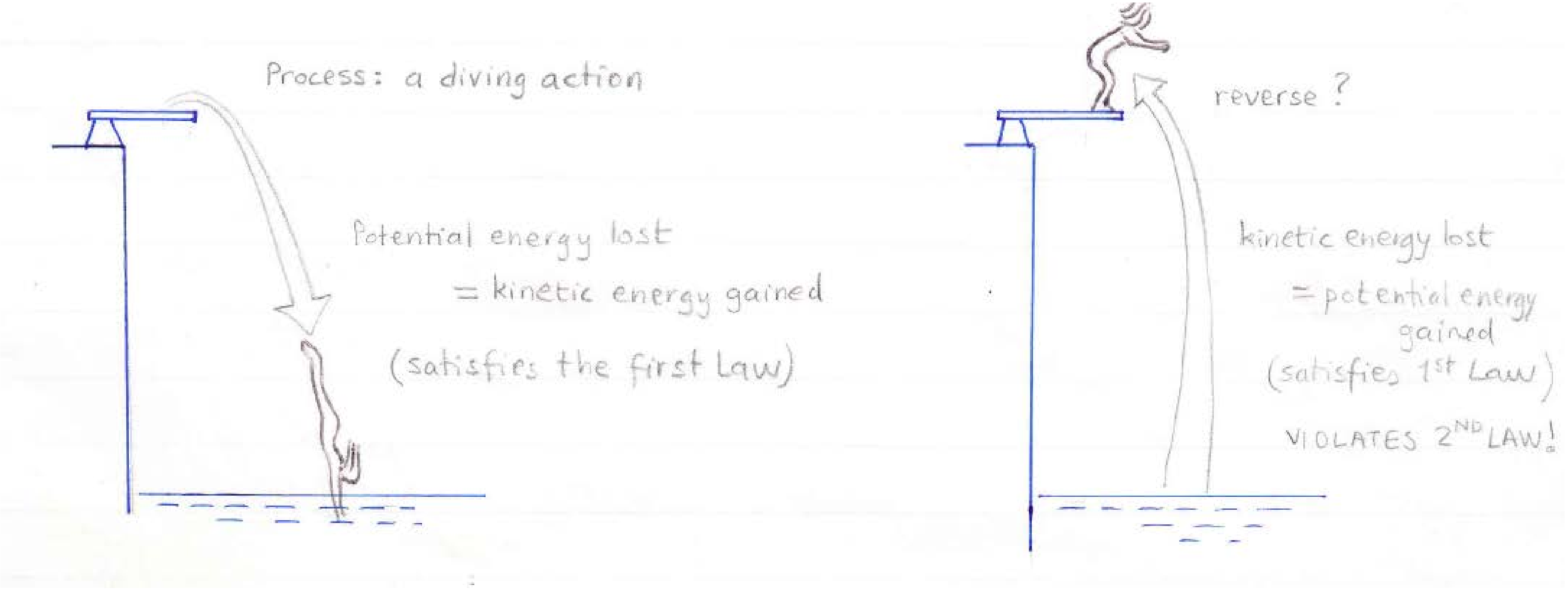
CHAPTER

5

The Second Law of Thermodynamics

→ **A process must satisfy the first law to occur**

→ **However, does it ensure that the process will actually take place?**

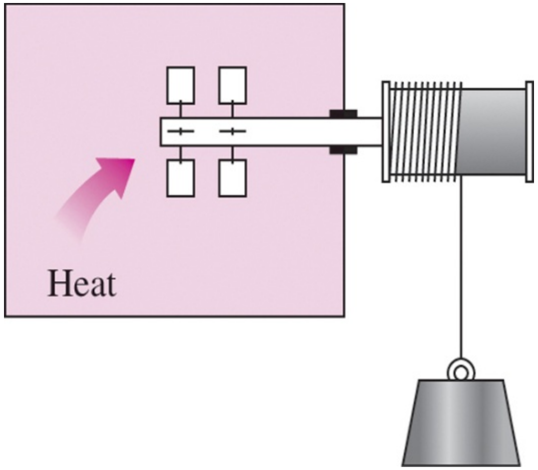


potential energy lost = kinetic energy gained
(satisfies the first law)

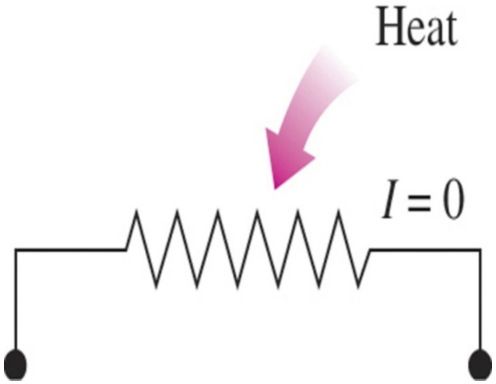
kinetic energy lost = potential energy gained
(satisfies the first law – VIOLATES the 2nd LAW!)

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.



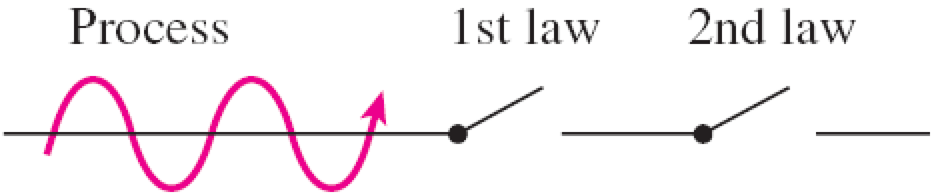
Transferring heat to a wire will not generate electricity.



It is clear from the above examples that <u>processes take place in a certain direction and not in the reverse direction</u>. First law alone is not enough to determine if a process will actually occur.

→ **Another principle is needed: <u>Second law of Thermodynamics</u>**

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

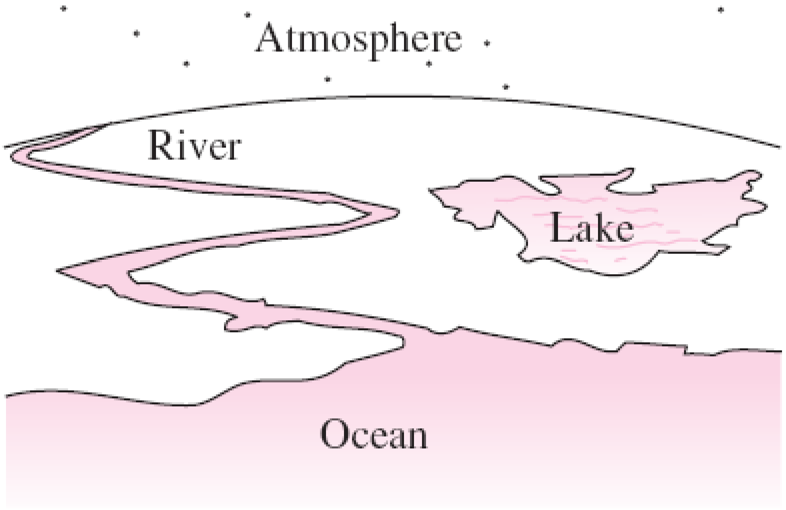


A process must satisfy both the first and second laws of thermodynamics to proceed.

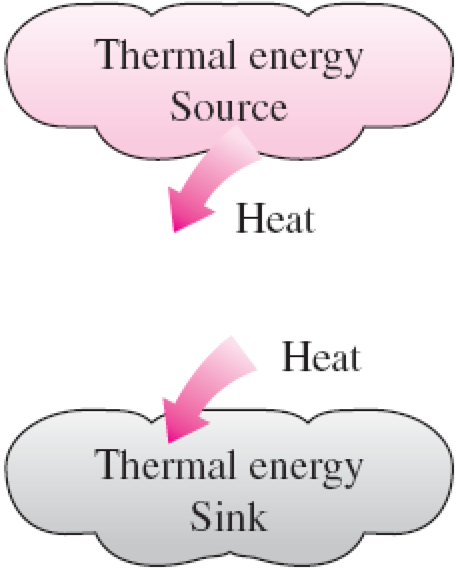
MAJOR USES OF THE SECOND LAW

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



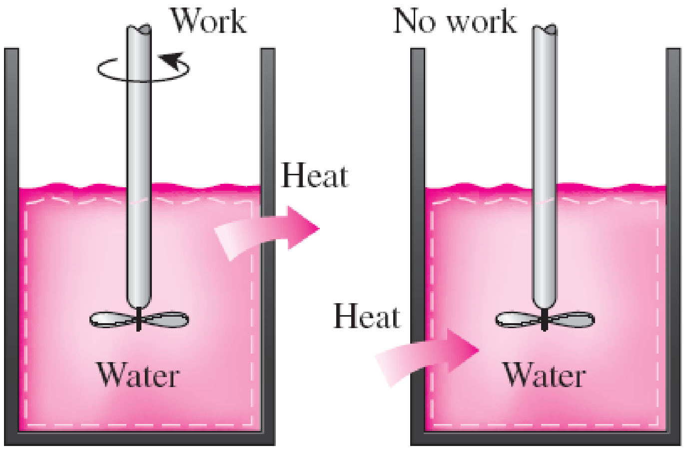
Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.



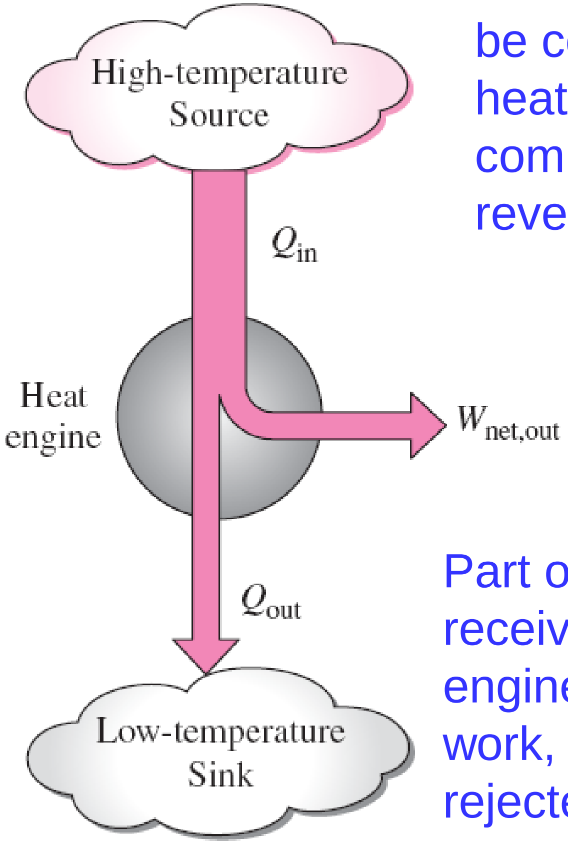
A **source** supplies energy in the form of heat, and a **sink** absorbs it.

- 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



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



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

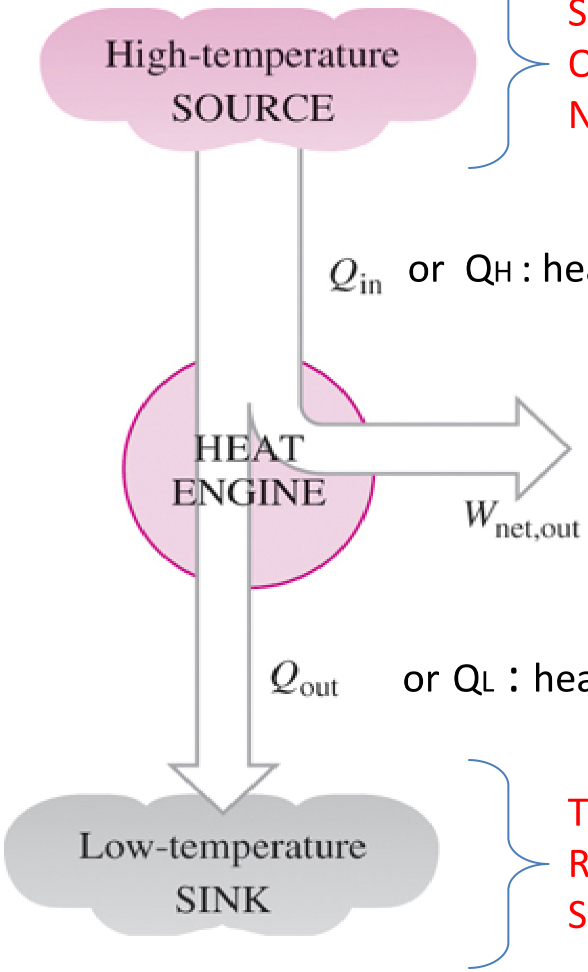
The devices that convert heat to work.

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***.

HEAT ENGINES:

→ **are thermodynamic systems operating in a cycle to which net heat is transferred and from which net work is delivered.**



Solar energy
Oil furnace
Nuclear reactor

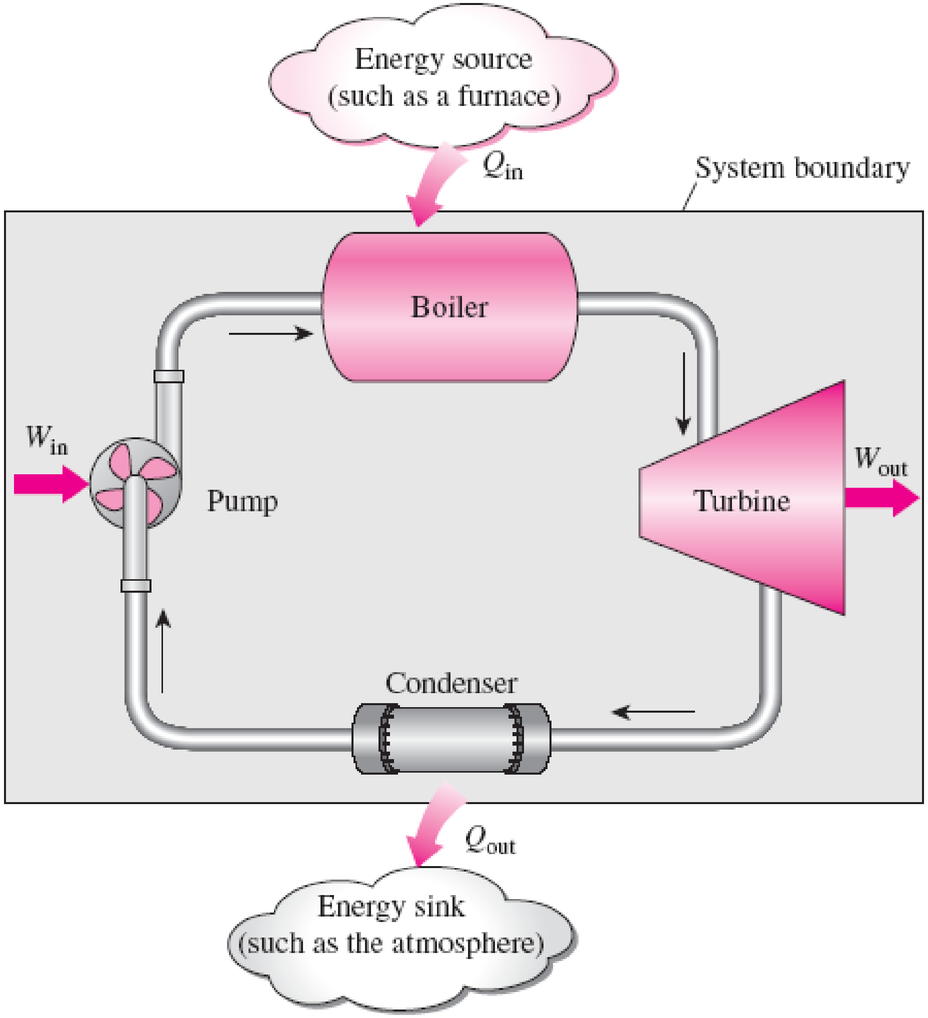
or Q_H : heat transfer between cyclic device and high temp. medium at T_H

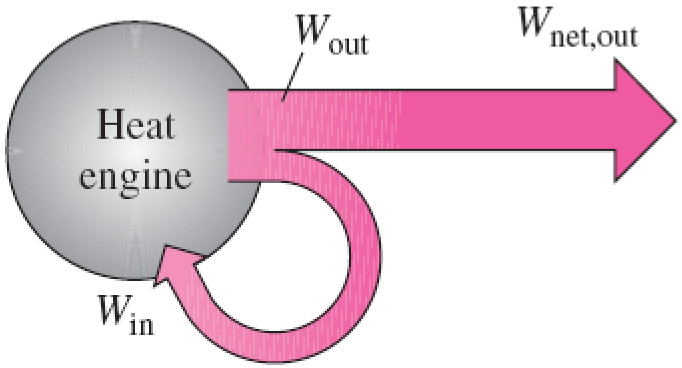
Rotating shaft

or Q_L : heat transfer between cyclic device and high temp. medium at T_H

The atmosphere
Rivers
Sea

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

DEFINITION of PERFORMANCE for any device

In general : performance = $\dfrac{\text{Desired output}}{\text{required input}} = \dfrac{\text{What I Get}}{\text{What I pay for}}$

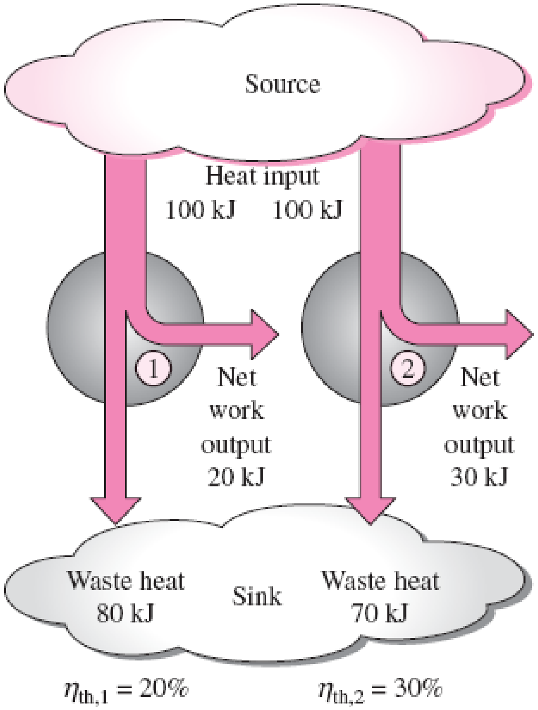
In heat engines: **the desired output = net work output** = $W_{net,out}$

the required input = heat supplied to system = Q_{in}

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

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

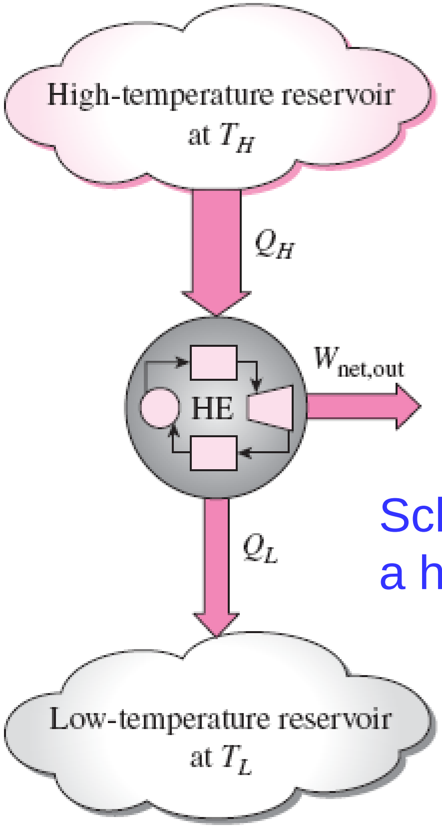
Thermal efficiency



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

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

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



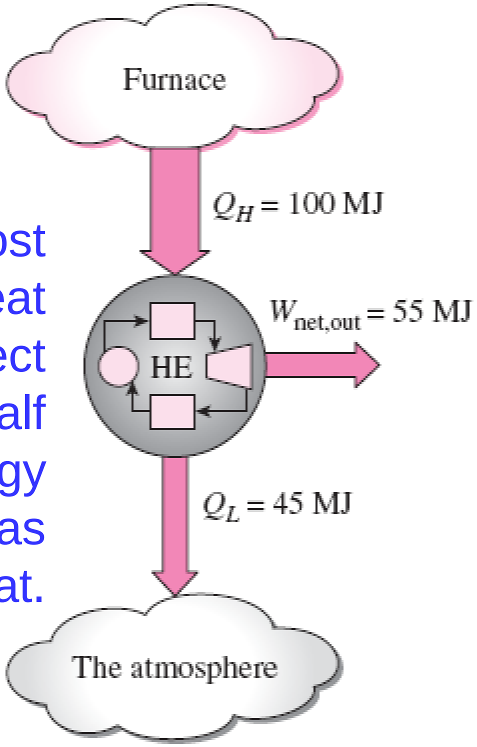
$$W_{net,out} = Q_H - Q_L$$

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

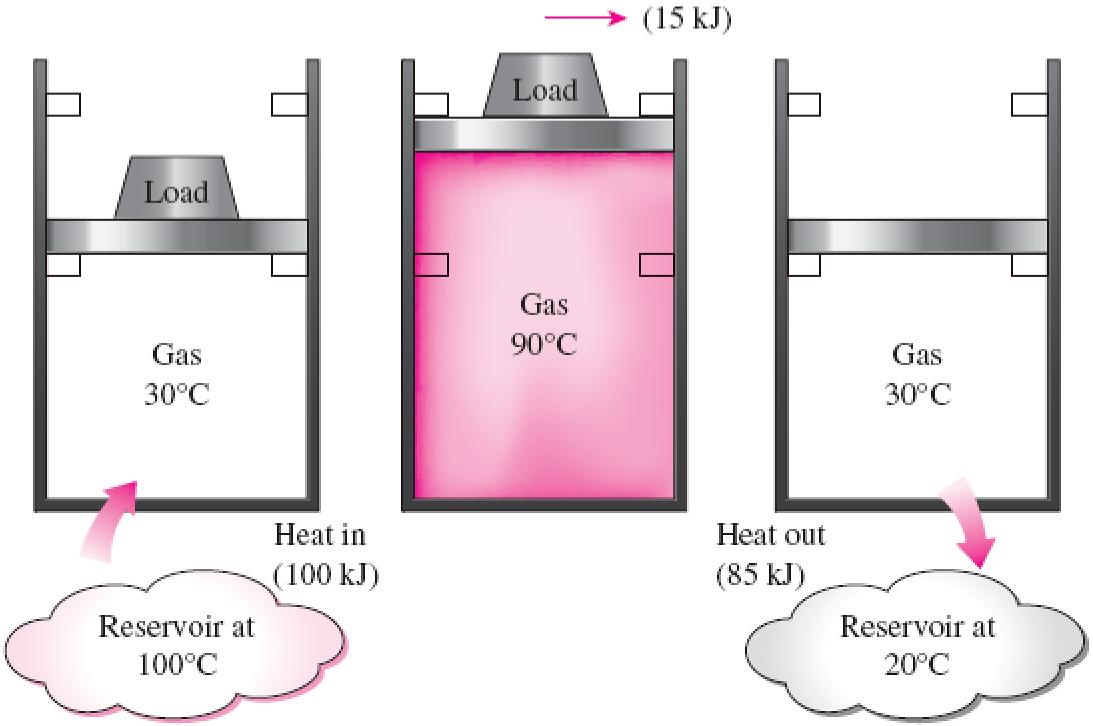
$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

Schematic of a heat engine.

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



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?

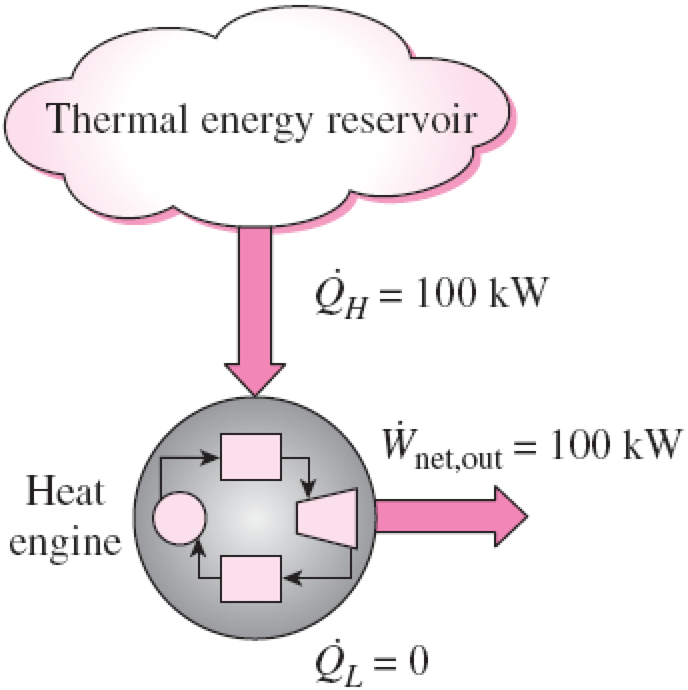
The answer is, unfortunately, a firm ***no*** for the simple reason that without a heat rejection process in a condenser, the cycle cannot be completed.

The Second Law of Thermodynamics: Kelvin–Planck Statement

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.

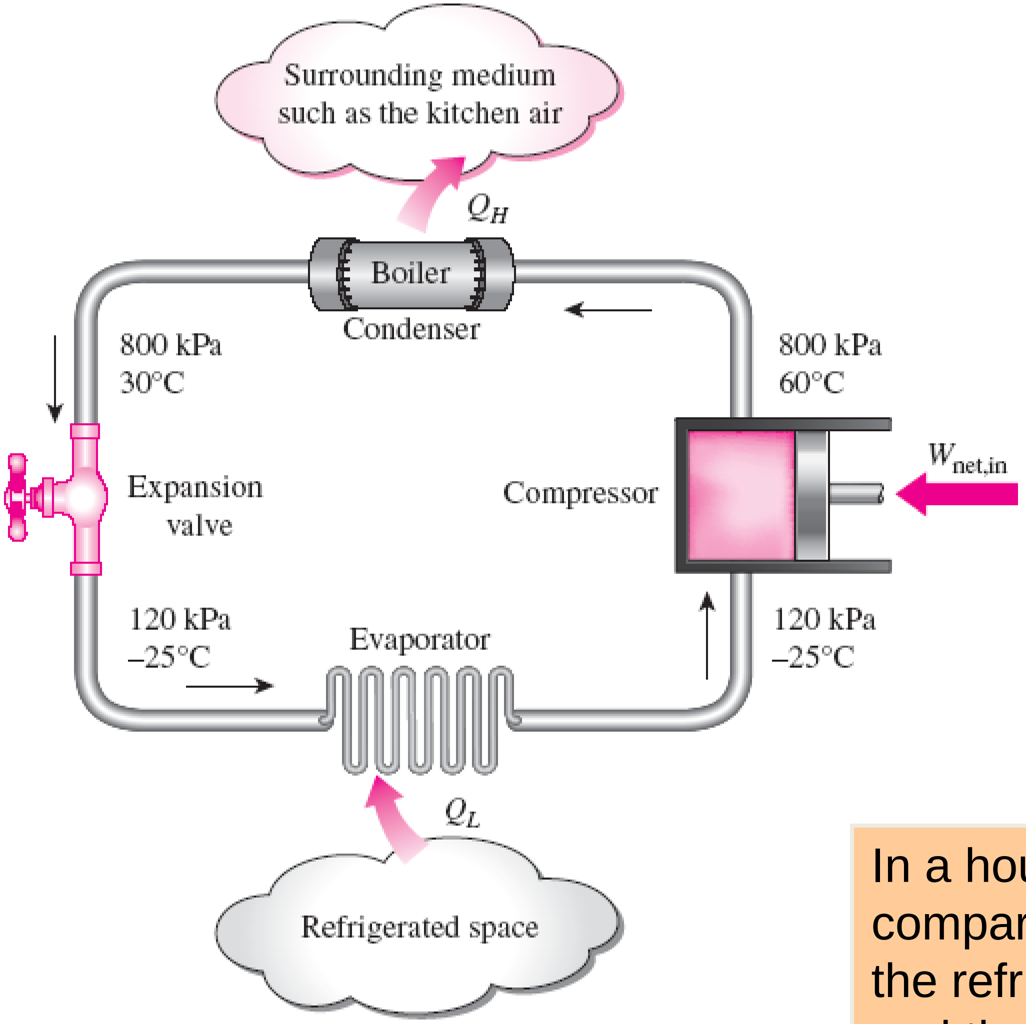
No heat engine can have a thermal efficiency of 100 percent, or *as for a power plant to operate, the working fluid must exchange heat with the environment as well as the furnace*.

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**.

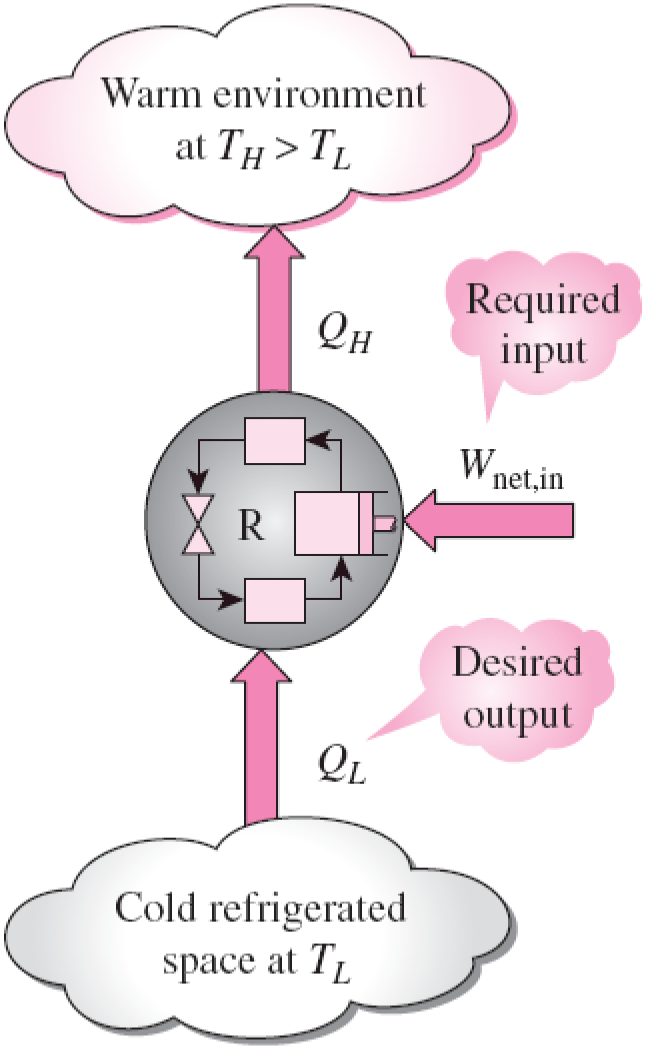
Refrigerators, like heat engines, are cyclic devices.

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

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.

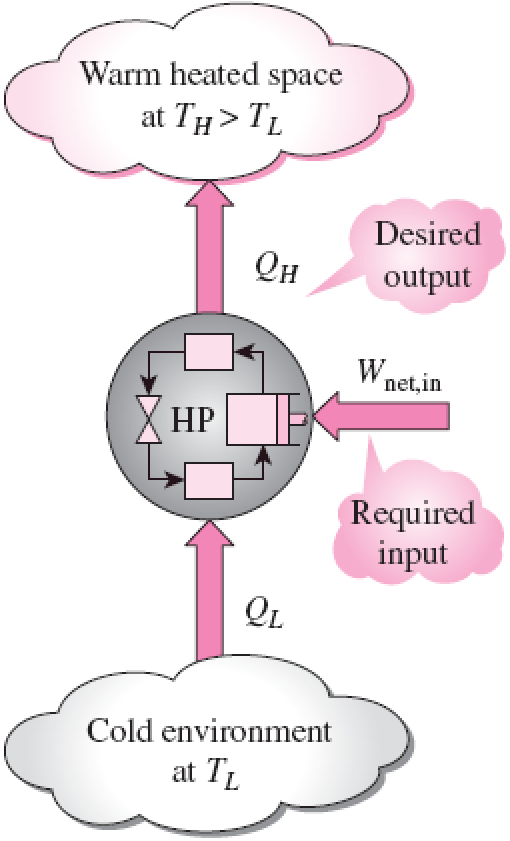
$$\text{COP}_\text{R} = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_L}{W_{\text{net,in}}}$$

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

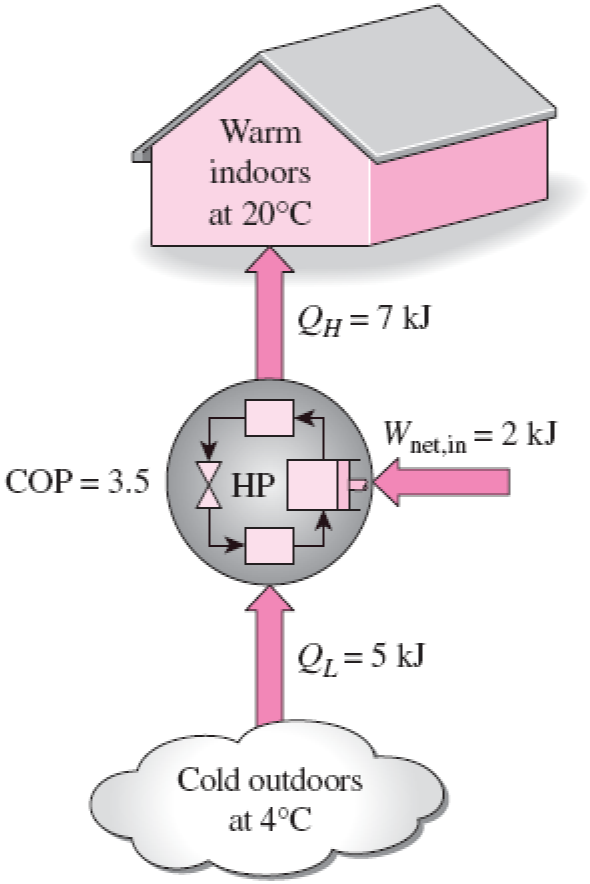
$$\text{COP}_\text{R} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1}$$

Can the value of COP_R be greater than unity?

Heat Pumps



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



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

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

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

$\text{COP}_{\text{HP}} = \text{COP}_{\text{R}} + 1$ for fixed values of Q_L and Q_H

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

What does $\text{COP}_{\text{HP}}=1$ 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.

Energy efficiency rating (EER): The amount of heat removed from the cooled space in Btu's for 1 Wh (watthour) of electricity consumed.

$$\text{EER} = 3.412\ \text{COP}_\text{R}$$

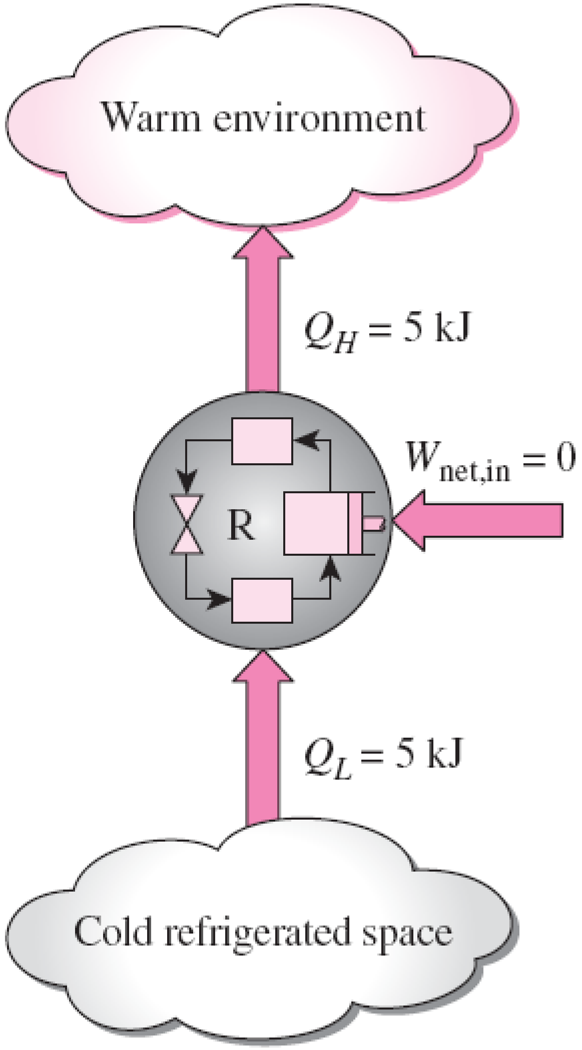
The Second Law of Thermodynamics: Clausius Statement

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.

It states that a refrigerator cannot operate unless its compressor is driven by an external power source, such as an electric motor.

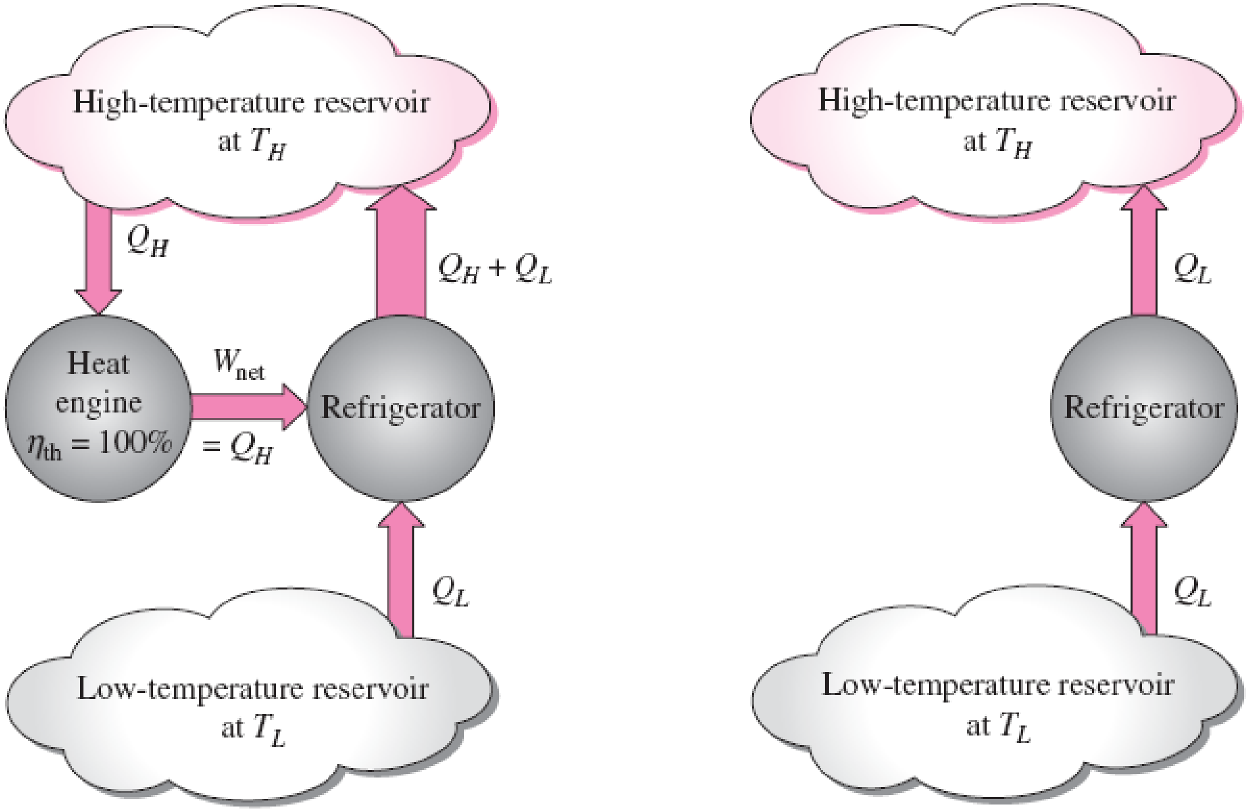
This way, the net effect on the surroundings involves the consumption of some energy in the form of work, in addition to the transfer of heat from a colder body to a warmer one.

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



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

Equivalence of the Two Statements



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

(*b*) The equivalent refrigerator

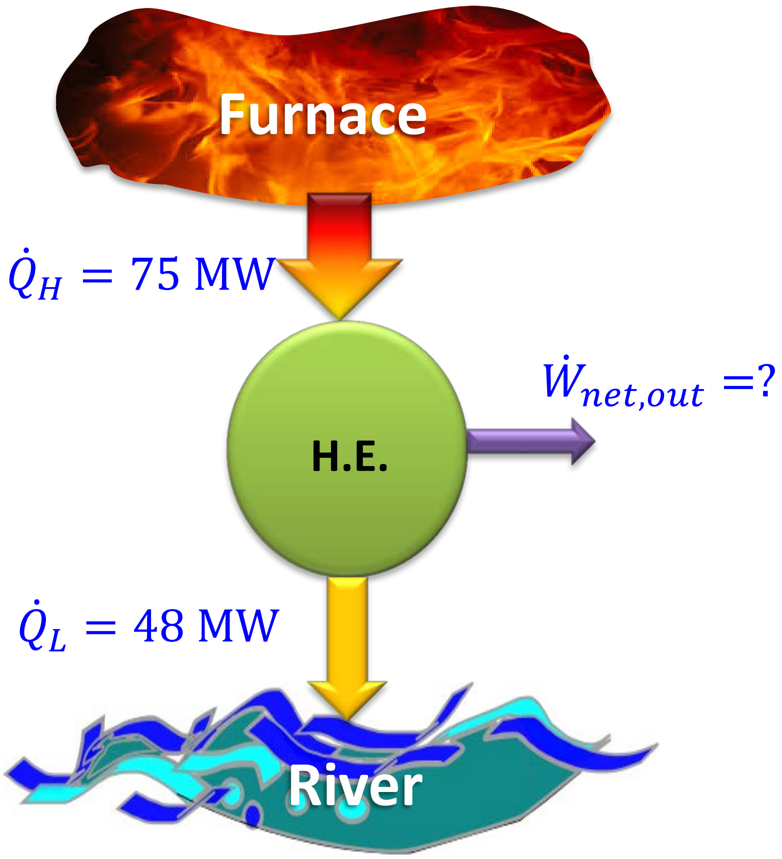
Proof that the violation of the Kelvin–Planck statement leads to the violation of the Clausius statement.

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.

Example 1:

Heat is transferred to a heat engine from a furnace at a rate of 75MW. If waste heat rejection to a nearby river is 48MW, determine the power output and the thermal efficiency for this heat engine.



$$\dot{W}_{net,out} = \dot{Q}_H - \dot{Q}_L$$

$$= (75 - 48)\text{MW} = 27\text{MW}$$

$$\eta_{th} = \frac{\dot{W}_{net,out}}{\dot{Q}_H}$$

$$= \frac{27\text{ MW}}{75\text{ MW}} = 0.36$$

or 36%

Example 2: Heat pump

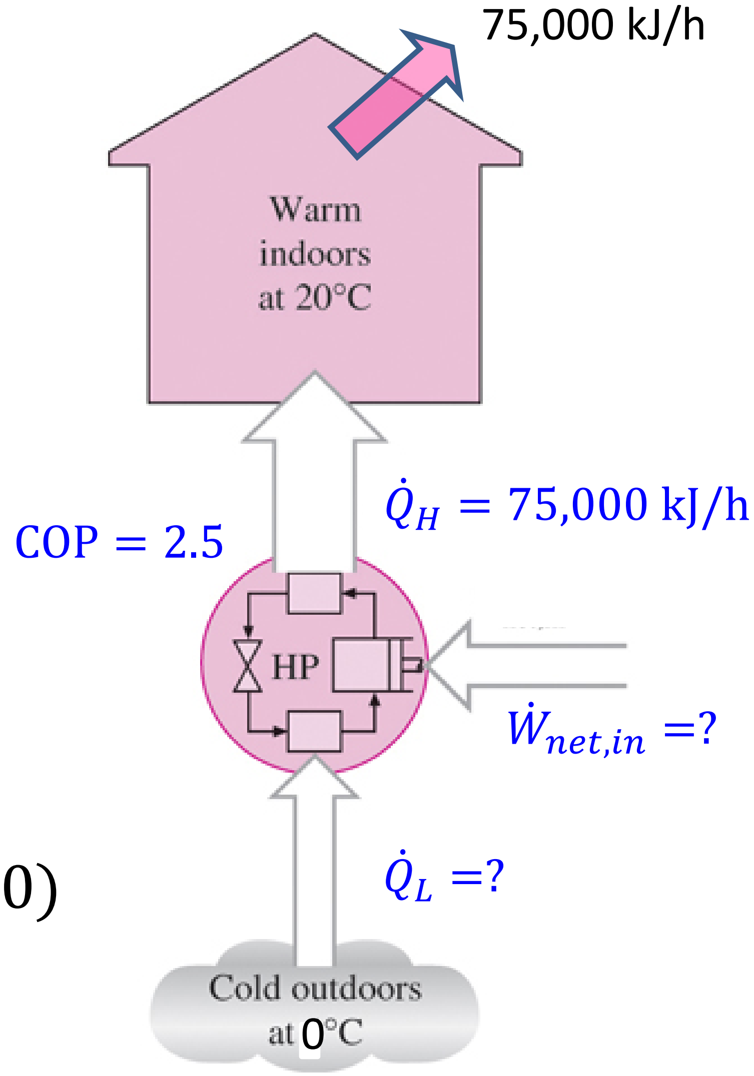
$$COP_{HP} = \frac{\dot{Q}_H}{\dot{W}_{net,in}}$$

$$\rightarrow \dot{W}_{net,in} = \frac{\dot{Q}_H}{COP_{HP}} = \frac{75{,}000}{2.5}$$

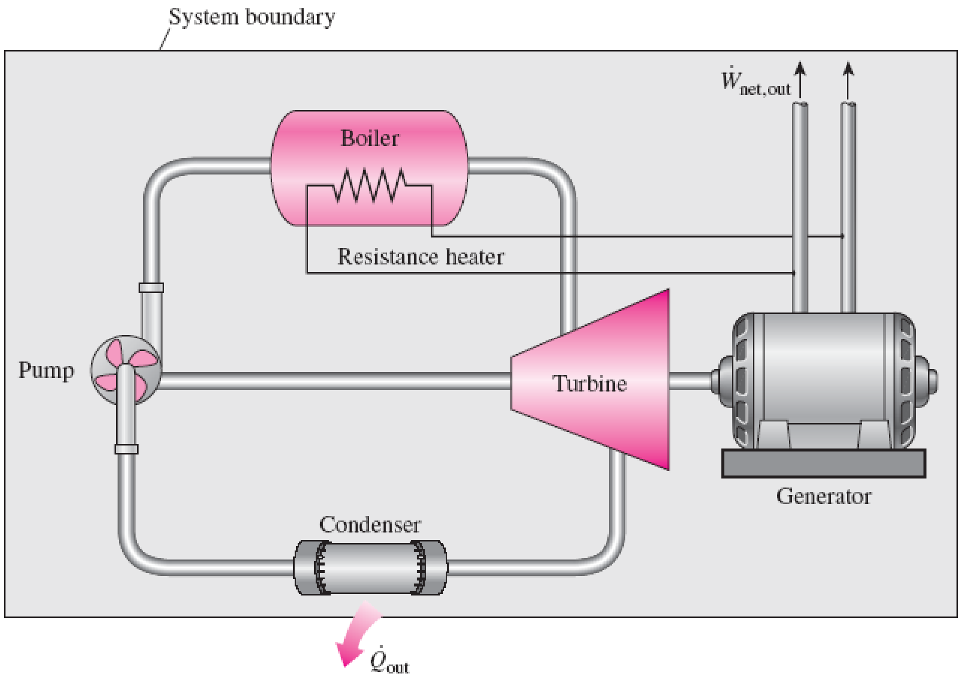
$$= 30{,}000 \ {}^{\text{kJ}}\!/_{\text{h}} \ (\text{or } 8.33\ \text{kW})$$

$$\dot{Q}_L = \dot{Q}_H - \dot{W}_{net,in} = (75{,}000 - 30{,}000)$$

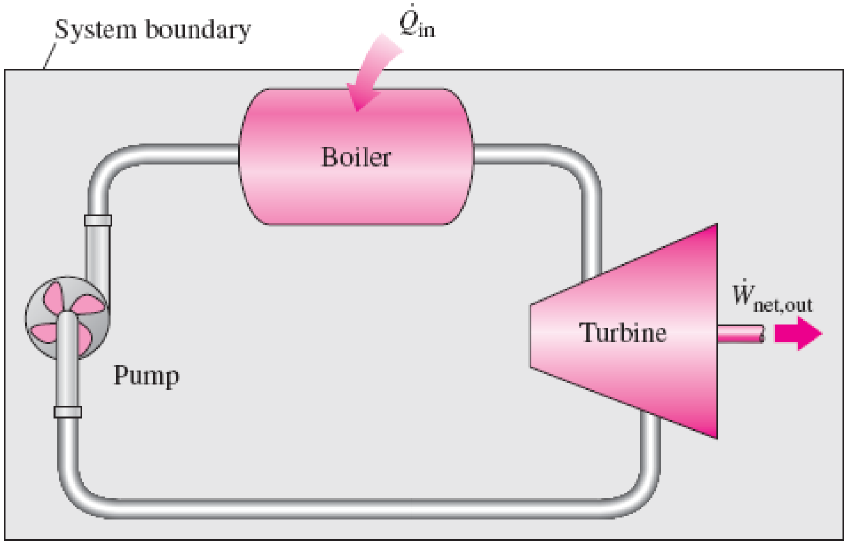
$$= 45{,}000 \ {}^{\text{kJ}}\!/_{\text{h}}$$



PERPETUAL-MOTION MACHINES



A perpetual-motion machine that violates the first law (PMM1).



A perpetual-motion machine that violates the second law of thermodynamics (PMM2).

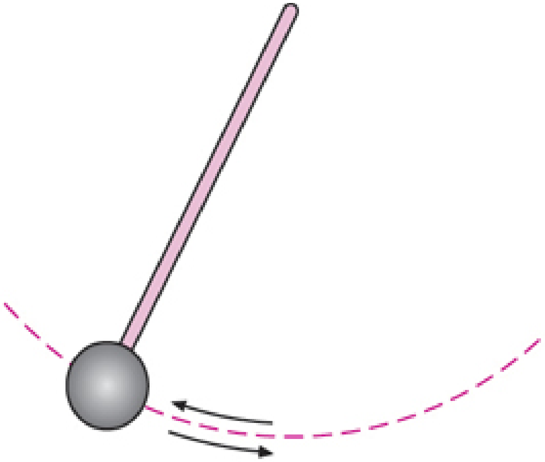
Perpetual-motion machine: Any device that violates the first or the second law.

A device that violates the first law (by *creating* energy) is called a PMM1.

A device that violates the second law is called a PMM2.

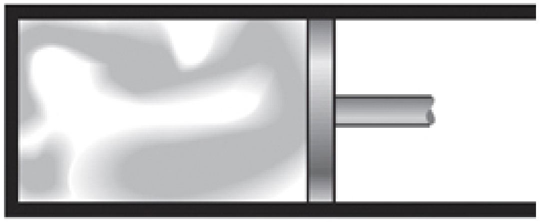
Despite numerous attempts, no perpetual-motion machine is known to have worked. ***If something sounds too good to be true, it probably is***.

REVERSIBLE AND IRREVERSIBLE PROCESSES:



(*a*) Frictionless pendulum

A pendulum could be a reversible process if it were frictionless



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

- **A process is <u>reversible</u> if, after it has occurred , both the system and the surroundings can be returned to their original states.**

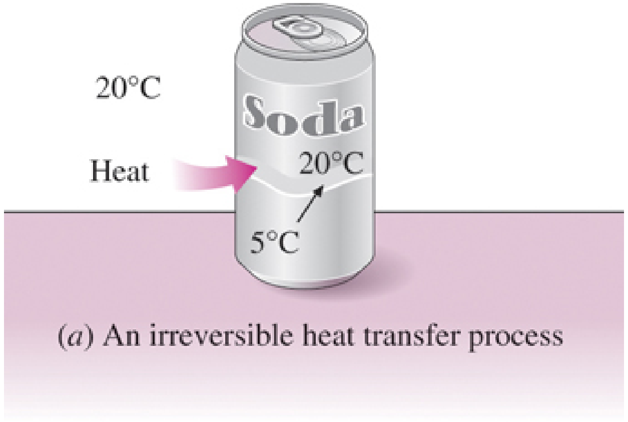
- **If the system can not be restored to its initial state then the process is called <u>irreversible</u>.**

- **The reversible processes do not occur in nature. They are only idealization of actual processes.**

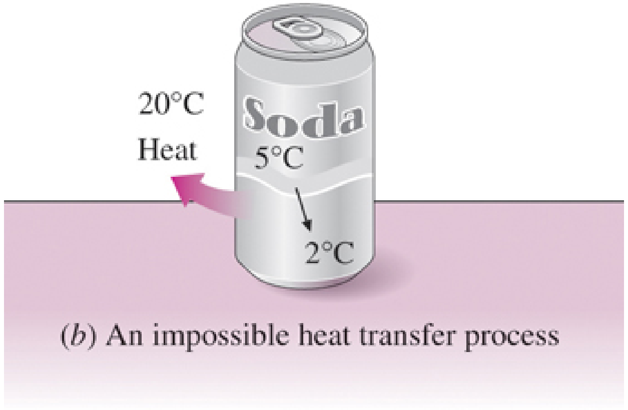
- **Reversible processes are important because they provide the maximum work from work-producing devices and the minimum work input to devices that absorb work to operate . (theoretical limitation of performance)**

- **The more close we approximate a reversible process the better.**

Irreversibilities:



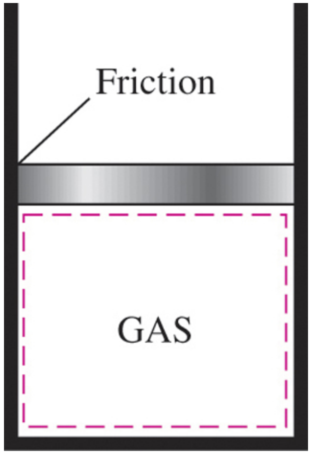
(*a*) An irreversible heat transfer process



(*b*) An impossible heat transfer process

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

- **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.**
- **When designing something we try to lower the irrevesibilities.**



Friction renders a process irreversible.

THE CARNOT CYCLE:

- **A reversible cycle, i.e. limiting case for both an engine and a refrigerator.**

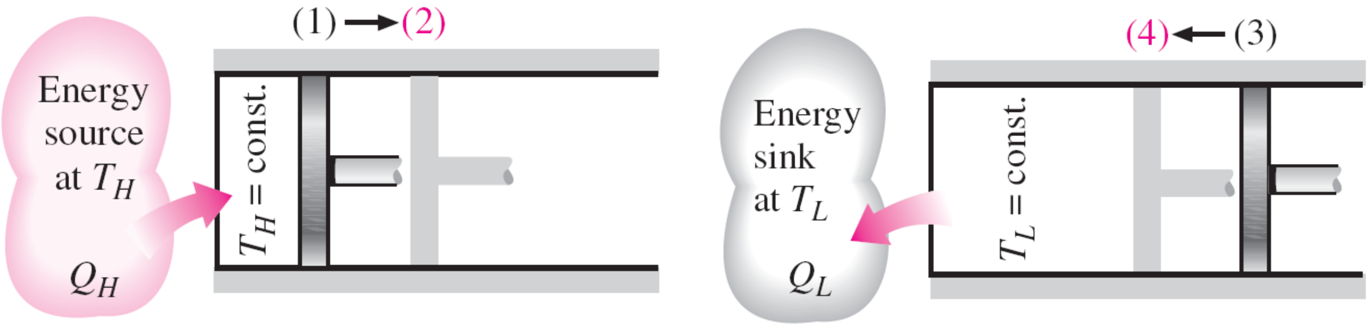
- **The Carnot engine is the heat engine that converts heat into work with the highest possible efficiency.**

- **The Carnot refrigerator is the refrigerator that uses the minimum amount of work to cool a space**

- **The Canot cycle is composed of four reversible processes(two isothermal and two adiabatic).**

- **Can be expected either in a closed system or a steady-flow system.**

Gas in an adiabatic piston-cylinder device:



(*a*) Process 1-2

(*c*) Process 3-4

(*b*) Process 2-3

(*d*) Process 4-1

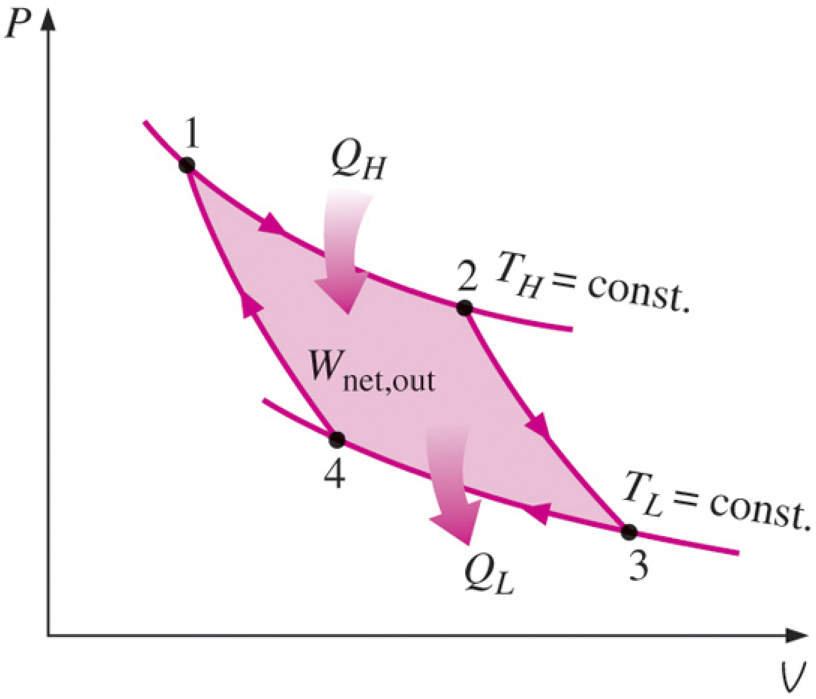
Execution of the Carnot cycle in a closed system.

Reversible Isothermal Expansion (process 1-2, T_H = constant)

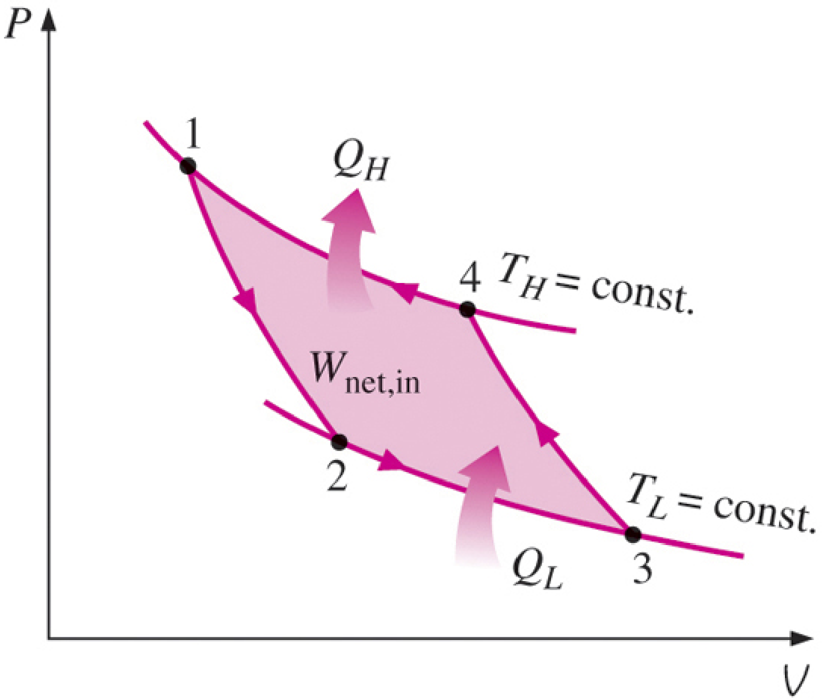
Reversible Adiabatic Expansion (process 2-3, temperature drops from T_H to T_L)

Reversible Isothermal Compression (process 3-4, T_L = constant)

Reversible Adiabatic Compression (process 4-1, temperature rises from T_L to T_H)



P-V diagram of the Carnot cycle.



P-V diagram of the reversed Carnot cycle.

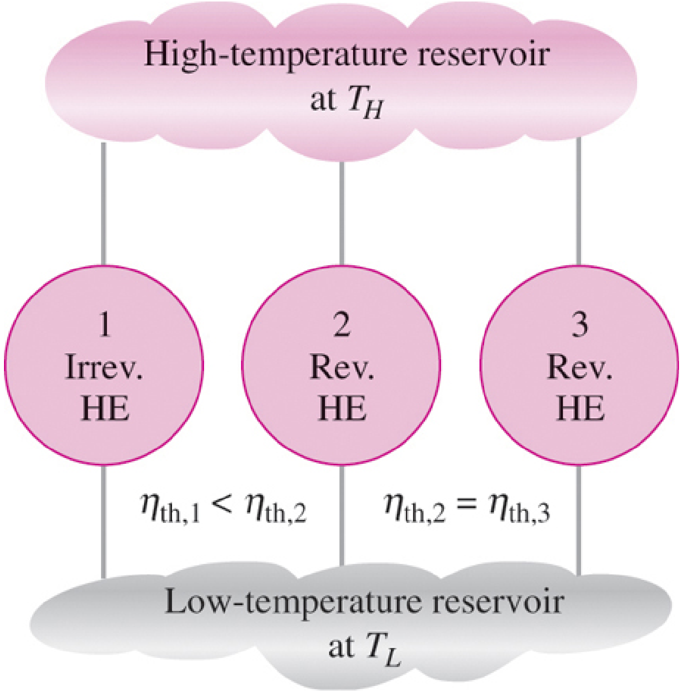
The Reversed Carnot Cycle:

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

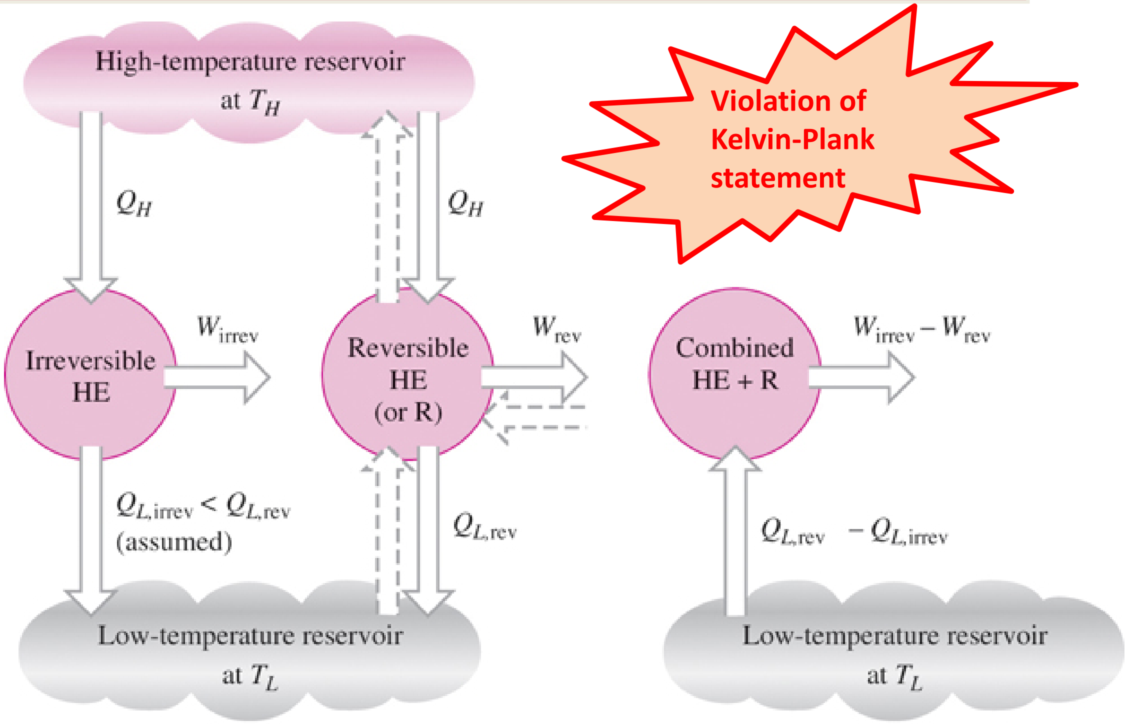
Therefore, all the processes that comprise it can be *reversed*, in which case it becomes the Carnot refrigeration cycle.

THE CARNOT PRINCIPLES:

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 principles.



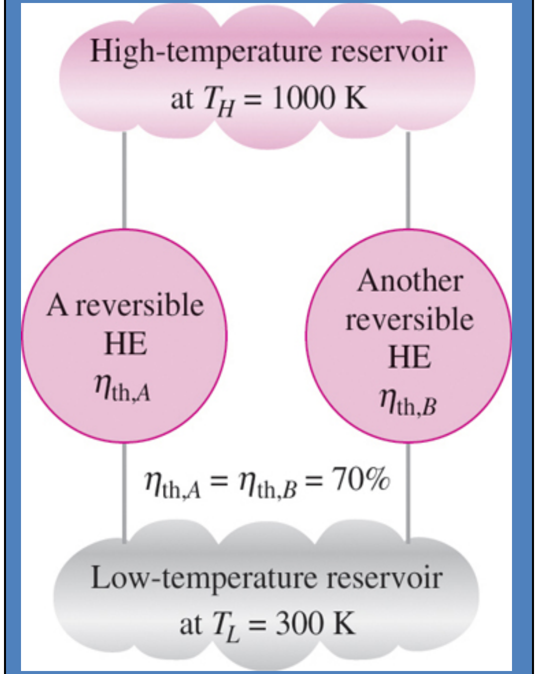
Violation of Kelvin-Plank statement

(*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.

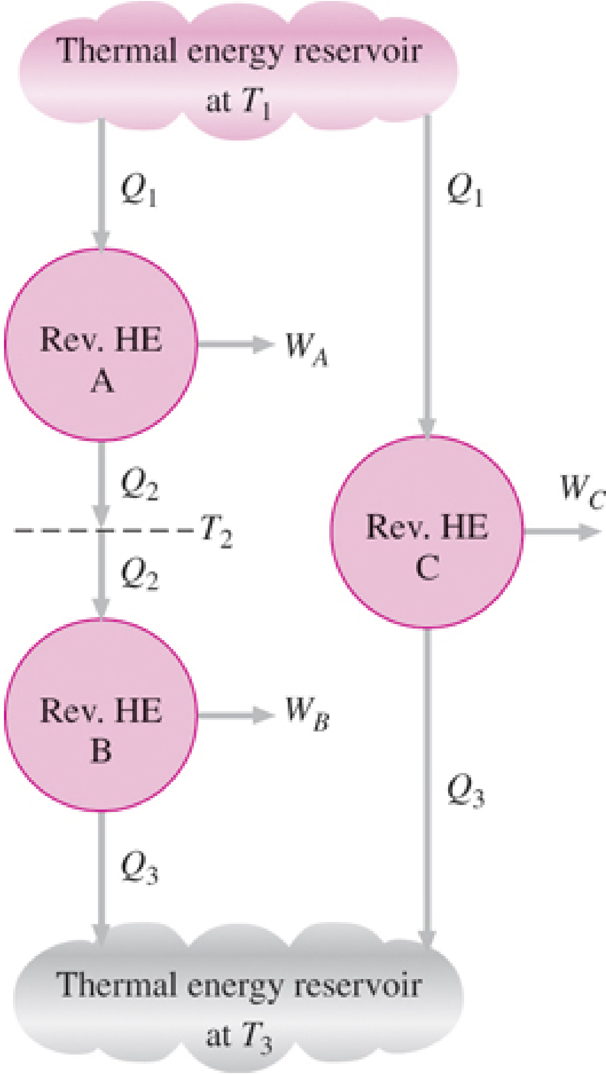
THE THERMODYNAMIC TEMPERATURE SCALE:



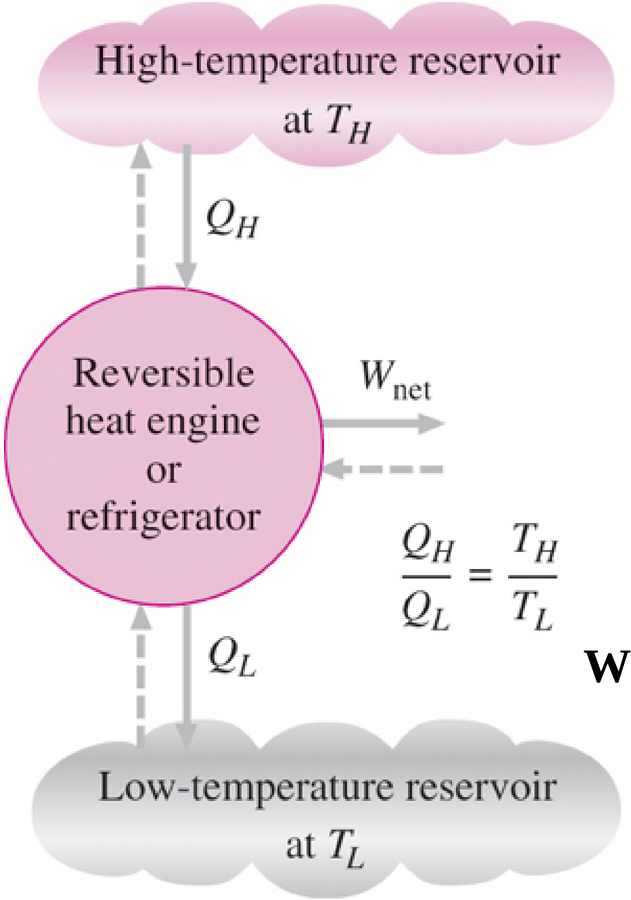
All reversible heat engines operating between the same two reservoirs have the same efficiency.

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.



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

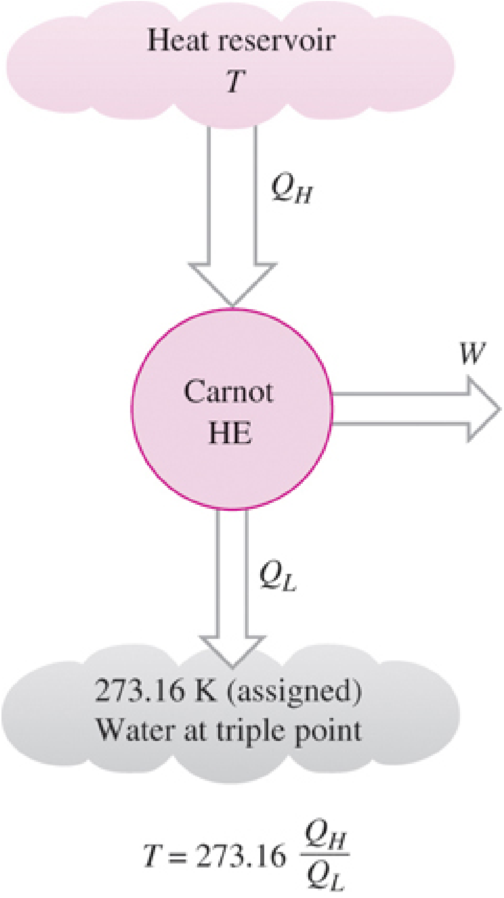


For a reversible heat engine operating between two reservoirs:

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

With Kelvin scale → $\phi(T) = T$

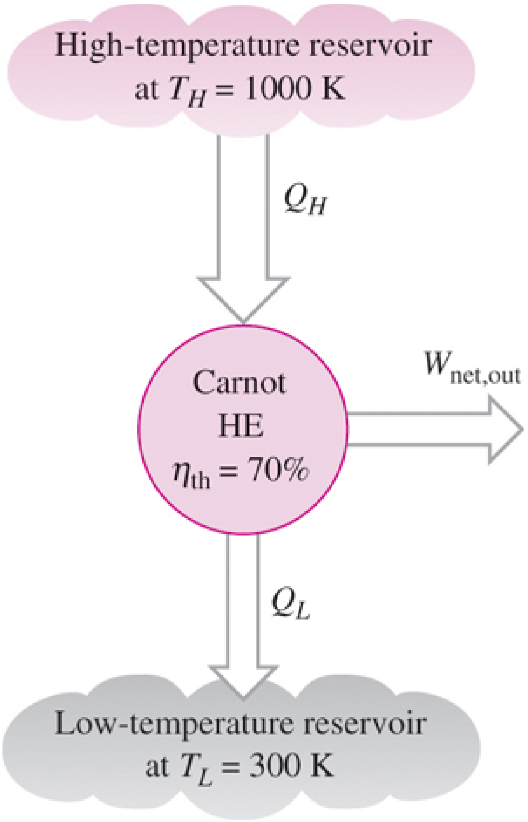
$$\left(\frac{Q_H}{Q_L}\right) = \frac{T_H}{T_L}$$



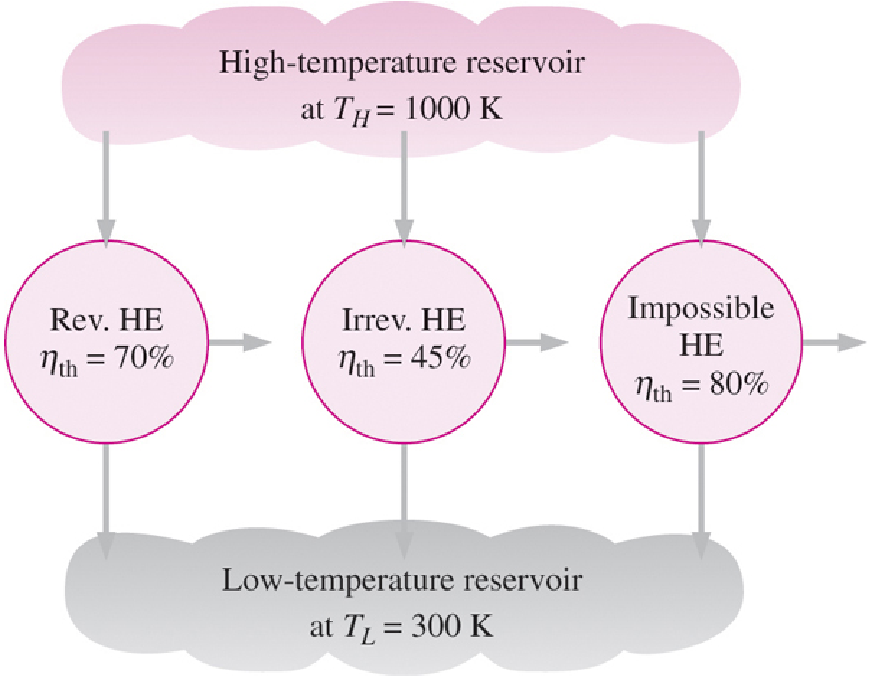
For reversible cycles, the heat transfer ratio Q_H/Q_L can be replaced by the absolute temperature ratio T_H/T_L.

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 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.

For any heat engine:

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

For a carnot engine(i.e. any reversible heat engine):

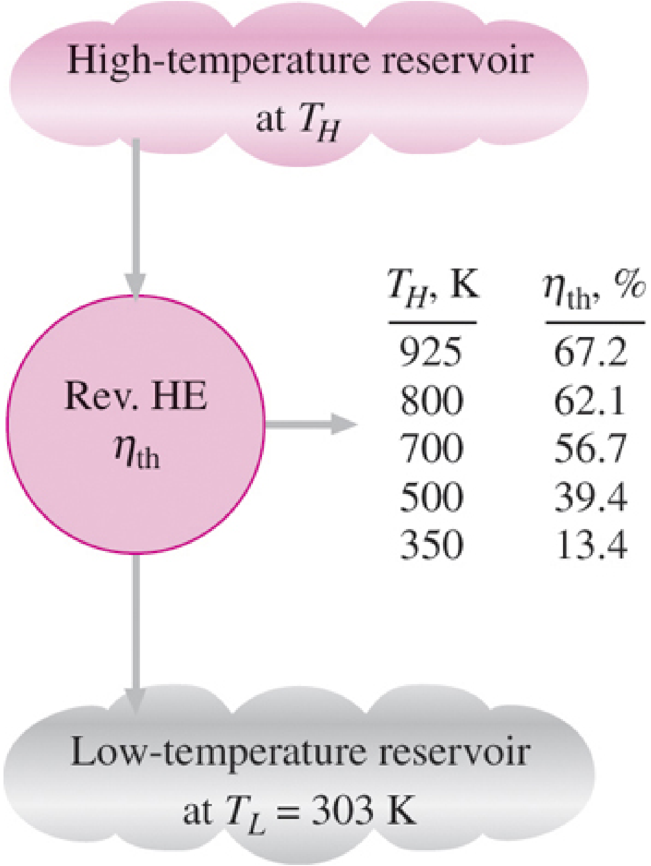
$$\eta_{th,rev} = 1 - \frac{T_L}{T_H}$$

Carnot efficiency: This is the highest efficiency a heat engine operating between the two reservoirs at T_L and T_H can have.

For a steam power plant operating between T_H=750K and T_L=300K the maximum efficiency is 60%.(In practicing they are under 40%)

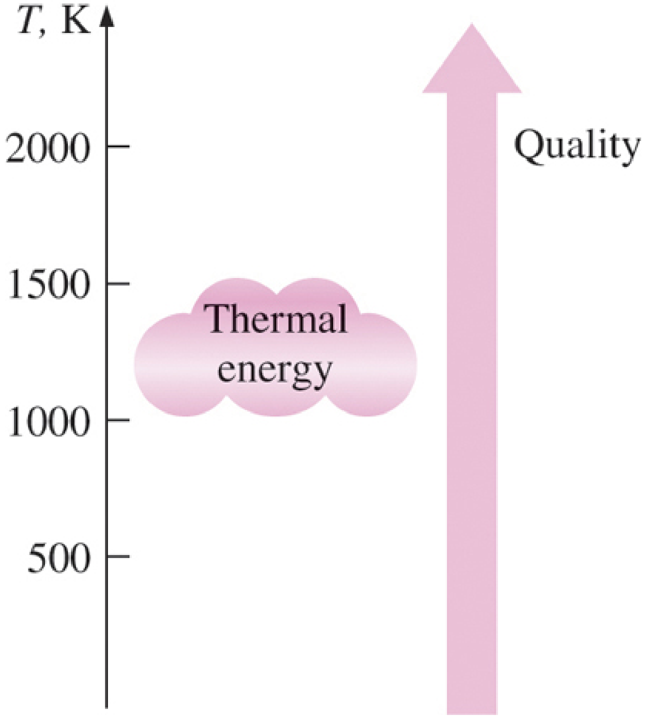
The Quality of Energy:

The carnot efficiency implies that, the higher the temperature TH, the higher the efficiency and hence the higher the quality of energy.



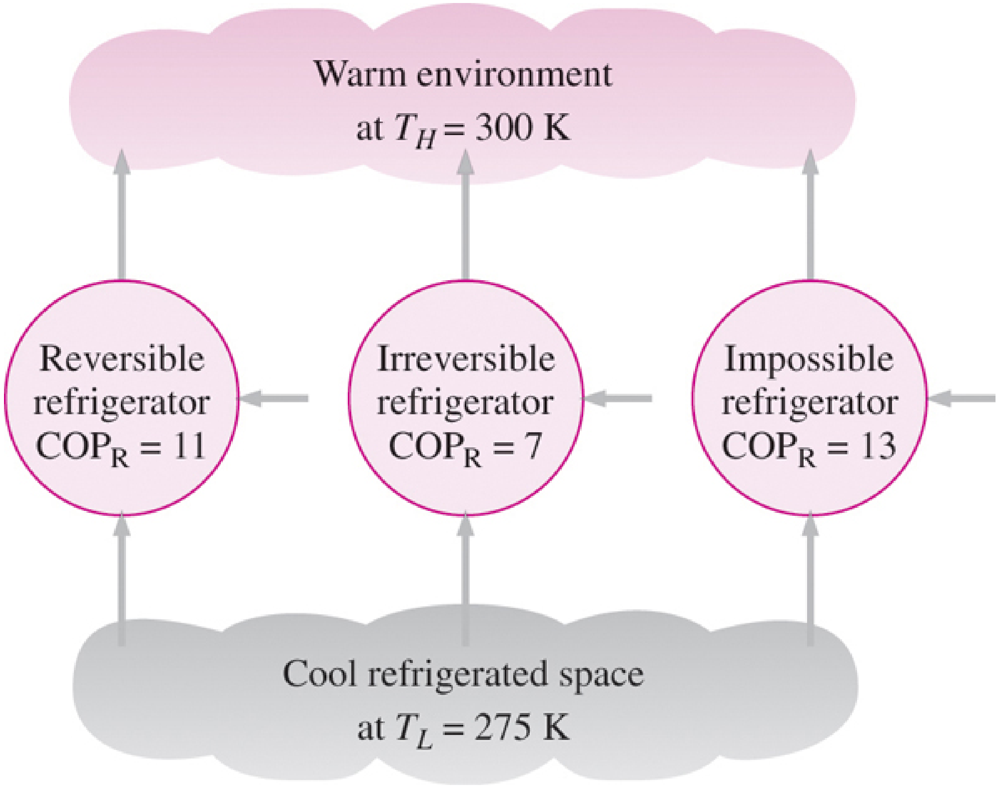
T_H, K	η_{th}, %
925	67.2
800	62.1
700	56.7
500	39.4
350	13.4

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



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

THE CARNOT REFRIGERATOR AND HEAT PUMP:



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

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

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

For <u>a carnot refrigerator:</u>

Q_H/Q_L **replace by** T_H/T_L

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

Highest COP between the limits T_L and T_H

For <u>a carnot heat pump:</u>

Q_L/Q_H **replace by** T_L/T_H

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