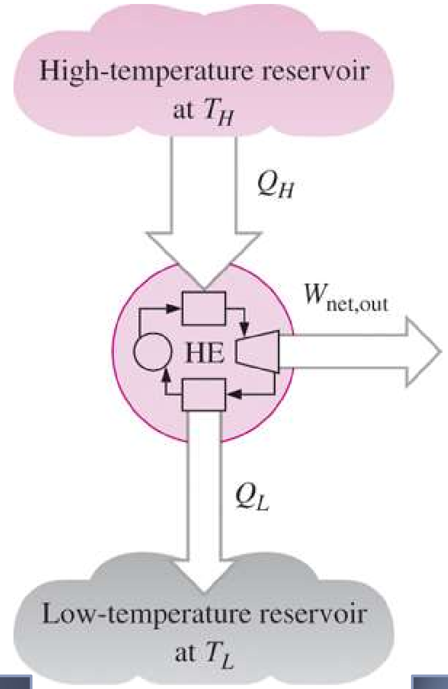
Thermal efficiency

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** η_{th}

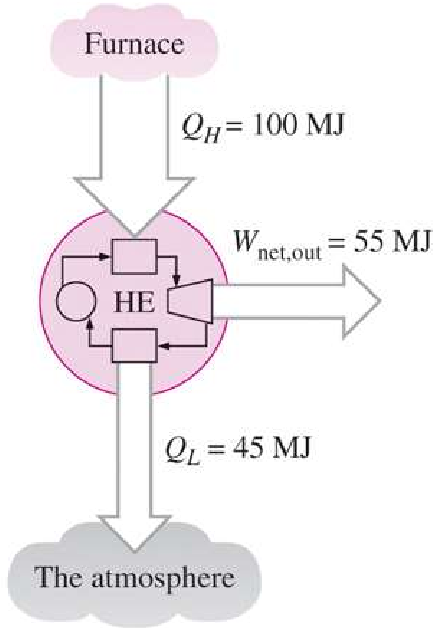
$$\text{Thermal efficiency} = \frac{\text{Net work output}}{\text{Total heat input}}$$



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



Schematic of a heat engine.



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

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

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

$$W_{net,out} = Q_H - Q_L$$

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

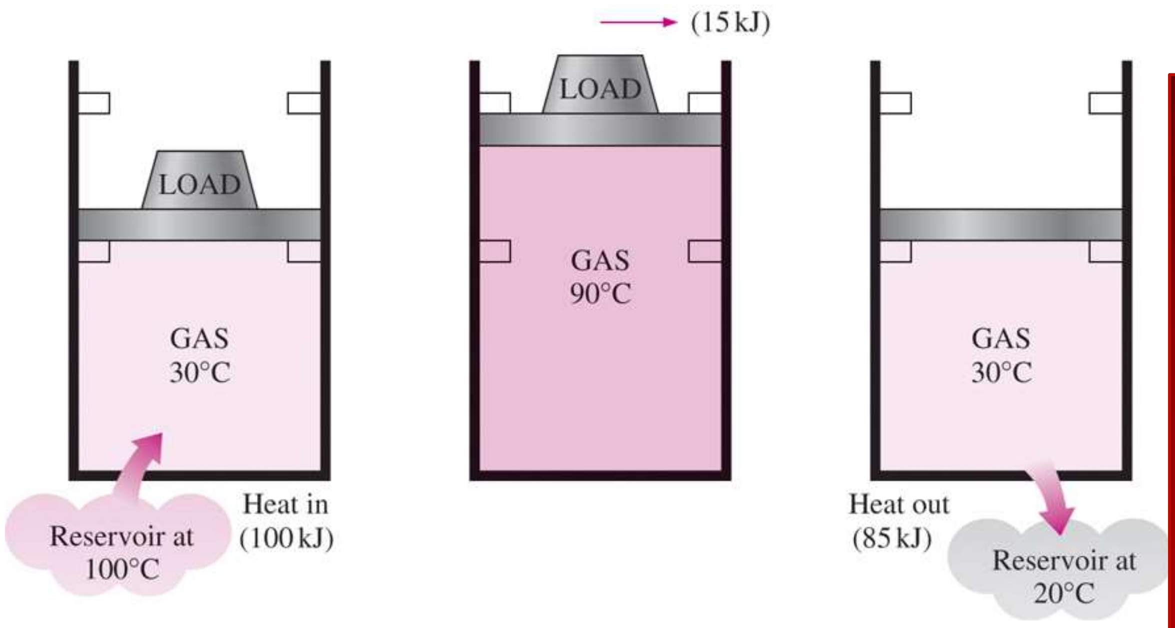
$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

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

Ordinary spark-ignition automobile engines have a thermal efficiency of about 25 percent. That is, an automobile engine converts about 25 percent of the chemical energy of **the gasoline** to mechanical work.

This number is as high as 40 percent for **diesel engines** and large gas-turbine plants and as high as 60 percent for large **combined gas-steam** power plants.

Can we save Q_{out}?



A heat-engine cycle cannot be completed without rejecting some heat to a low-temperature sink.

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.

In a steam power plant, the condenser is the device where large quantities of waste heat is rejected to rivers, lakes, or the atmosphere.

Can we not just take the condenser out of the plant and save all that waste energy?

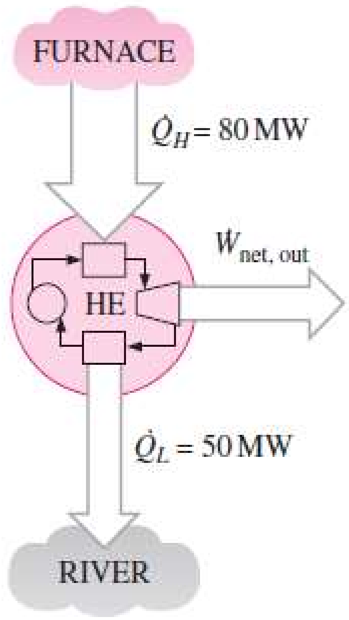
The answer is, unfortunately, a firm ***no*** for the simple reason that without a heat rejection process in a condenser, the cycle cannot be completed.

Example 6-1

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 The rates of heat transfer to and from a heat engine are given. The net power output and the thermal efficiency are to be determined.

Assumptions Heat losses through the pipes and other components are negligible.



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

The net power output of this heat engine is

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

Then the thermal efficiency is

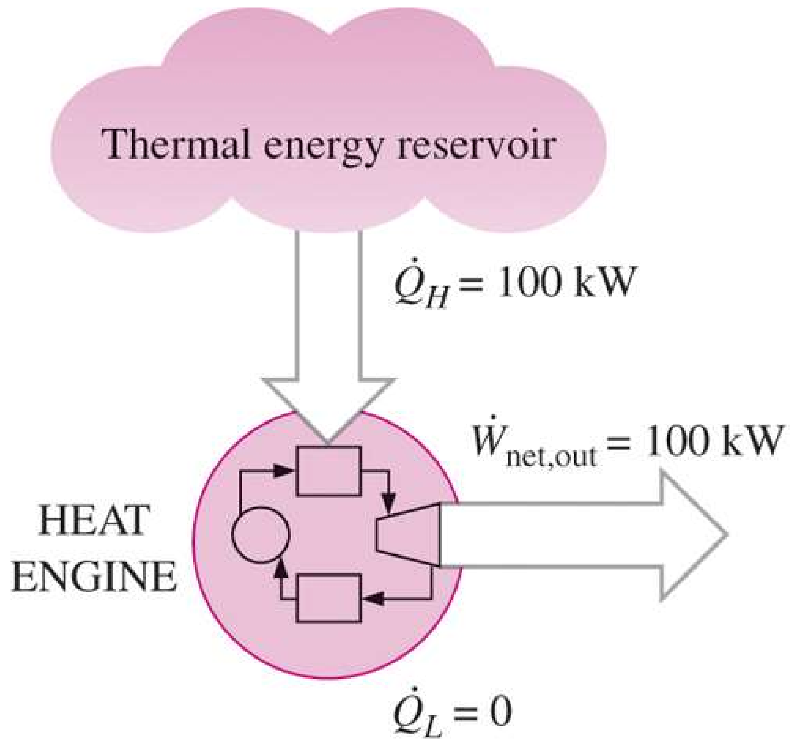
$$\eta_{\text{th}} = \frac{\dot{W}_{\text{net, out}}}{\dot{Q}_H} = \frac{30\ \text{MW}}{80\ \text{MW}} = \mathbf{0.375}\ (\text{or } 37.5\%)$$

Discussion Note that the heat engine converts 37.5 percent of the heat it receives to work.

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.

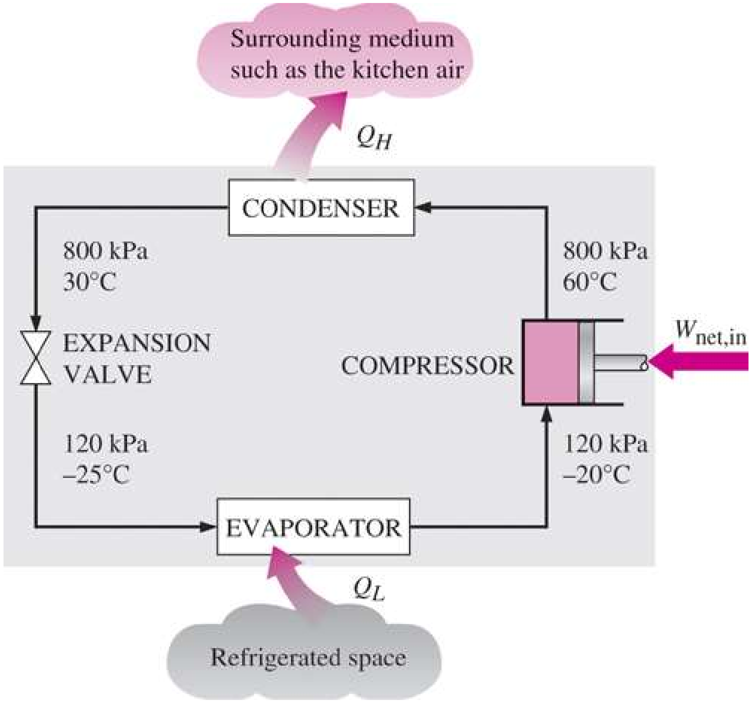
No heat engine can have a thermal efficiency of 100 percent, or as for a *power plant to operate, the working fluid must exchange heat with the environment as well as the furnace*.

The impossibility of having a 100% 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.



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

REFRIGERATORS AND HEAT PUMPS

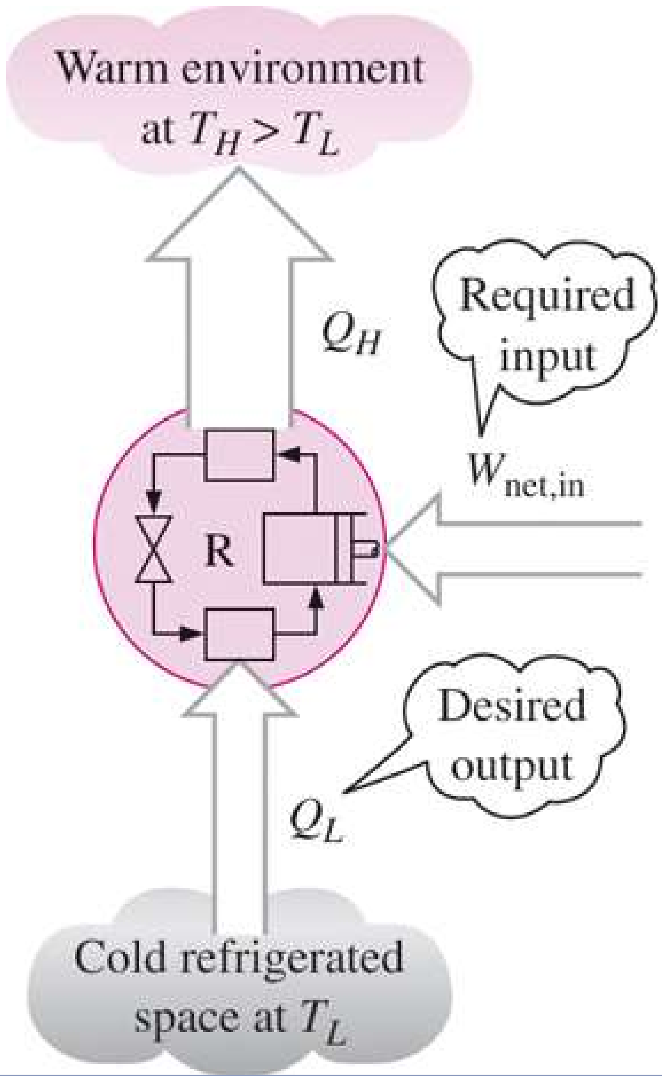


Basic components of a refrigeration system and typical operating conditions.

- 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***.

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

Coefficient of Performance



The *efficiency* of a refrigerator is expressed in terms of the **coefficient of performance (COP).**

The objective of a refrigerator is to remove heat (Q_L) from the refrigerated space.

$$COP_R = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_L}{W_{net,in}}$$

$$W_{net,in} = Q_H - Q_L \qquad \text{(kJ)}$$

$$COP_R = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1}$$

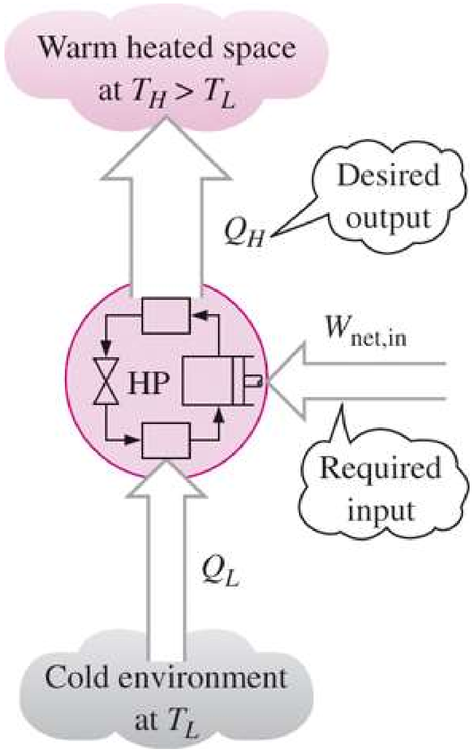
Can the value of COP_R be greater than unity?

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

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.

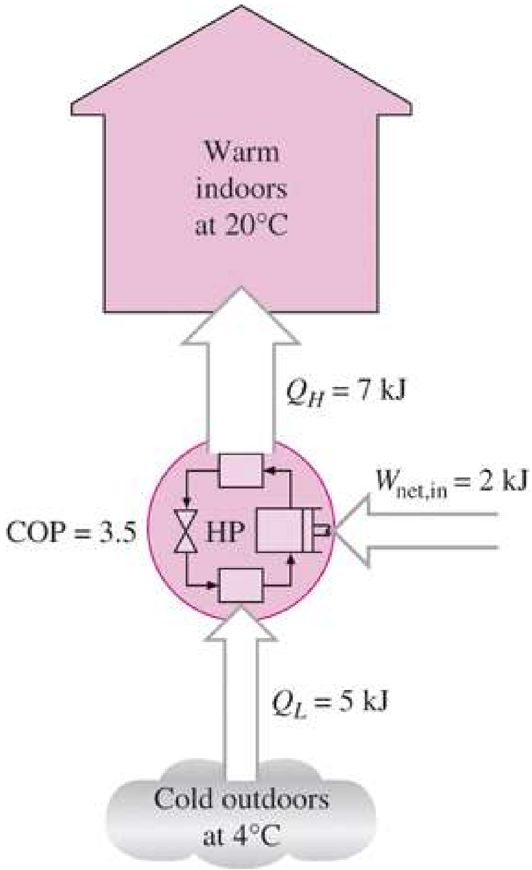


The objective of a heat pump, however, is to maintain a heated space at a high temperature. This is accomplished by absorbing heat from a low-temperature source, such as well water or cold outside air in winter, and supplying this heat to the high-temperature medium such as a house

The objective of a heat pump is to supply heat Q_H into the warmer space.

$$\mathrm{COP_{HP}} = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_H}{W_{net,in}}$$

$$\mathrm{COP_{HP}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$



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

for fixed values of Q_L and Q_H

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

Can the value of COP_{HP} be lower than unity?

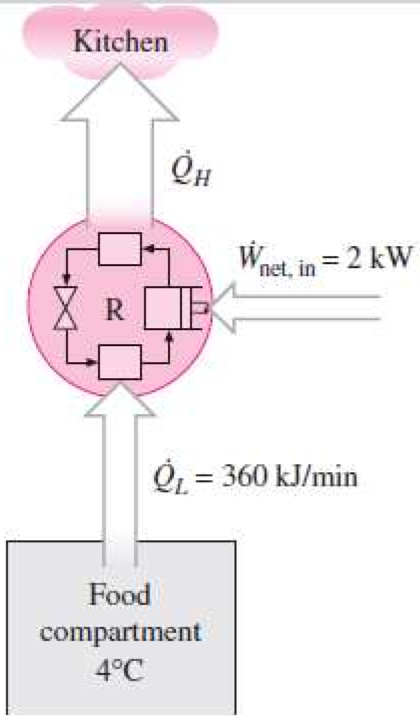
What does $COP_{HP}=1$ represent?

When installed backward, an air conditioner functions as a heat pump.

- Most heat pumps in operation today have a seasonally averaged COP of 2 to 3.
- Most existing heat pumps use the cold outside air as the heat source in winter (*air-source* HP).
- In cold climates their efficiency drops considerably when temperatures are below the freezing point.
- In such cases, *geothermal* (*ground-source*) HP that use the ground as the heat source can be used.
- Such heat pumps are more expensive to install, but they are also more efficient.
- **Air conditioners** are basically refrigerators whose refrigerated space is a room or a building instead of the food compartment.
- The COP of a refrigerator decreases with decreasing refrigeration temperature.
- Therefore, it is not economical to refrigerate to a lower temperature than needed.

Example 6-3

The food compartment of a refrigerator is maintained at 4C 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 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.

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

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

(*b*) The rate at which heat is rejected to the room that

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

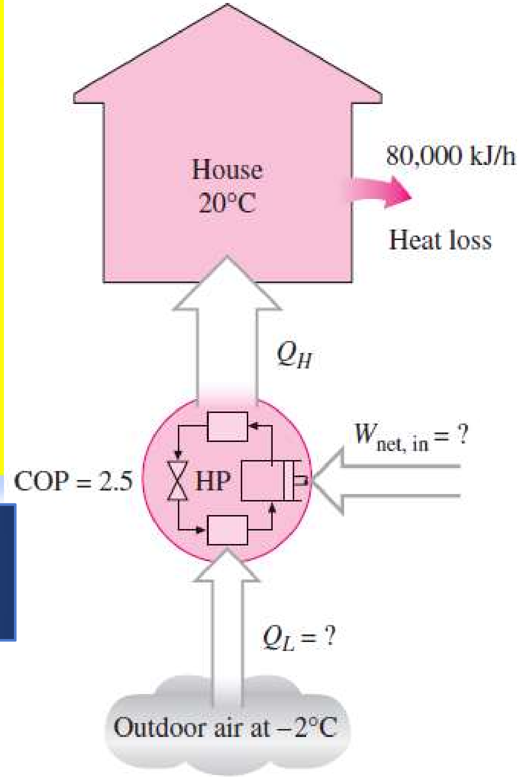
Discussion Both the energy removed from the refrigerated space as heat and the energy supplied to the refrigerator as electrical work eventually show up in the room air and become part of the internal energy of the air. This demonstrates that energy can change from one form to another, can move from one place to another, but is never destroyed during a process.

Example 6-4

A heat pump is used to meet the heating requirements of a house and maintain it at 20^{0}C. On a day when the outdoor air temperature drops to -2^{0}C, the house is estimated to lose heat at a rate of 80,000 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.



Solution The COP of a heat pump is given.

Assumptions Steady operating conditions exist.

(*a*) The power consumed by this heat pump

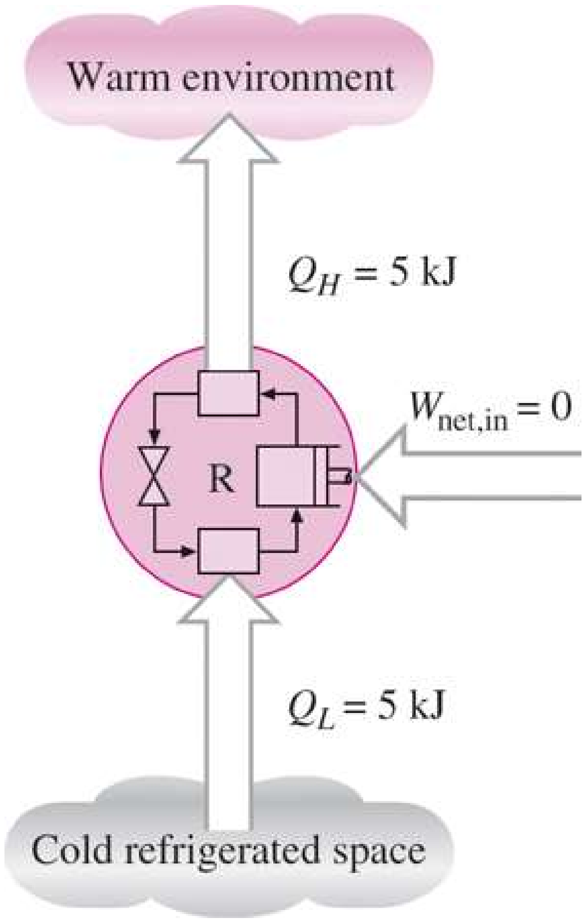
$$\dot{W}_{net,\,in} = \frac{\dot{Q}_H}{COP_{HP}} = \frac{80{,}000 \text{ kJ/h}}{2.5} = \mathbf{32{,}000 \text{ kJ/h}} \text{ (or 8.9 kW)}$$

(*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^{o}C, the heat pump must deliver heat to the house at the same rate, that is, at a rate of 80,000 kJ/h. Then the rate of heat transfer from the outdoor becomes

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

The Second Law of Thermodynamics: Clasius Statement

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.



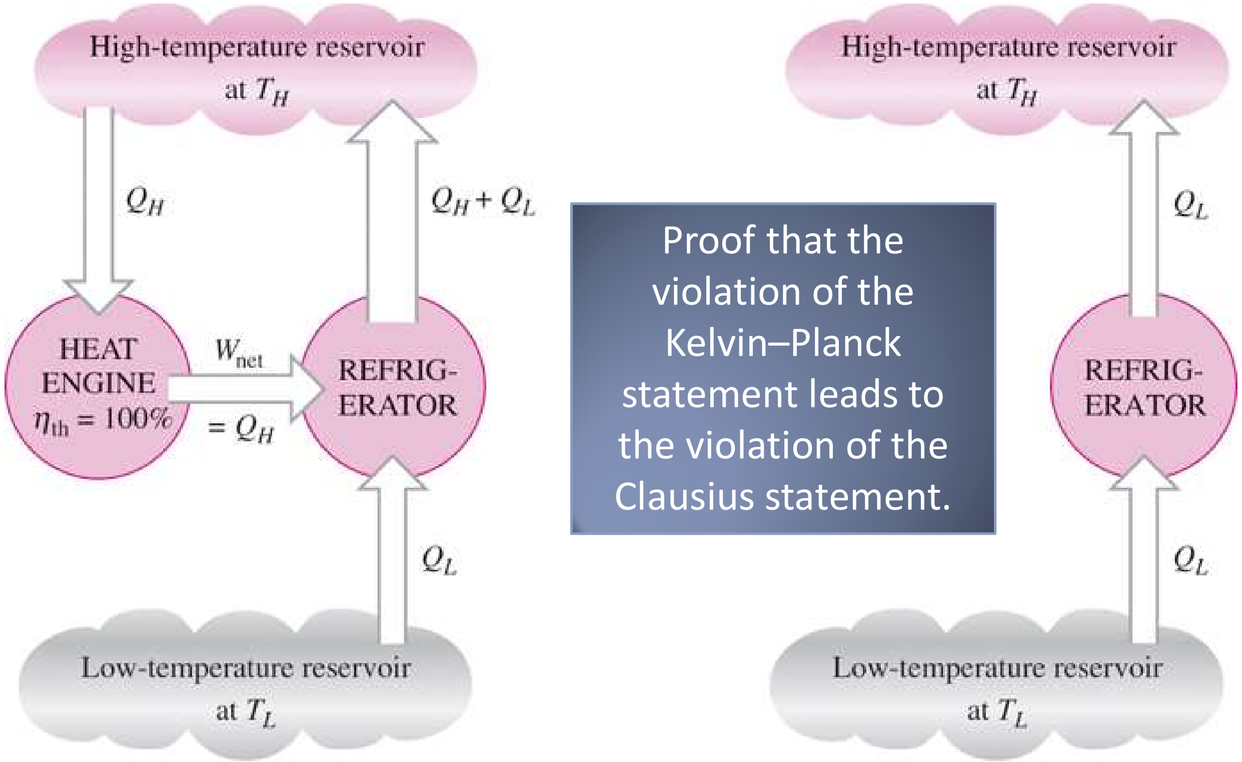
A refrigerator that violates the Clausius statement of the second law.

It 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.

To date, no experiment has been conducted that contradicts the second law, and this should be taken as sufficient proof of its validity.

Equivalence of the two Statements



(*a*) A refrigerator that is powered by a 100 percent efficient heat engine

(*b*) The equivalent refrigerator

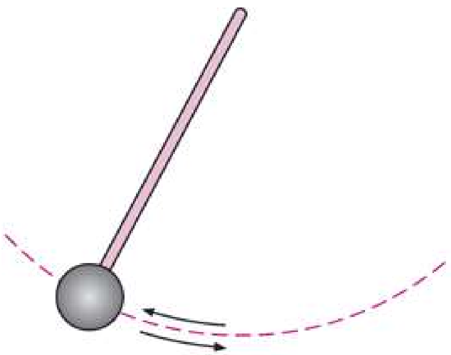
Proof that the violation of the Kelvin–Planck statement leads to the violation of the Clausius statement.

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.

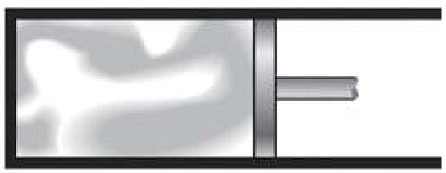
REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible process: *A process that can be reversed without leaving any trace on the surroundings.*
Irreversible process: A process that is not reversible.



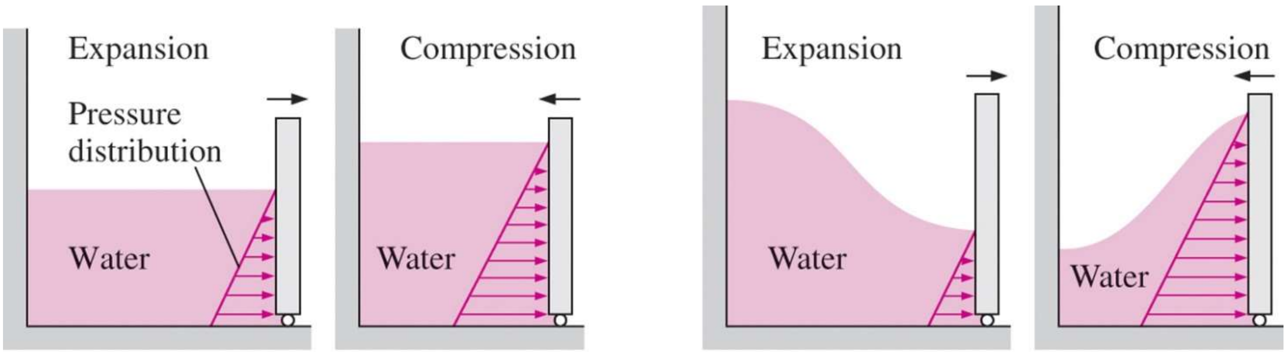
(*a*) Frictionless pendulum

- All the processes occurring in nature are irreversible.
- ***Why are we interested*** **in reversible processes?**
- **(1)** they are easy to analyze and **(2)** they serve as idealized models (theoretical limits) to which actual processes can be compared.
- Some processes are more irreversible than others.



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

Two familiar reversible processes.

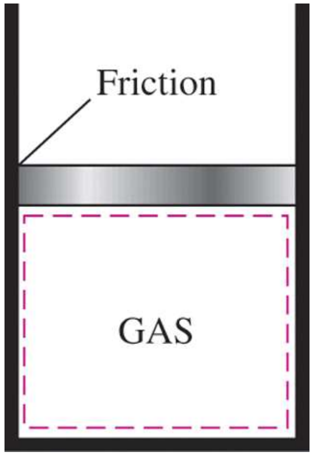


(*a*) Slow (reversible) process (*b*) Fast (irreversible) process

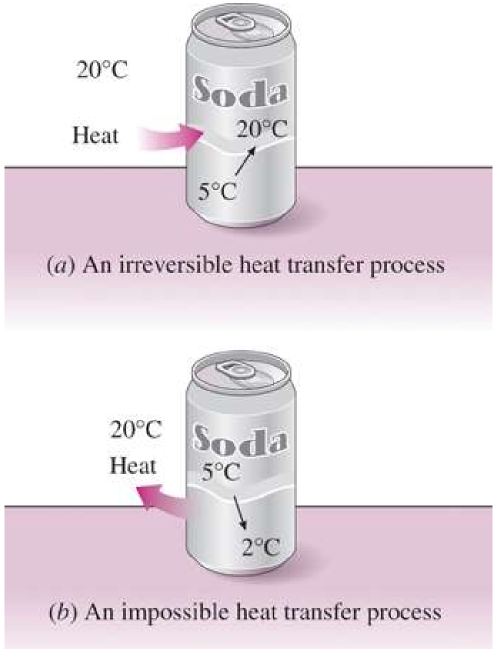
Reversible processes deliver the most and consume the least work.

Irreversibilities

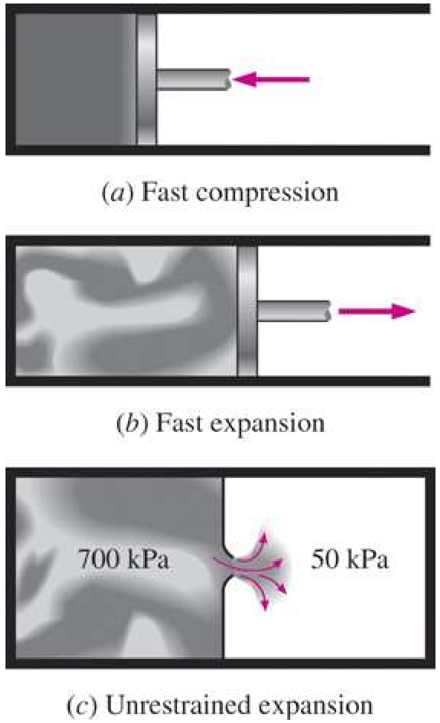
- The factors that cause a process to be irreversible are called **irreversibilities**.
- They include friction, unrestrained expansion, mixing of two fluids, heat transfer across a finite temperature difference, electric resistance, inelastic deformation of solids, and chemical reactions.
- The presence of any of these effects renders a process irreversible.



Friction renders a process irreversible.



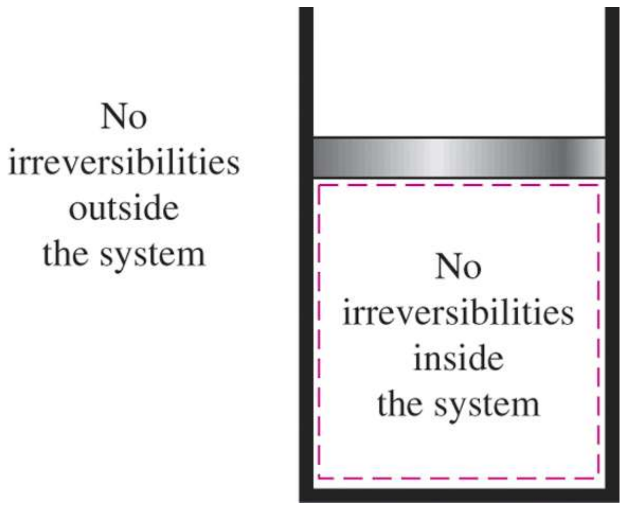
(*a*) Heat transfer through a temperature difference is irreversible, and (*b*) the reverse process is impossible.



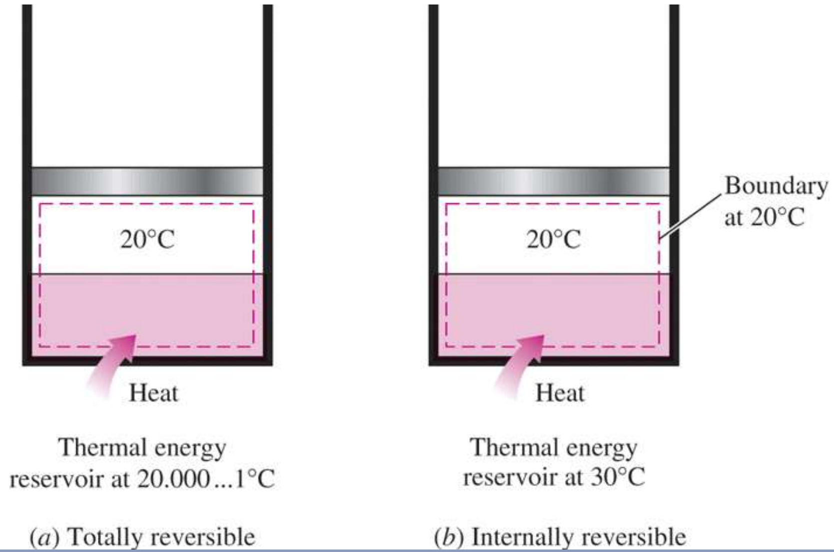
Irreversible compression and expansion processes.

Internally and Externally Reversible Processes

- **Internally reversible process:** If no irreversibilities occur within the boundaries of the system during the process.
- **Externally reversible:** If no irreversibilities occur outside the system boundaries.
- **Totally reversible process:** It involves no irreversibilities within the system or its surroundings.
- A totally reversible process involves no heat transfer through a finite temperature difference, no nonquasi-equilibrium changes, and no friction or other dissipative effects.

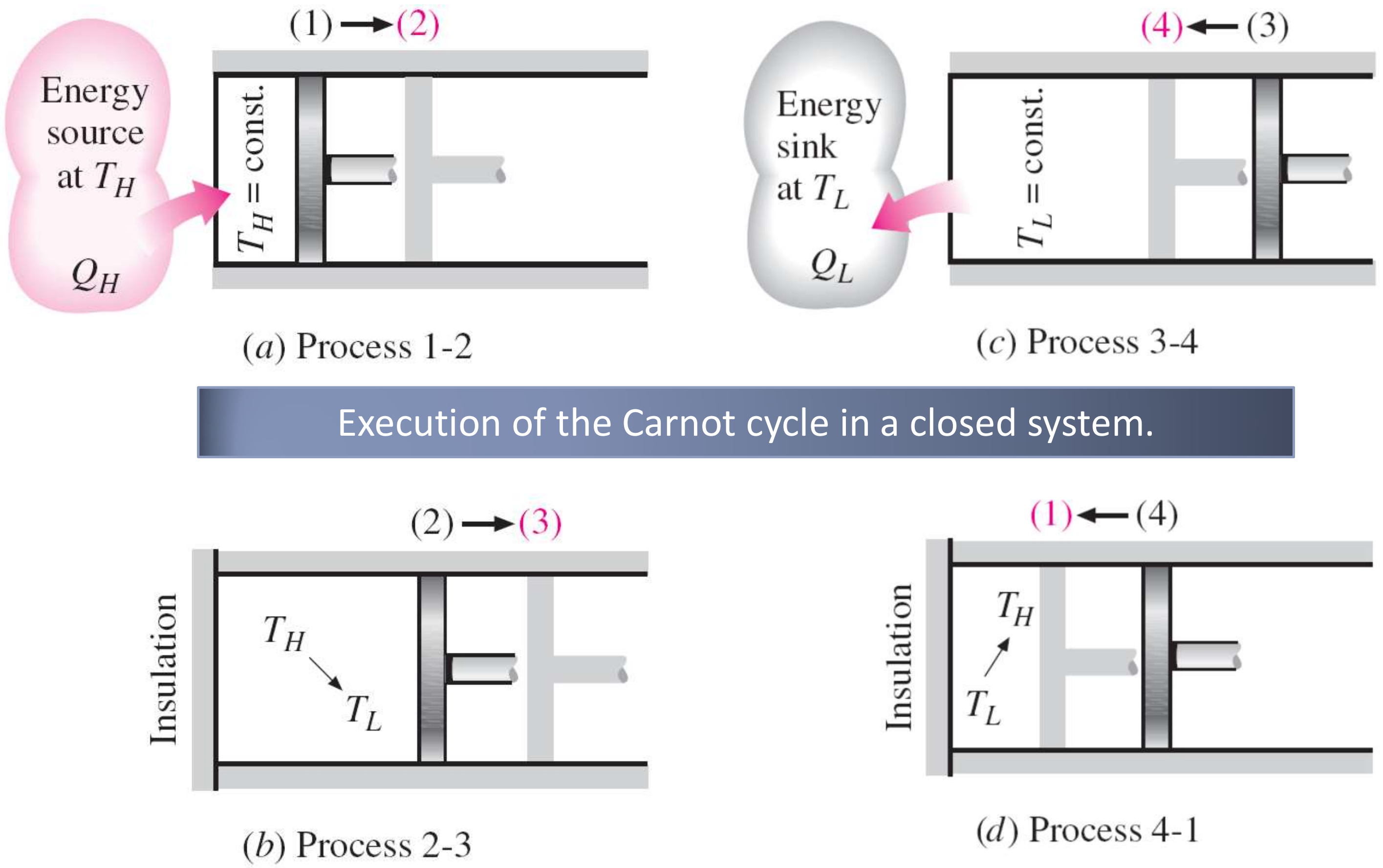


A reversible process involves no internal and external irreversibilities



Totally and internally reversible heat transfer processes.

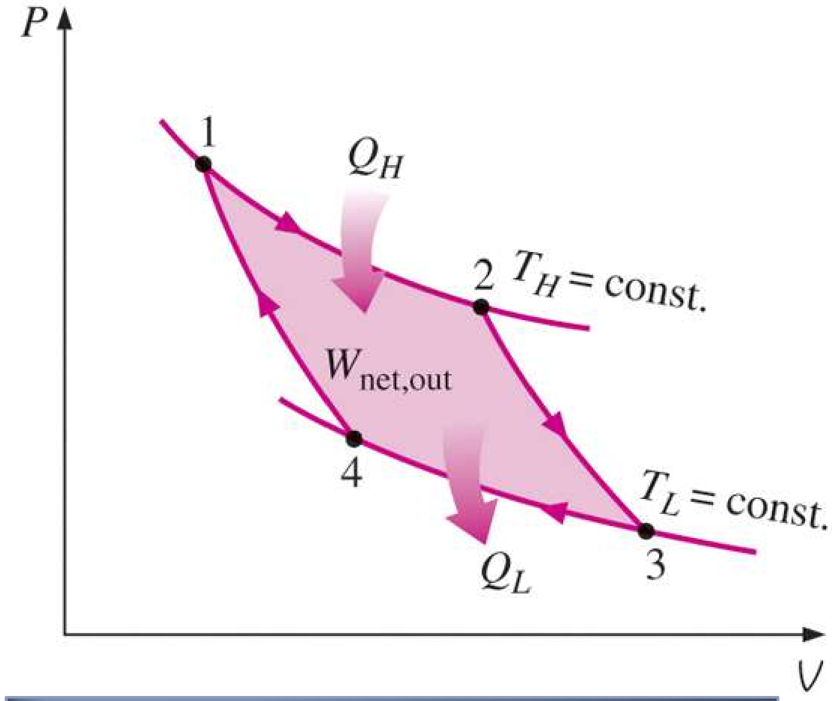
THE CARNOT CYCLE



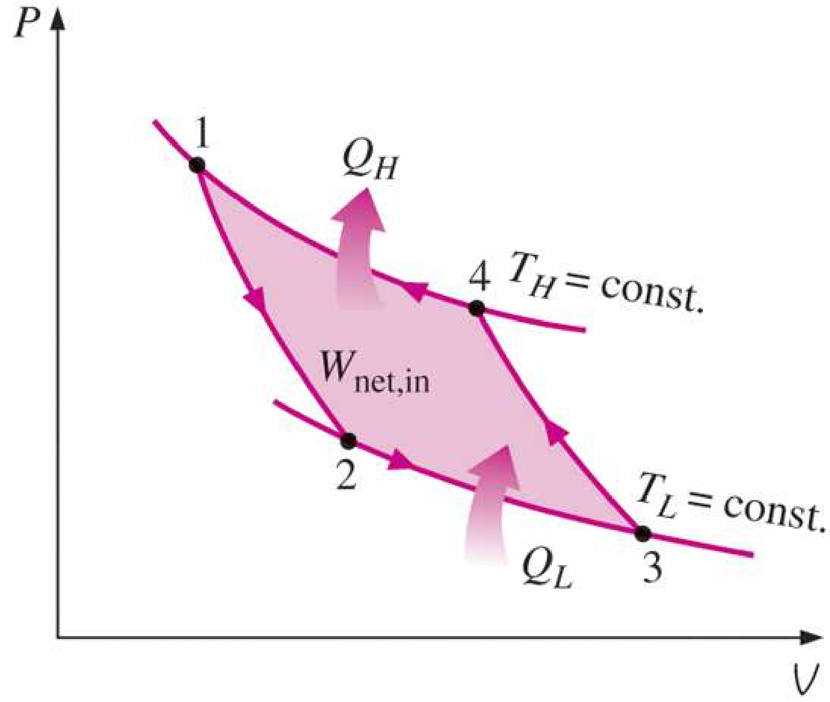
Execution of the Carnot cycle in a closed system.

Reversible Isothermal Expansion (process 1-2, T_H = constant)
Reversible Adiabatic Expansion (process 2-3, temperature drops from T_H to T_L)
Reversible Isothermal Compression (process 3-4, T_L = constant)
Reversible Adiabatic Compression (process 4-1, temperature rises from T_L to T_H)

The Reversed Carnot Cycle



P-V diagram of the Carnot cycle.

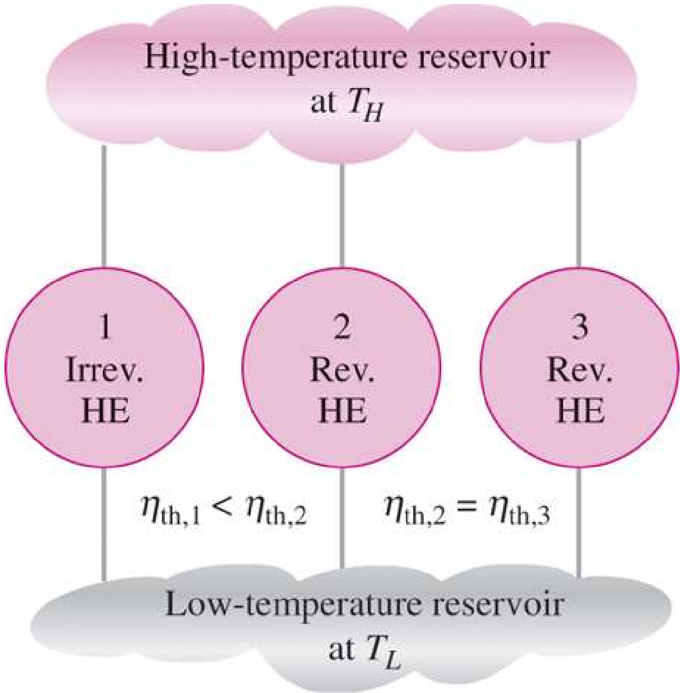


P-V diagram of the reversed Carnot cycle.

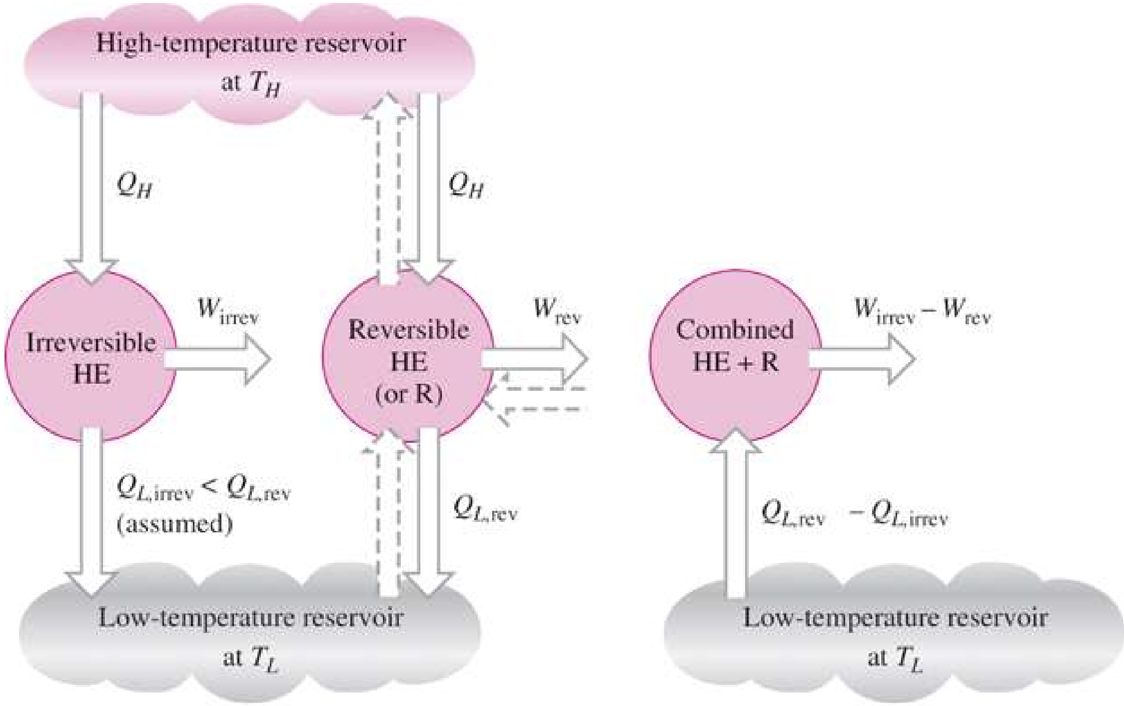
The Carnot heat-engine cycle is a totally reversible cycle.

Therefore, all the processes that comprise it can be *reversed*, in which case it becomes the **Carnot refrigeration cycle**.

THE CARNOT PRINCIPLES



The Carnot principles.



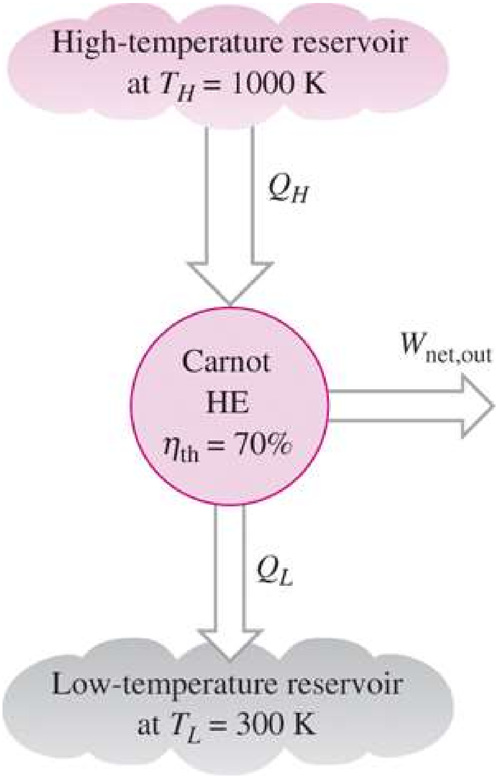
(*a*) A reversible and an irreversible heat engine operating between the same two reservoirs (the reversible heat engine is then reversed to run as a refrigerator)

(*b*) The equivalent combined system

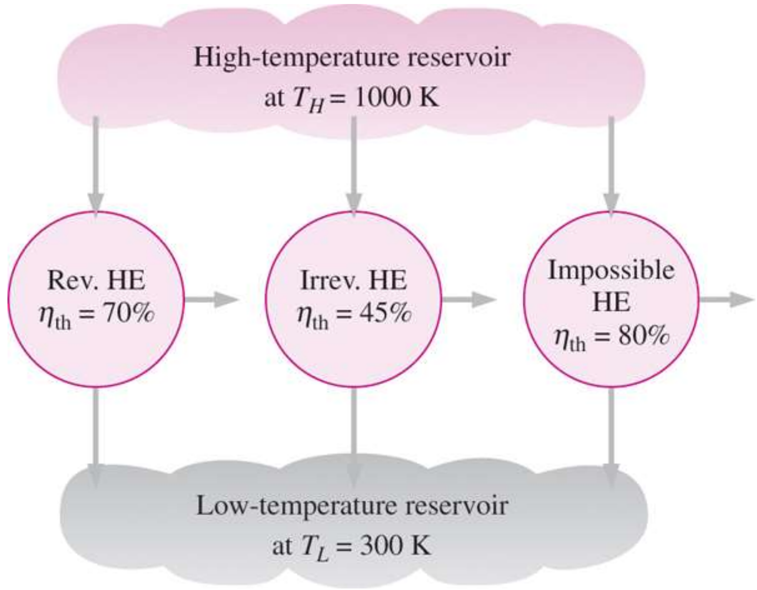
Proof of the first Carnot principle.

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.

THE CARNOT HEAT ENGINE



The Carnot heat engine is the most efficient of all heat engines operating between the same high- and low-temperature reservoirs.



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

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

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

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

Example 6-5

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 The heat supplied to a Carnot heat engine is given. The thermal efficiency and the heat rejected are to be determined.

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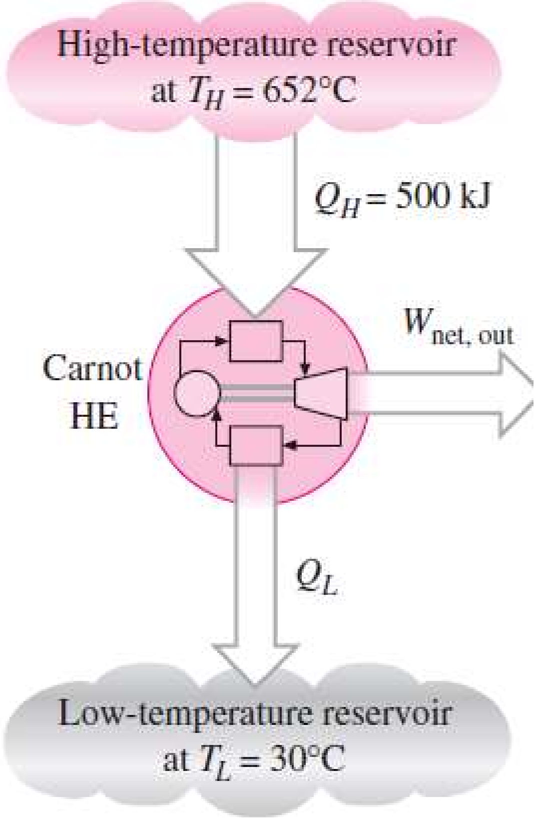


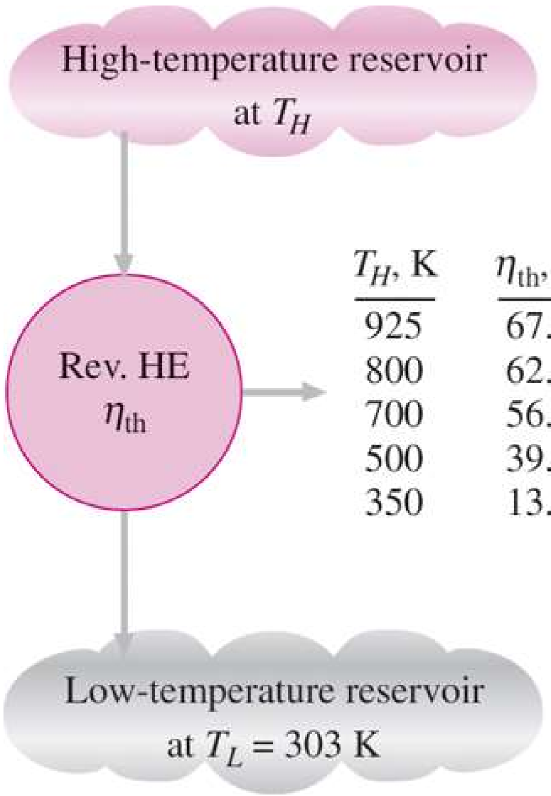
(*a*) The Carnot heat engine is a reversible heat engine, and so its efficiency can be determined

$$\eta_{th, C} = \eta_{th, rev} = 1 - \frac{T_L}{T_H} = 1 - \frac{(30 + 273)\text{ K}}{(652 + 273)\text{ K}} = \mathbf{0.672}$$

b) The amount of heat rejected Q_L by this reversible heat engine is easily determined

$$Q_{L, rev} = \frac{T_L}{T_H} Q_{H, rev} = \frac{(30 + 273)\text{ K}}{(652 + 273)\text{ K}} (500\text{ kJ}) = \mathbf{164\ kJ}$$

Discussion Note that this Carnot heat engine rejects to a low-temperature sink 164 kJ of the 500 kJ of heat it receives during each cycle



T_H, K	η_{th}, %
925	67.2
800	62.1
700	56.7
500	39.4
350	13.4

The fraction of heat that can be converted to work as a function of source temperature.

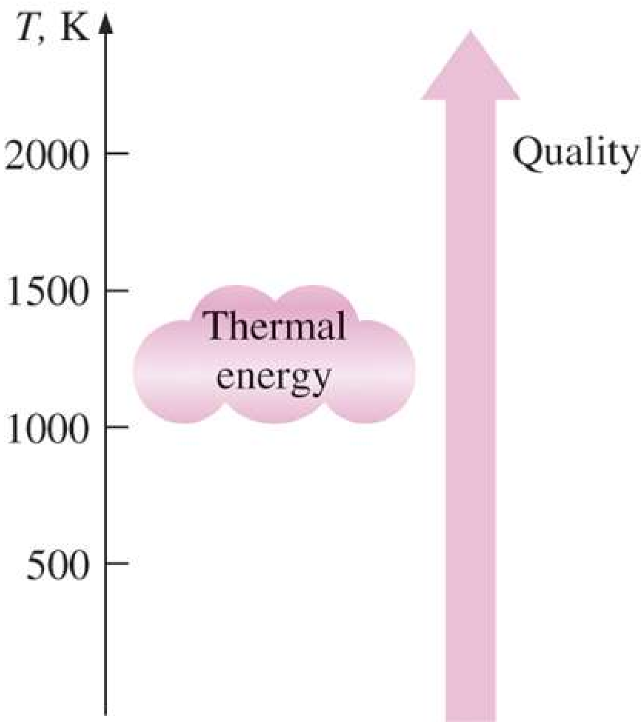
$$\eta_{th,rev} = 1 - \frac{T_L}{T_H}$$

The Carnot heat engine in Example 6–5 receives heat from a source at 925 K and converts 67.2 % of it to work while rejecting the rest (32.8 %) to a sink at 303 K.

Now let us examine how the thermal efficiency varies with the source temperature when the sink temperature is held constant.

Can we use °C unit for temperature here?

How do you increase the thermal efficiency of a Carnot heat engine? How about for actual heat engines?

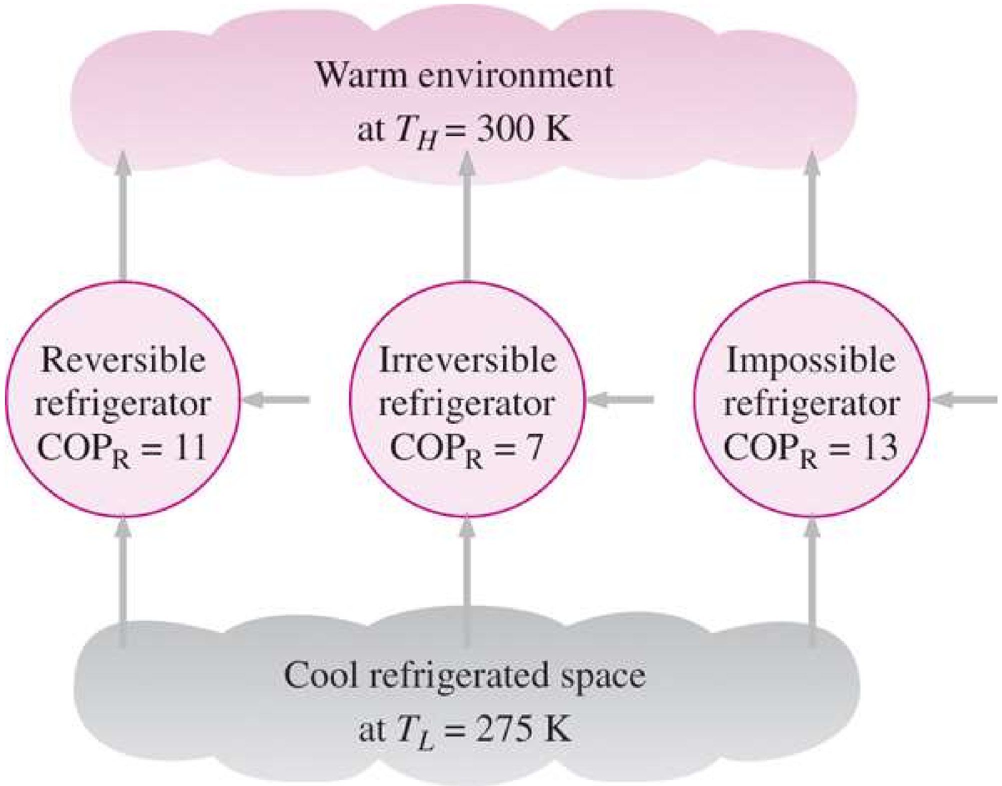


The higher the temperature of the thermal energy, the higher its quality.

more of the high-temperature thermal energy can be converted to work. Therefore, the higher the temperature, the higher the quality of the energy

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.**



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

Any refrigerator or heat pump

$$COP_R = \frac{1}{Q_H/Q_L - 1}$$

$$COP_{HP} = \frac{1}{1 - Q_L/Q_H}$$

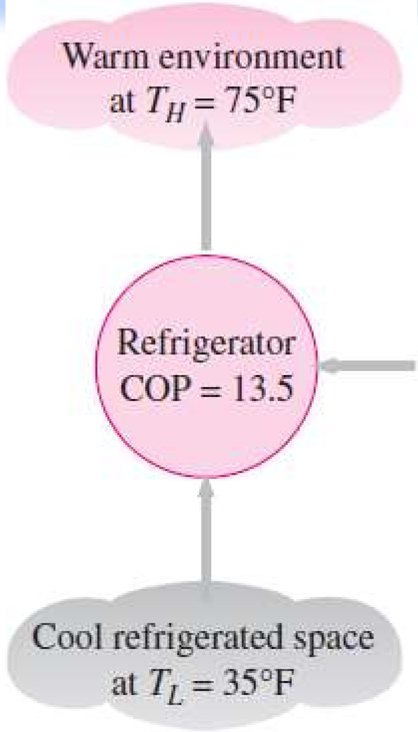
Carnot refrigerator or heat pump

$$COP_{HP,rev} = \frac{1}{1 - T_L/T_H}$$

$$COP_{R,rev} = \frac{1}{T_H/T_L - 1}$$

Example 6-6

An inventor claims to have developed a refrigerator that maintains the refrigerated space at 2°C while operating in a room where the temperature is 25°C and that has a COP of 13.5. Is this claim reasonable?



Solution An extraordinary claim made for the performance of a refrigerator is to be evaluated.
Assumptions Steady operating conditions exist.

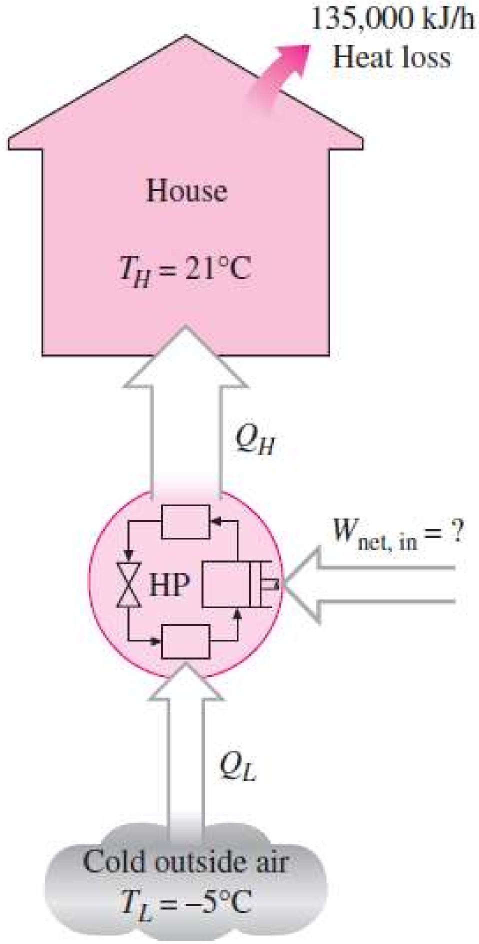
$$COP_{SM,\ maks} = COP_{SM,\ tr} = \frac{1}{T_H/T_L - 1}$$

$$= \frac{1}{(25 + 273)\,/\,(2 + 273) - 1} = 12.0$$

Discussion This is the highest COP a refrigerator can have when removing heat from a cool medium at 2°C to a warmer medium at 25°C. Since the COP claimed by the inventor is above this maximum value, the claim is *false*.

Example 6-7

A heat pump is to be used to heat a house during the winter. The house is to be maintained at 21C at all times. The house is estimated to be losing heat at a rate of 135,000 kJ/h when the outside temperature drops to 5C. Determine the minimum power required to drive this heat pump.



Solution A heat pump maintains a house at a fixed temperature. The required minimum power input to the heat pump is to be determined.

Assumptions Steady operating conditions exist.

$$COP_{HP, rev} = \frac{1}{1 - T_L/T_H} = \frac{1}{1 - (-5 + 273\text{ K})/(12 + 273\text{ K})} = 11.3$$

$$\dot{W}_{net, in} = \frac{Q_H}{COP_{HP}} = \frac{37.5\text{ kW}}{11.3} = 3.32\text{ kW}$$

Discussion This heat pump can meet the heating requirements of this house by consuming electric power at a rate of 3.32 kW only. If this house were to be heated by electric resistance heaters instead, the power consumption would jump up 11.3 times to 37.5 kW. Notice that the heat pump does not create energy. It merely transports it from one medium (the cold outdoors) to another (the warm indoors).

SUMMARY

- Introduction to the second law
- Thermal energy reservoirs
- Heat engines
  - Thermal efficiency
  - The 2^{nd} law: Kelvin-Planck statement
- Refrigerators and heat pumps
  - Coefficient of performance (COP)
  - The 2^{nd} law: Clasius statement
- Perpetual motion machines
- Reversible and irreversible processes
  - Irreversibilities, Internally and externally reversible processes
- The Carnot cycle
  - The reversed Carnot cycle
- The Carnot principles
- The thermodynamic temperature scale
- The Carnot heat engine
  - The quality of energy
- The Carnot refrigerator and heat pump