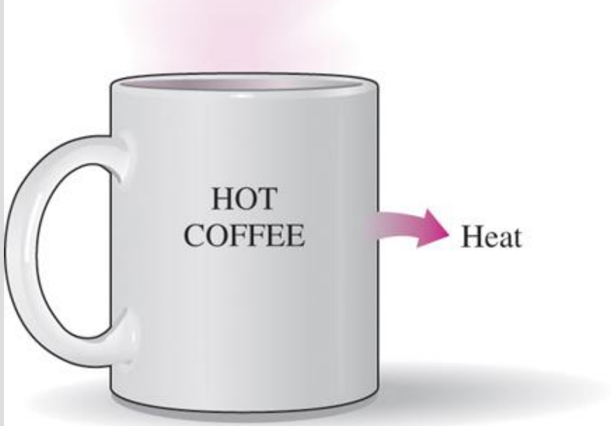
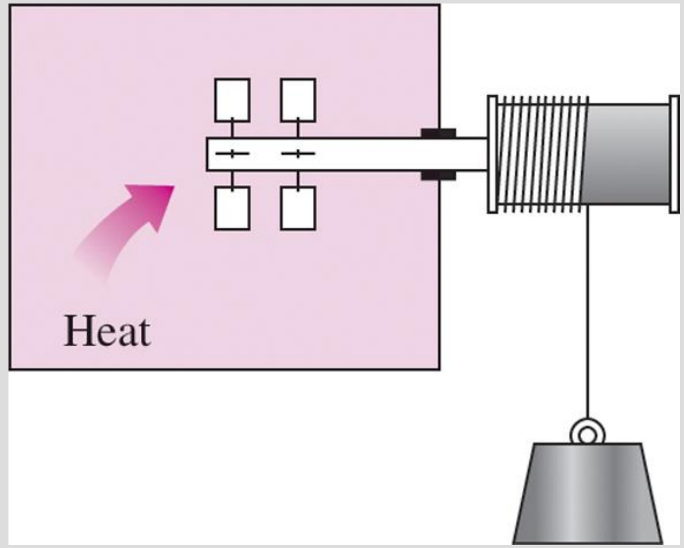
Chapter 6

THE SECOND LAW OF THERMODYNAMICS

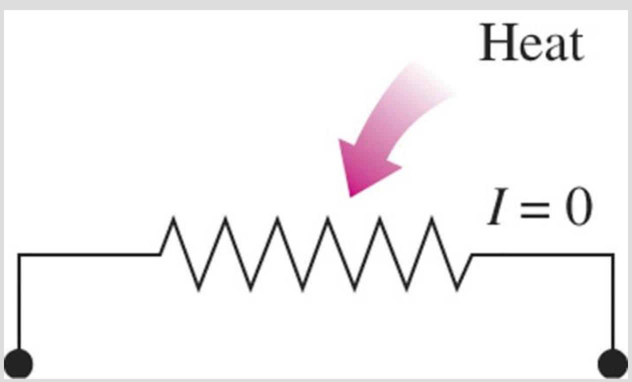
INTRODUCTION TO THE SECOND LAW

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





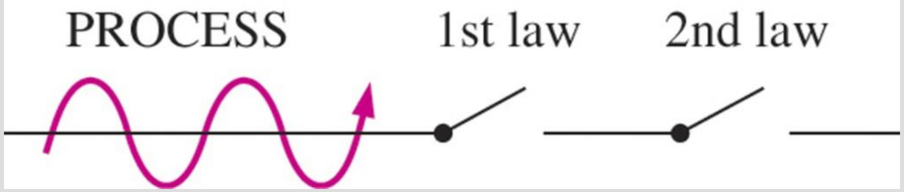
Transferring heat to a paddle wheel will not cause it to rotate.



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.

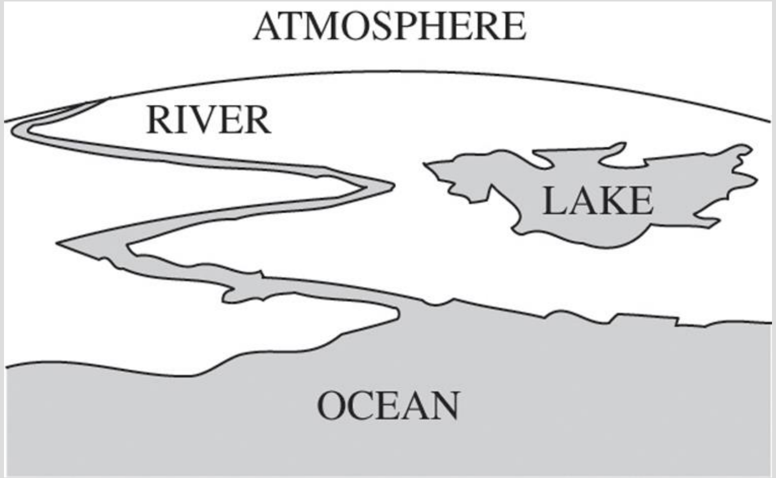


A process must satisfy both the first and second laws of thermodynamics to proceed.

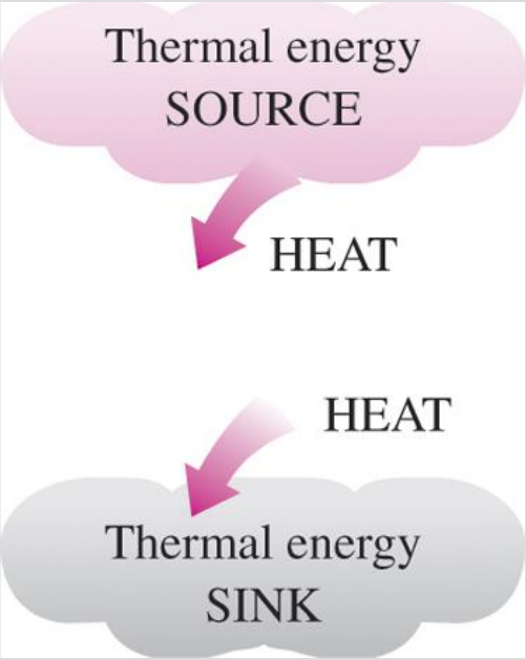
MAJOR USES OF THE SECOND LAW

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



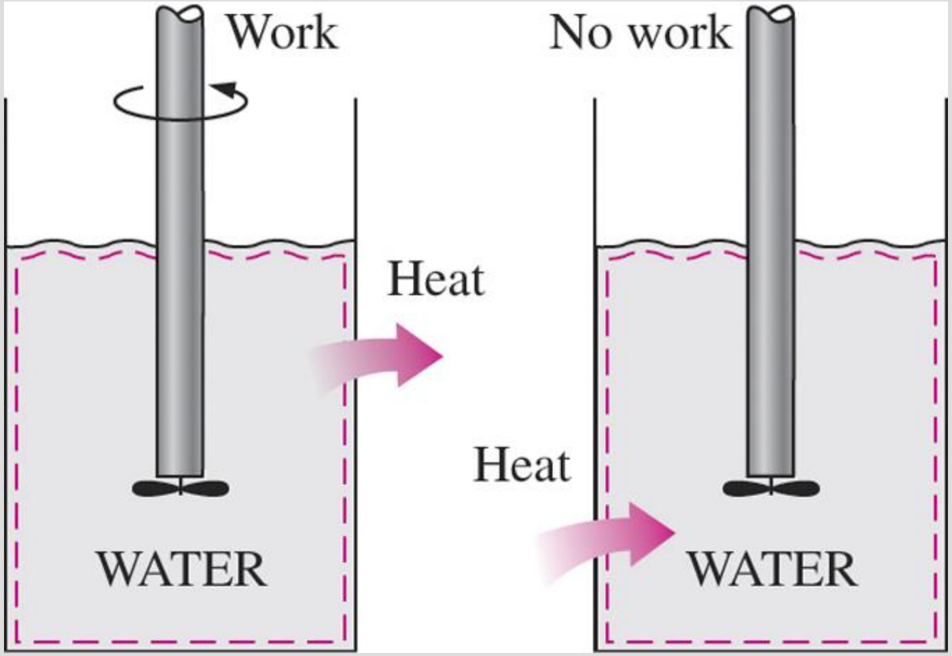
Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.



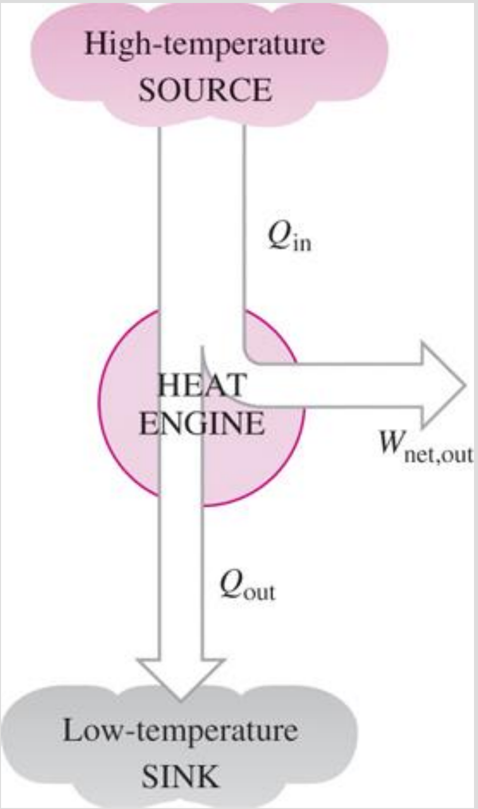
A source supplies energy in the form of heat, and a sink absorbs it.

- 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



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.

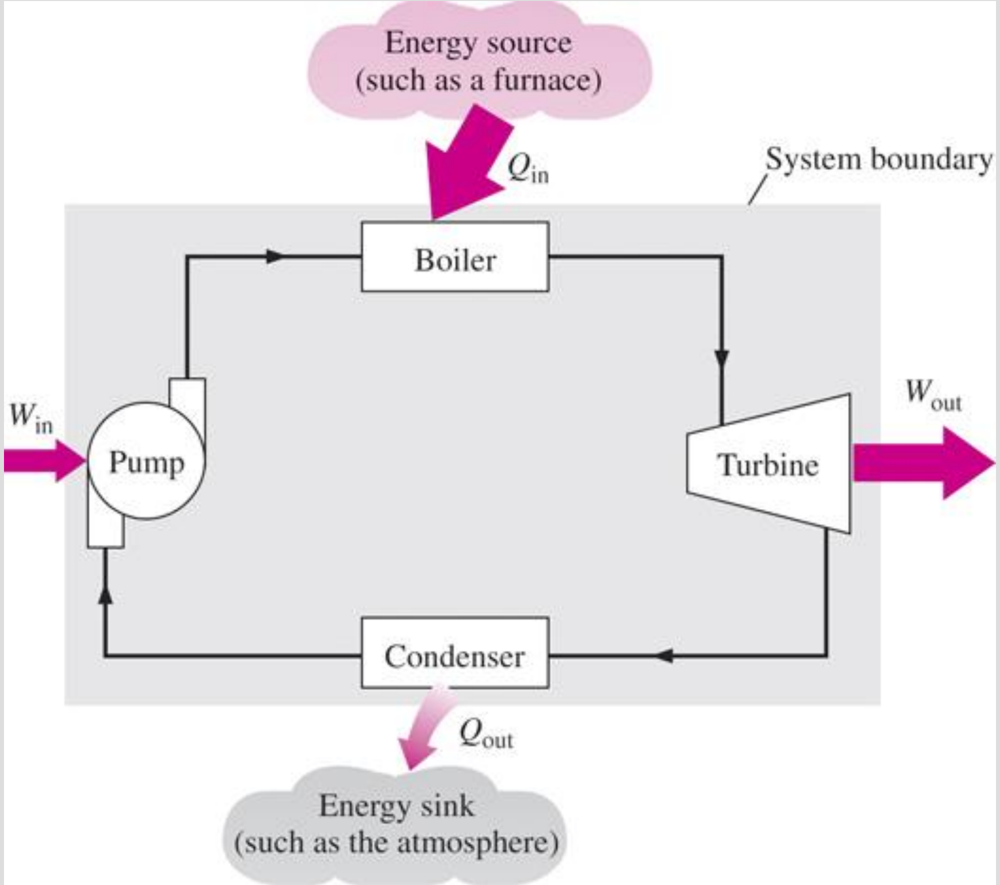
HEAT ENGINES

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**.

A steam power plant



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

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

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

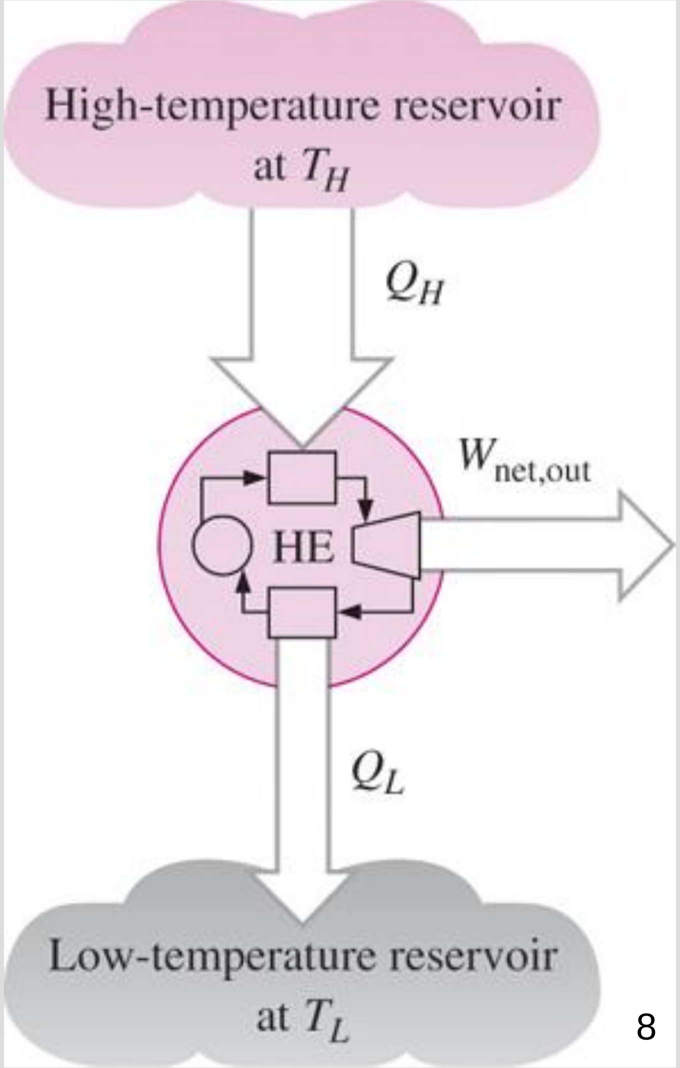
Thermal efficiency

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

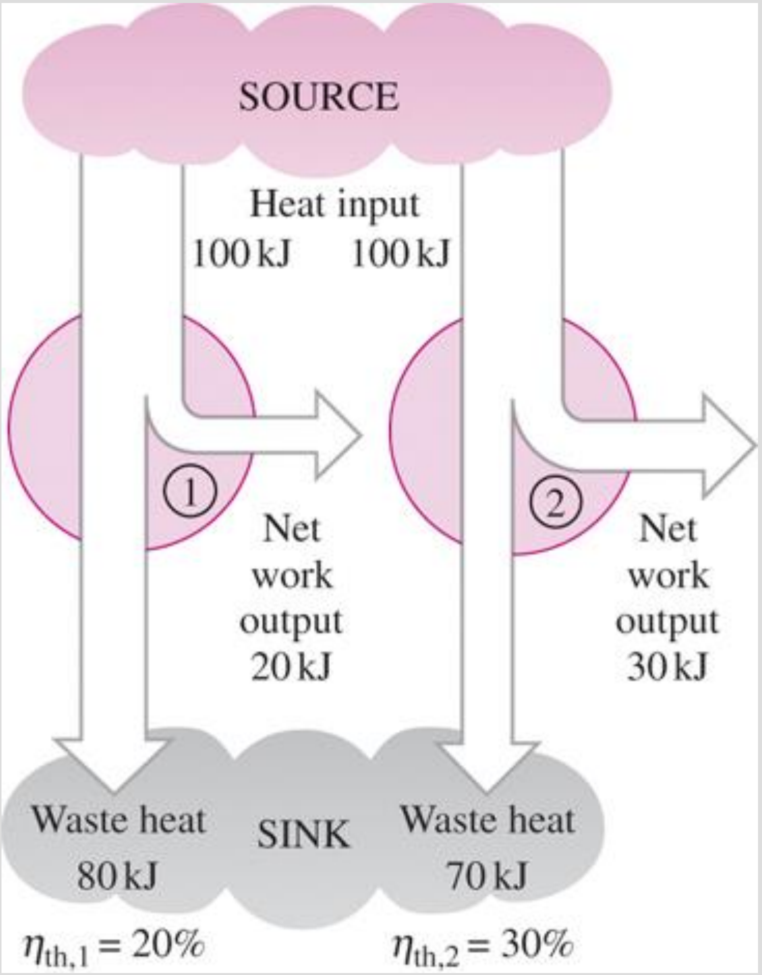
$$\eta_{th} = \frac{W_{net,out}}{Q_H}$$

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

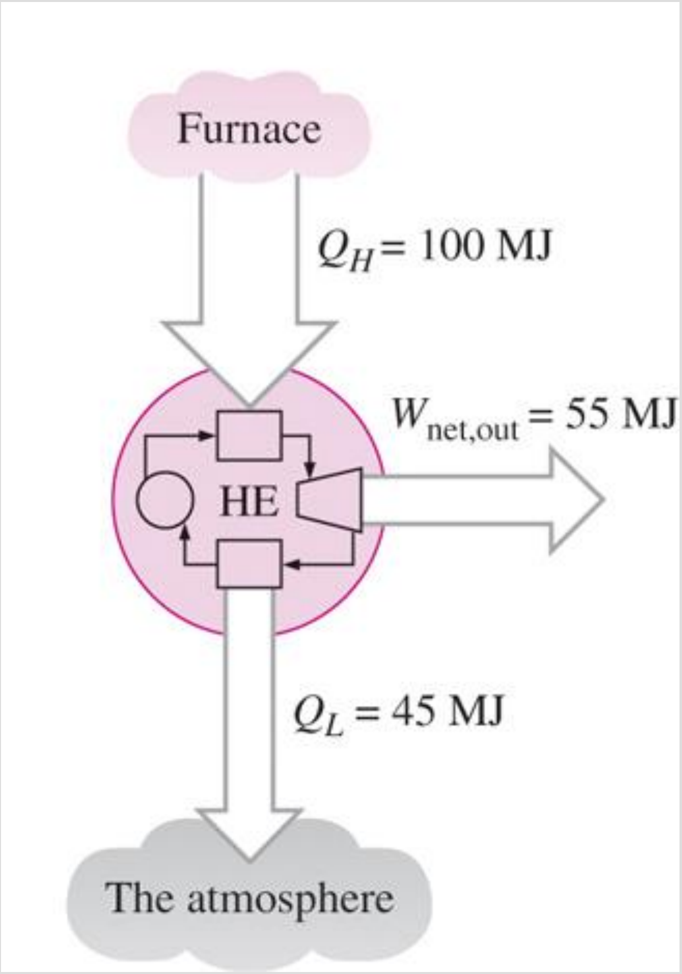
$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$



Thermal efficiency



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

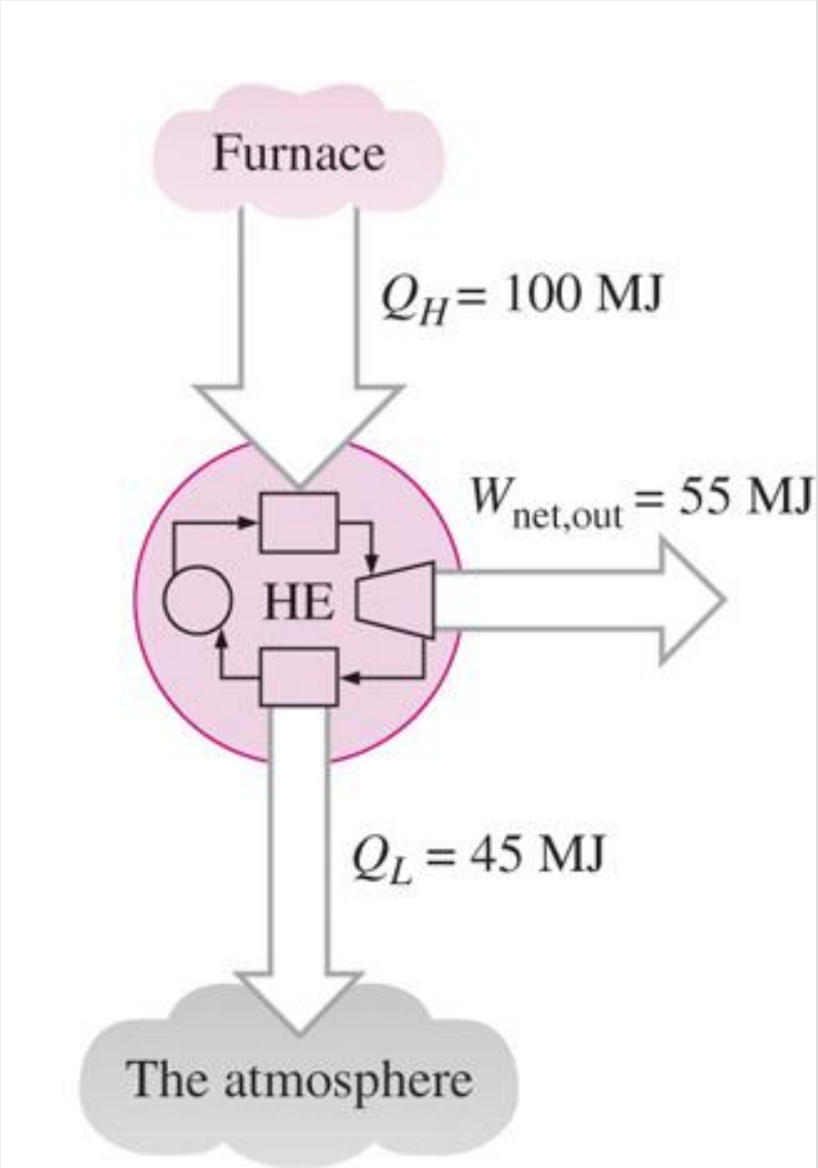


Even the most efficient heat engines reject almost one-half of the energy they receive as waste heat.

Can we save Q_{out}?

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.

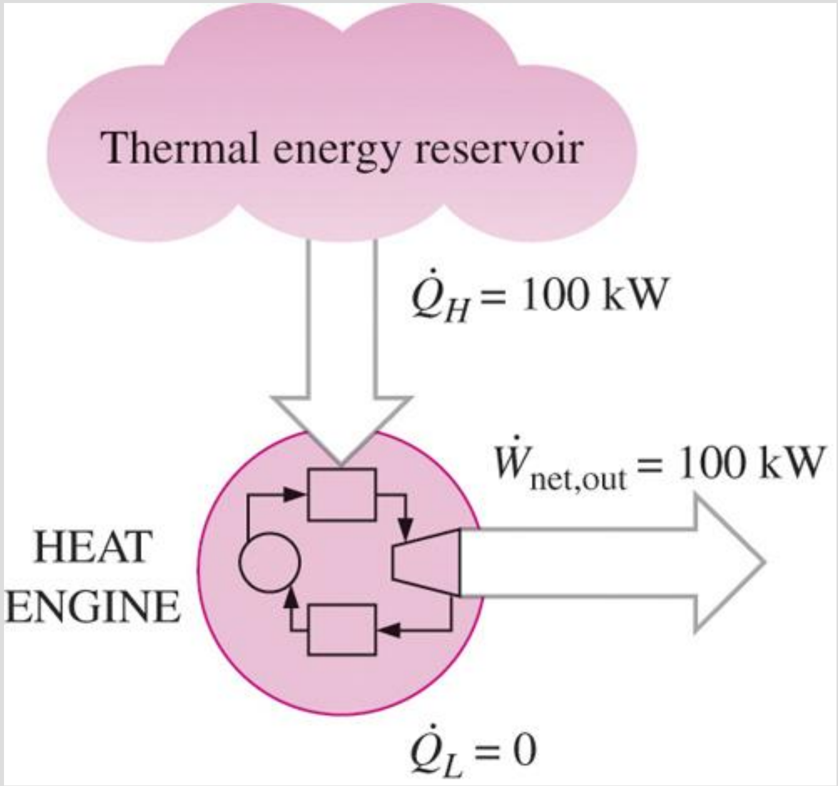
In a steam power plant, without a heat rejection process in a condenser, the cycle cannot be completed.



The Second Law of Thermodynamics: Kelvin–Planck Statement

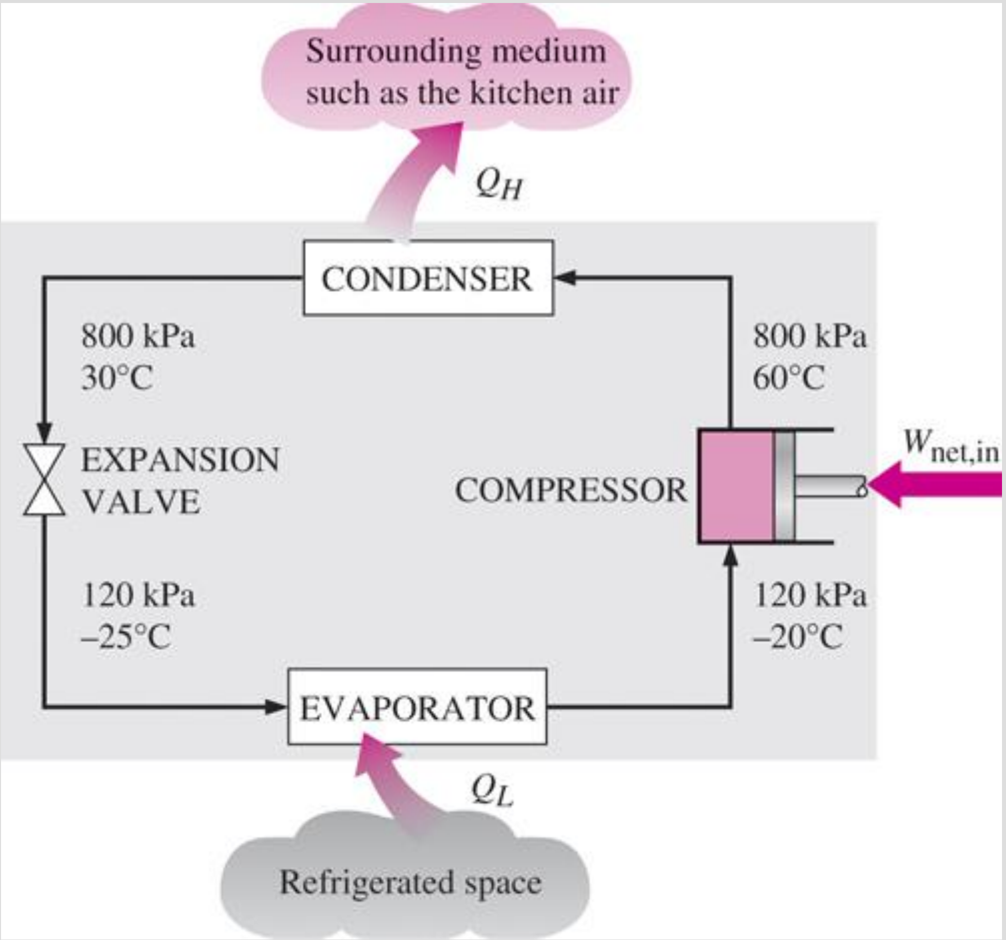
It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.

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*.

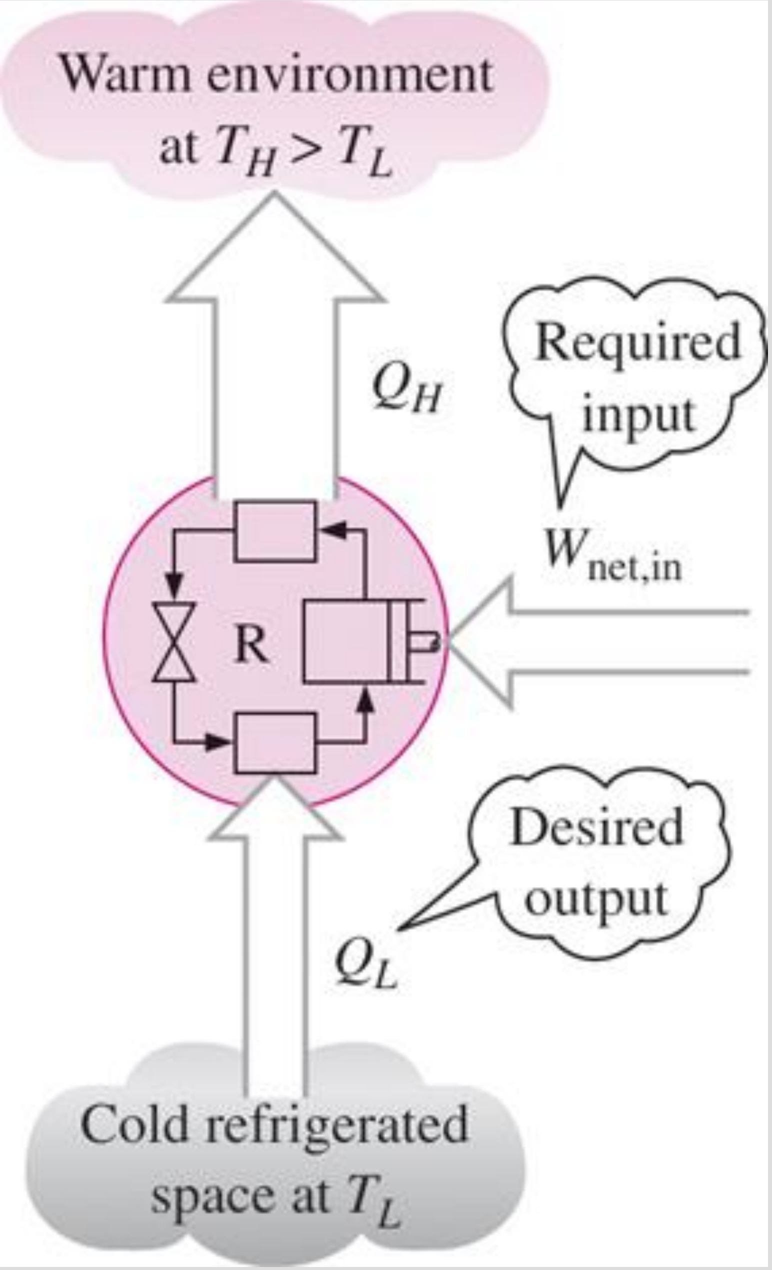


A heat engine that violates the Kelvin–Planck statement of the second law.

REFRIGERATORS AND HEAT PUMPS



- 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*.



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.

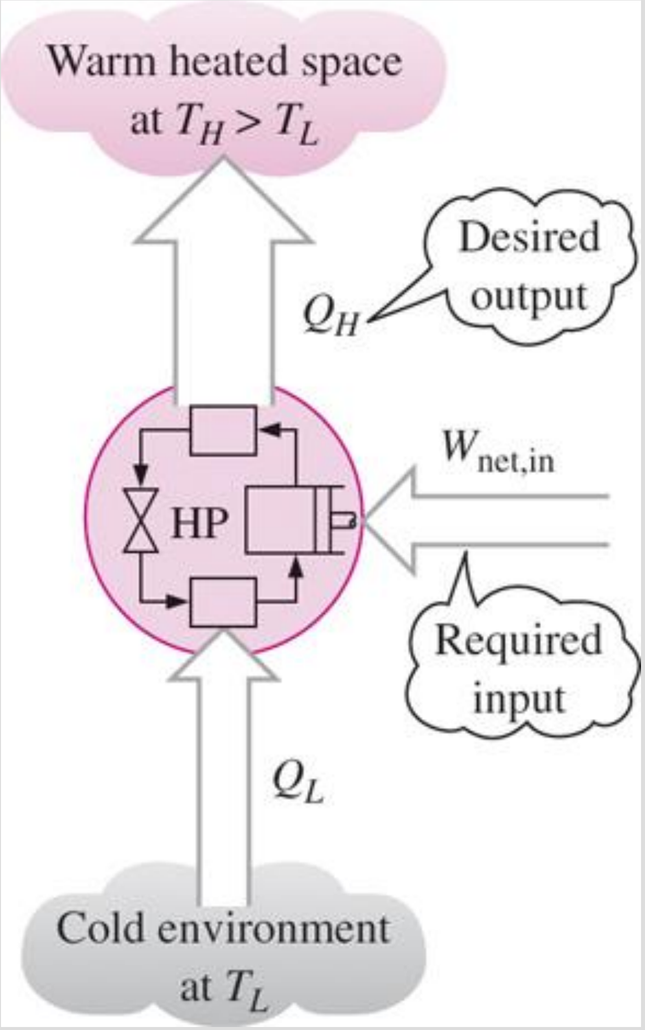
$$\mathrm{COP_R} = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_L}{W_{\text{net,in}}}$$

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

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

Can the value of $\mathrm{COP_R}$ be > 1?

Heat Pumps



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

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

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

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

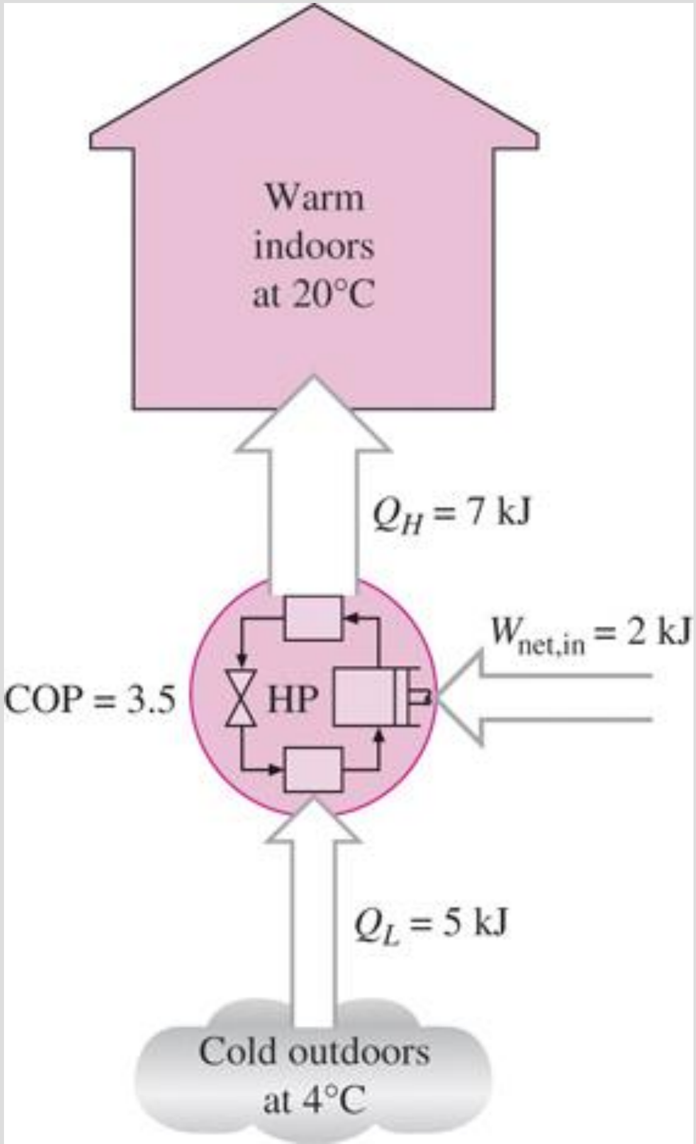
for fixed values of Q_L and Q_H

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

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

Heat Pumps

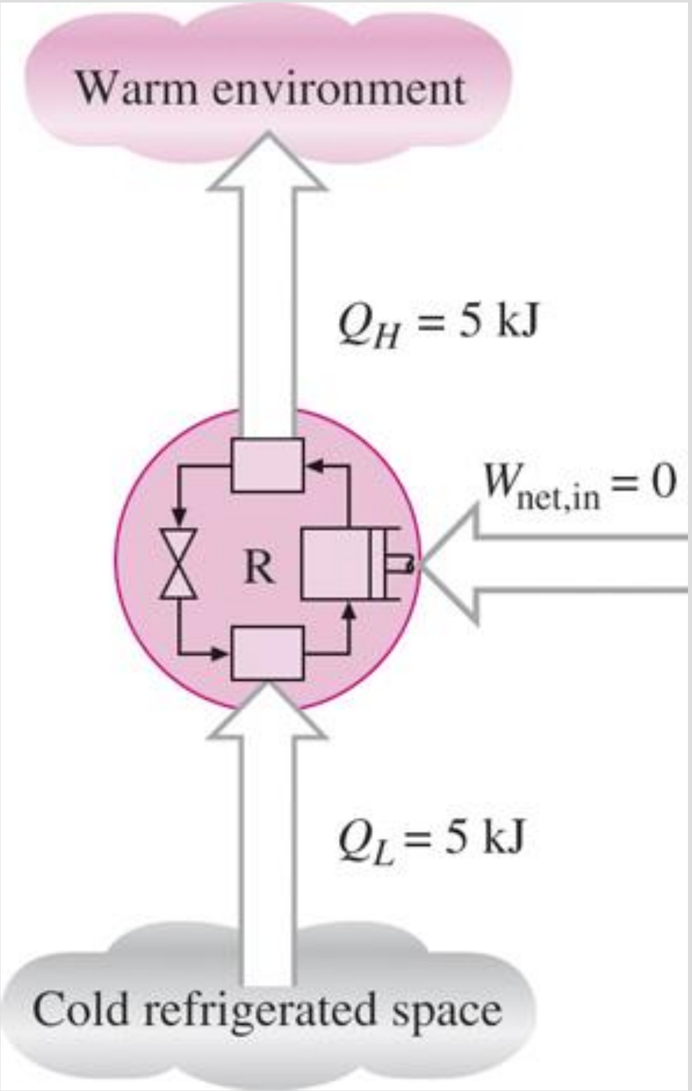
The work supplied to a heat pump is used to extract energy from the cold outdoors and carry it into the warm indoors.



The Second Law of Thermodynamics: Clasius Statement

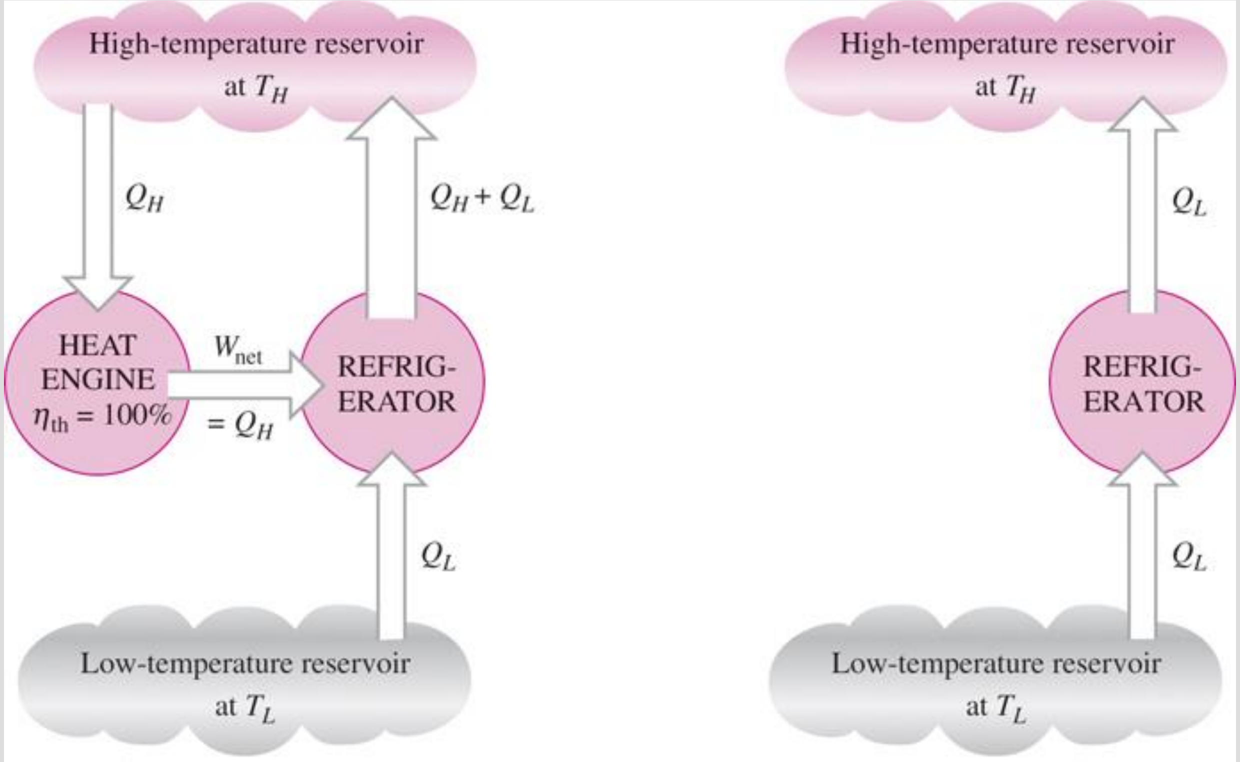
It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.

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



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

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.

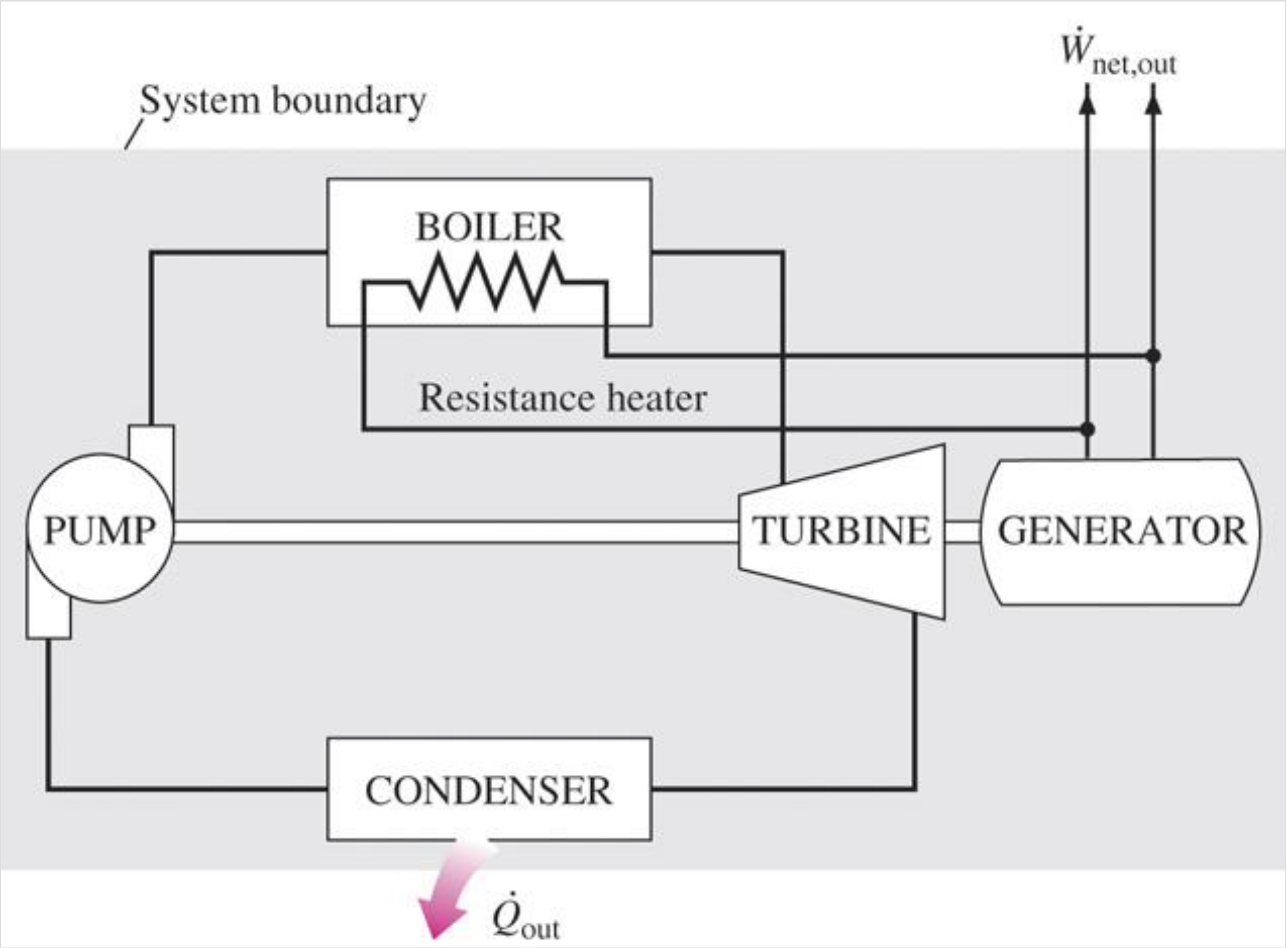
PERPETUAL-MOTION MACHINES

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.

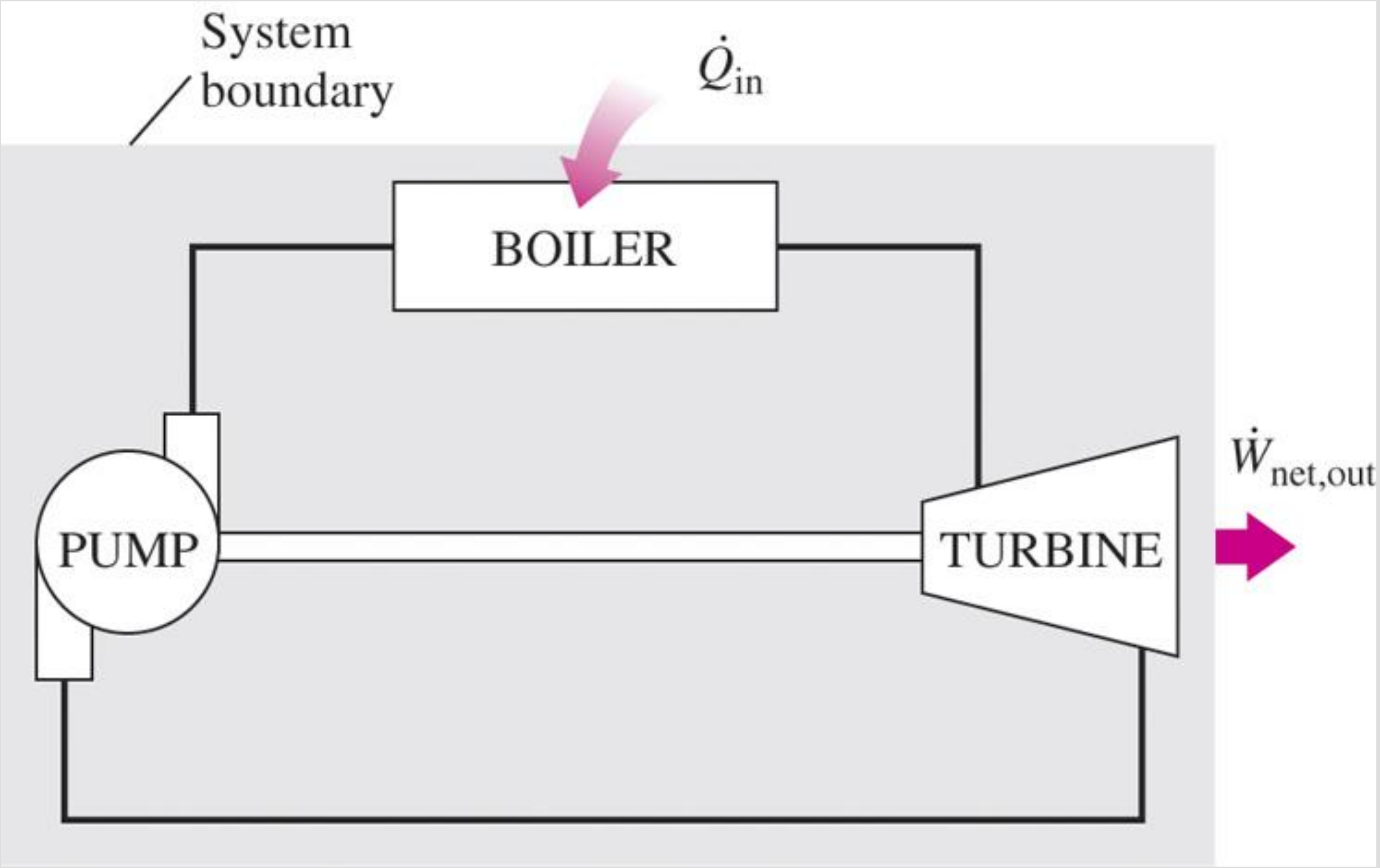
A device that violates the second law is called a PMM2.

PERPETUAL-MOTION MACHINES



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

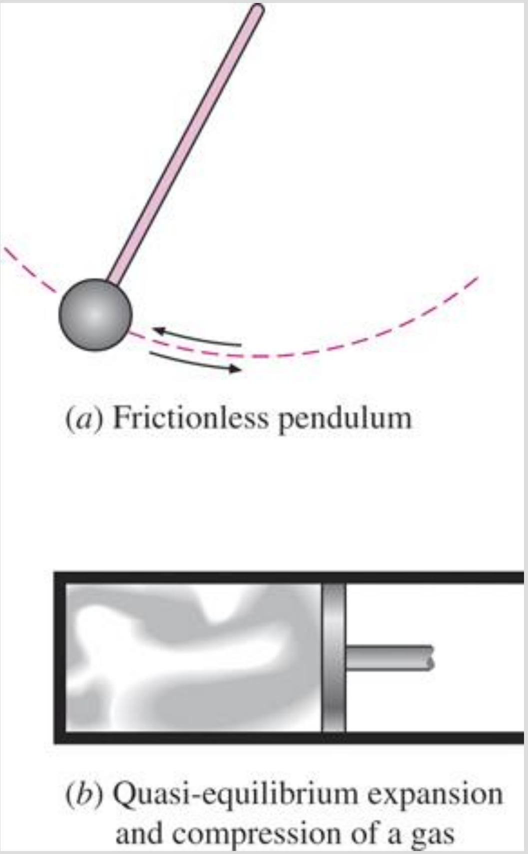
PERPETUAL-MOTION MACHINES



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

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.

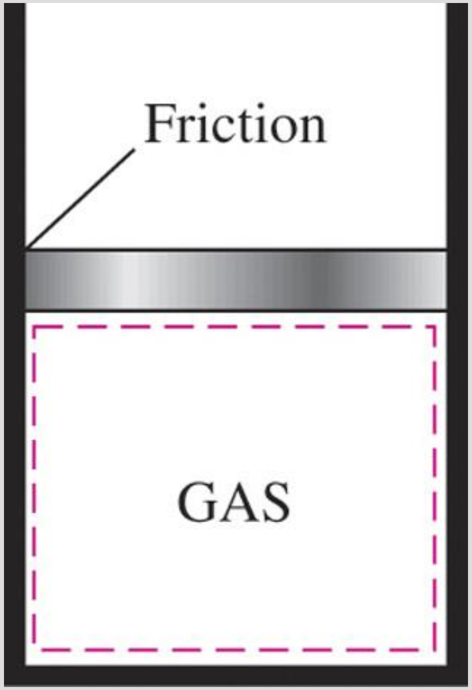


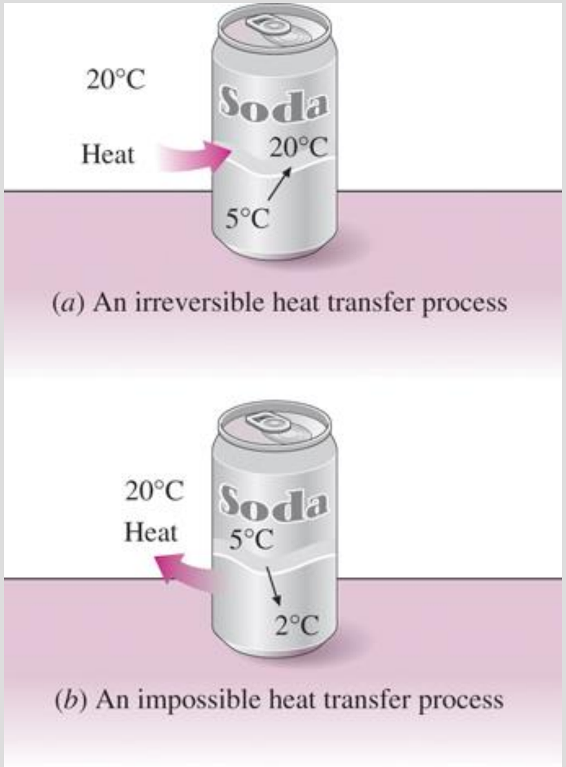
Two familiar reversible processes.

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

Types of Irreversibilities

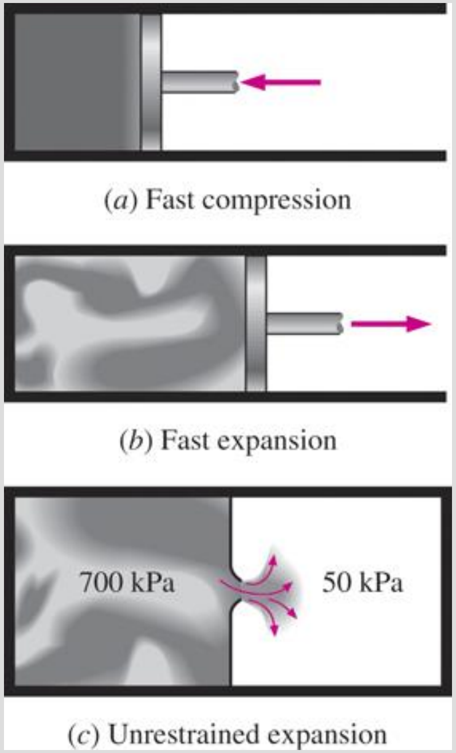
- The factors that cause a process to be irreversible are called **irreversibilities**.
- **Examples:** friction, heat transfer across a finite temperature difference, unrestrained expansion, mixing of two fluids,, electric resistance, inelastic deformation of solids, and chemical reactions.





(*a*) An irreversible heat transfer process

(*b*) An impossible heat transfer process



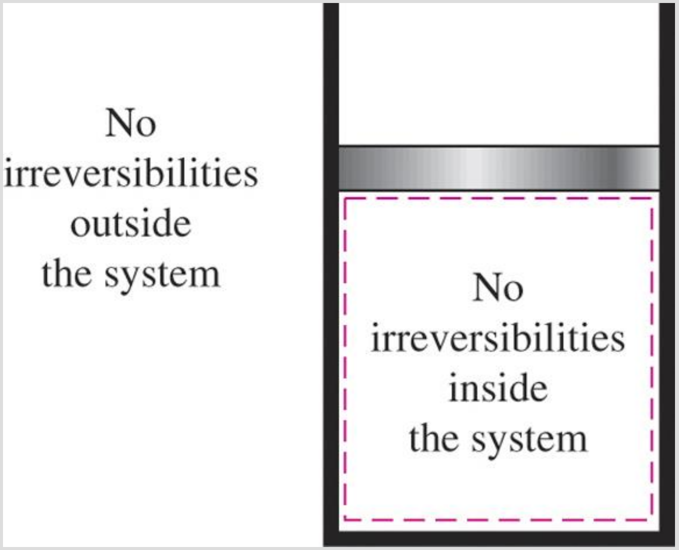
(*a*) Fast compression

(*b*) Fast expansion

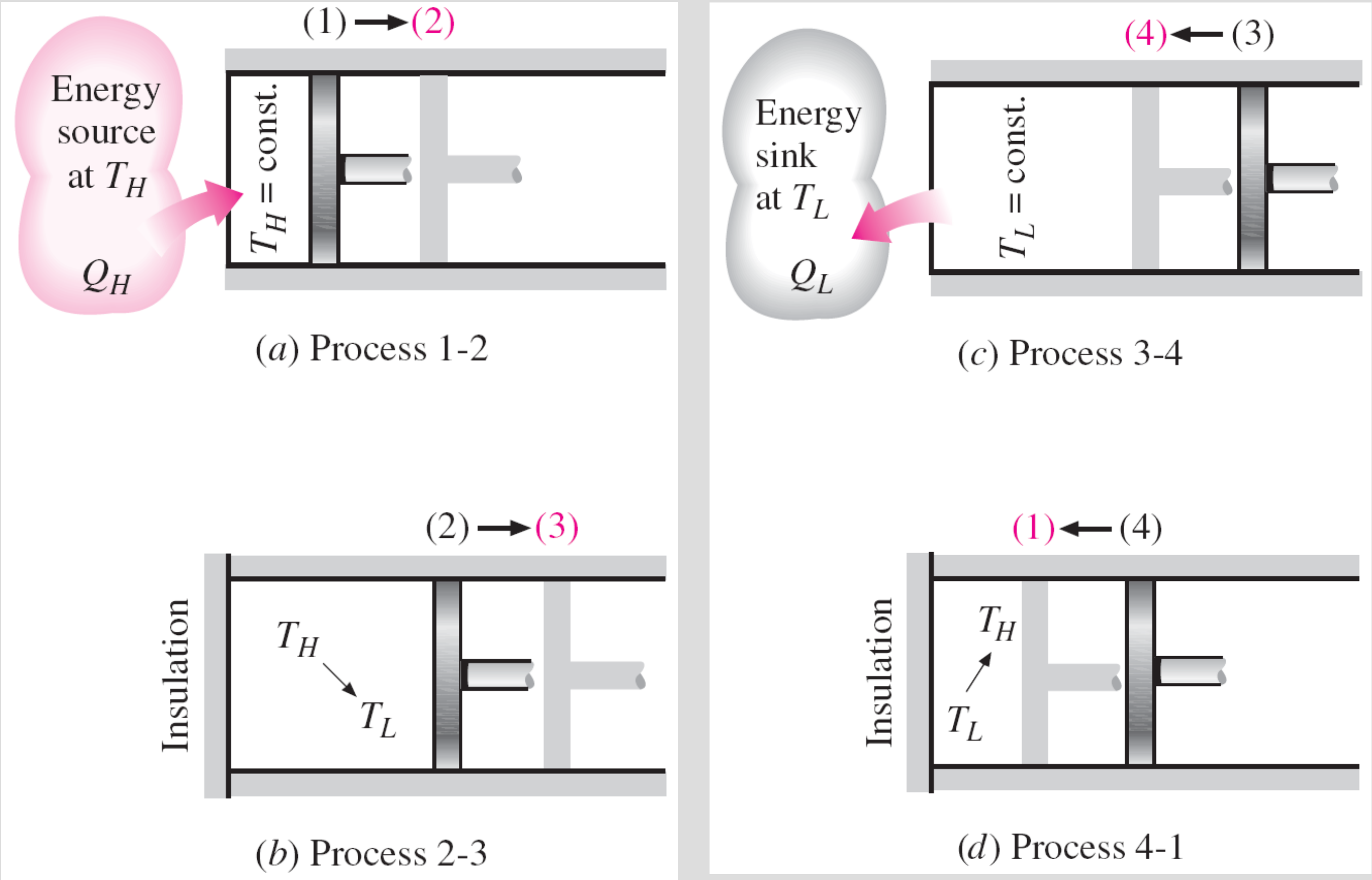
(*c*) Unrestrained expansion

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.

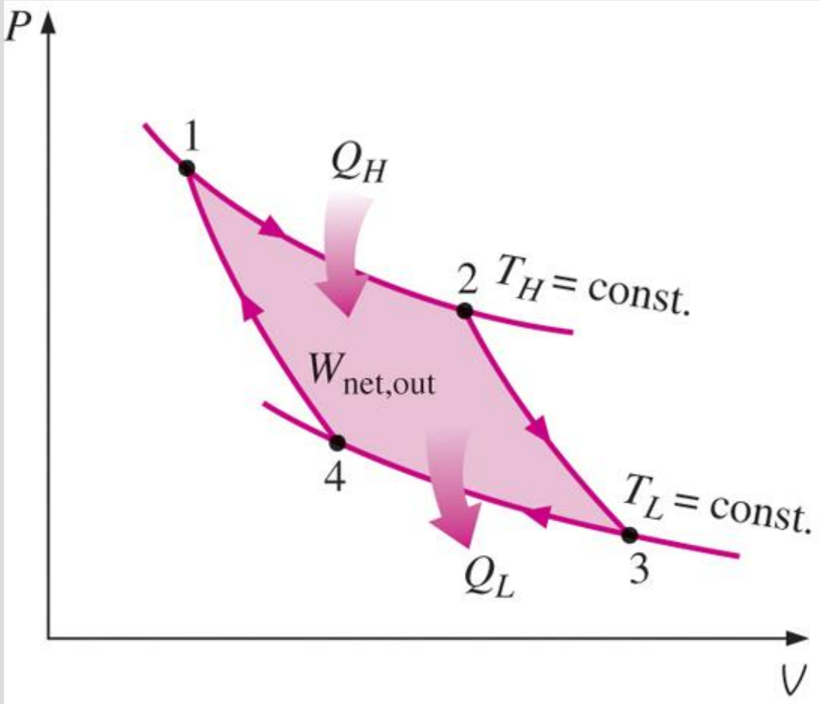


THE CARNOT CYCLE

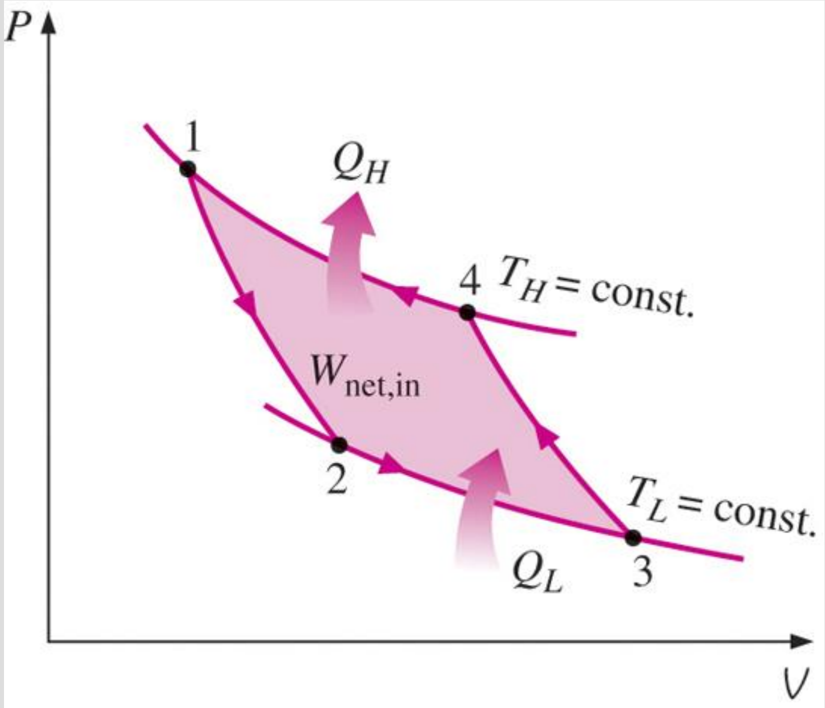


Execution of the Carnot cycle in a closed system.

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)



P-V diagram of the Carnot cycle.



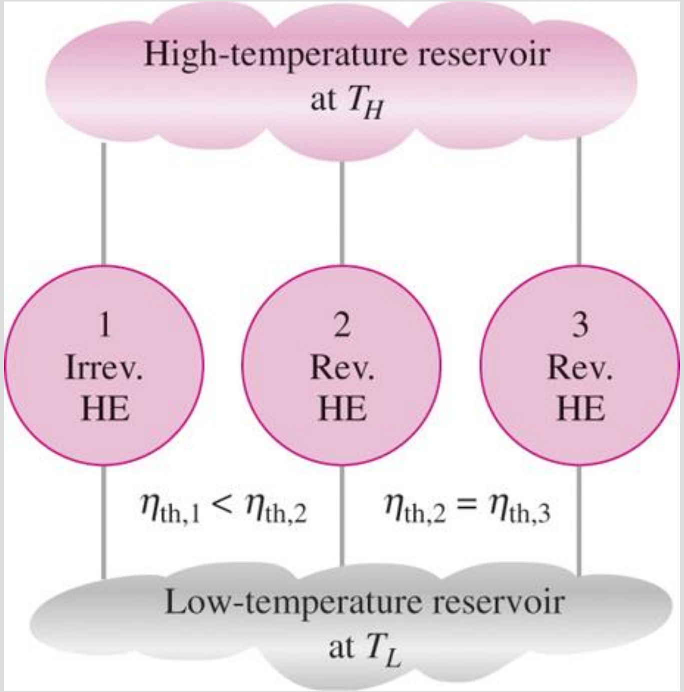
P-V diagram of the reversed Carnot cycle.

The Reversed Carnot Cycle

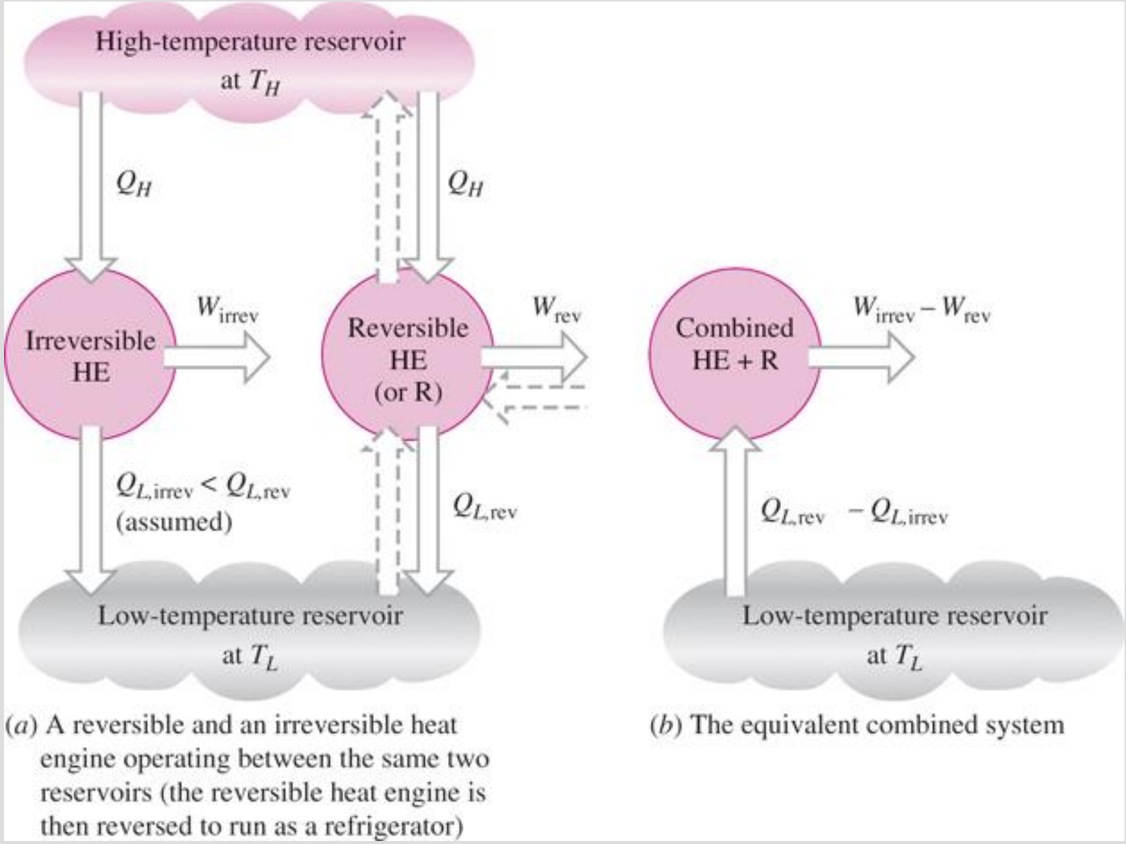
The Carnot heat-engine cycle is a totally reversible cycle.

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

THE CARNOT PRINCIPLES

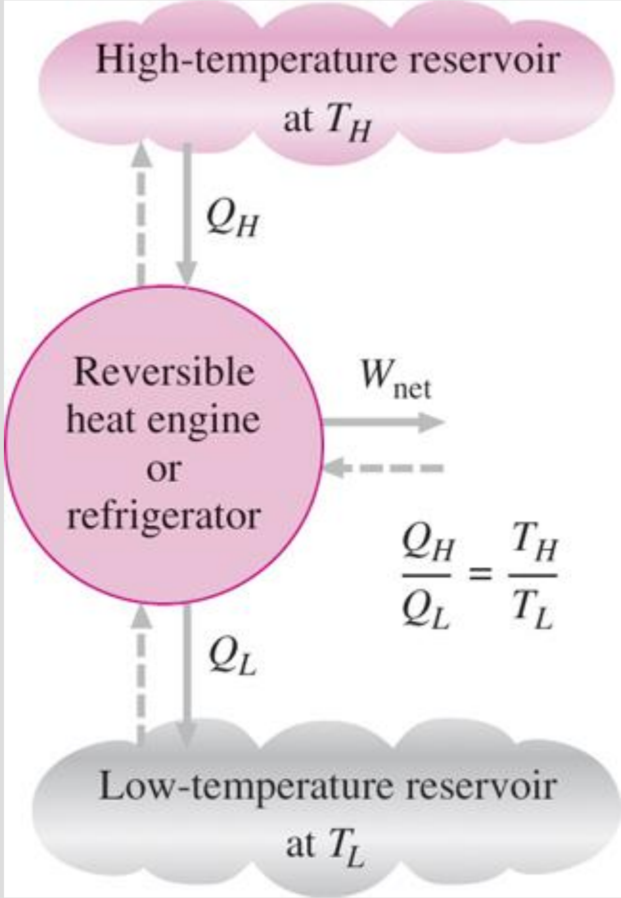


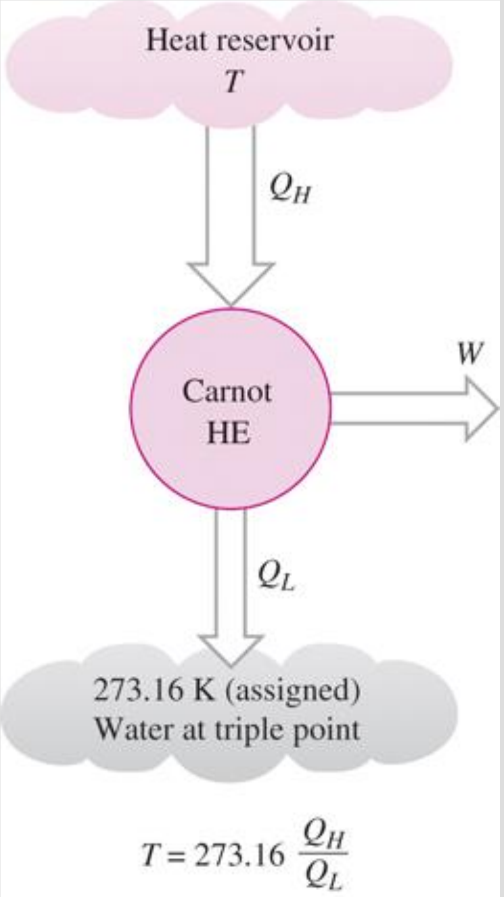
The Carnot principles.



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.





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

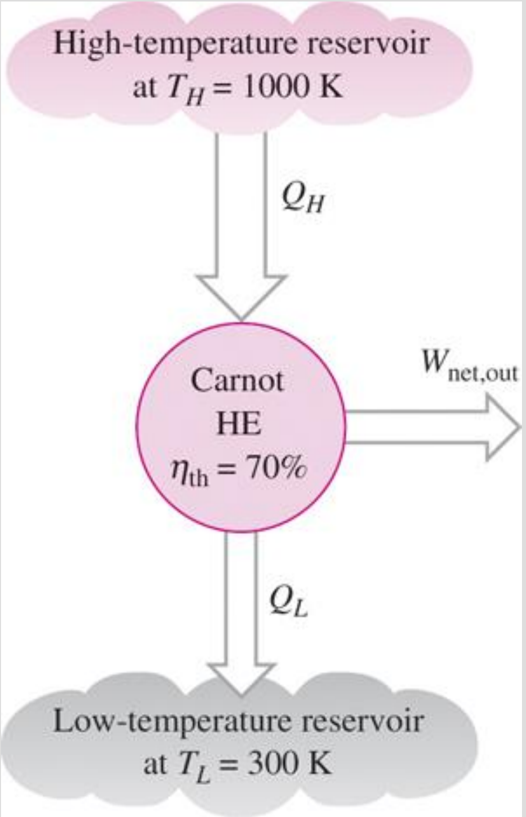
This temperature scale is called the **Kelvin scale**, and the temperatures on this scale are called **absolute temperatures**.

$$T(°C) = T(K) - 273.15$$

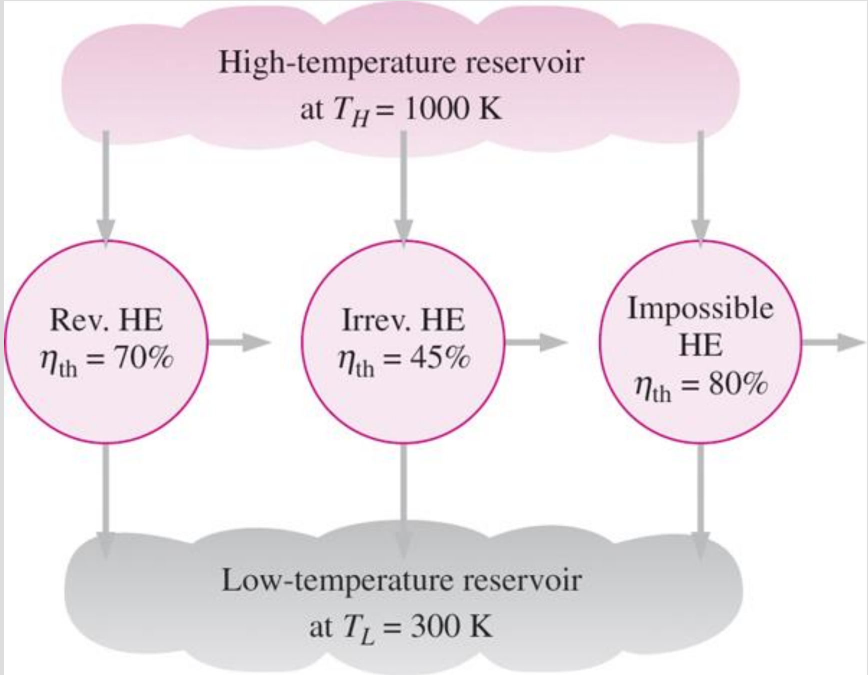
For reversible cycles, the heat transfer ratio Q_H/Q_L can be replaced by the absolute temperature ratio T_H/T_L.

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.

Any heat engine

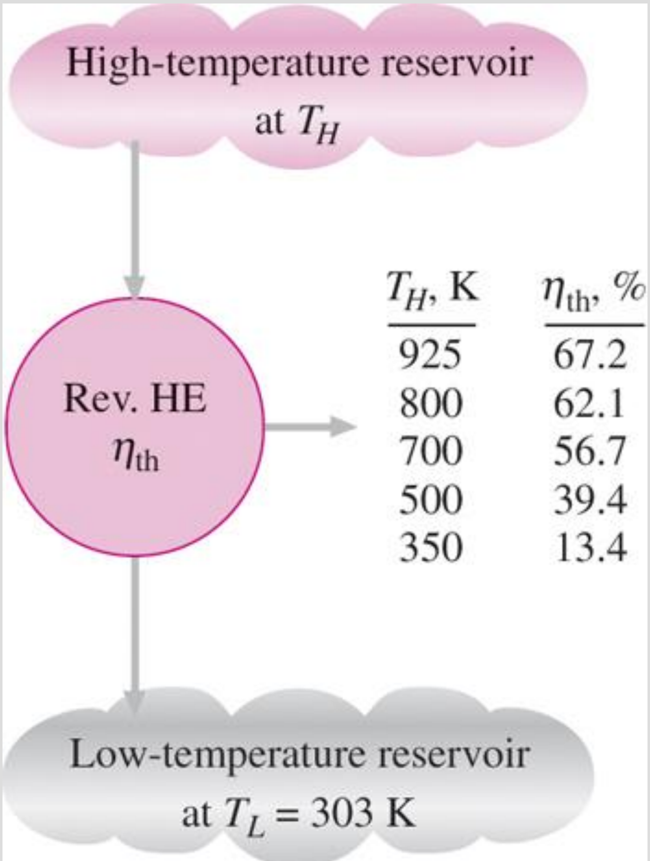
$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

Carnot heat engine

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

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

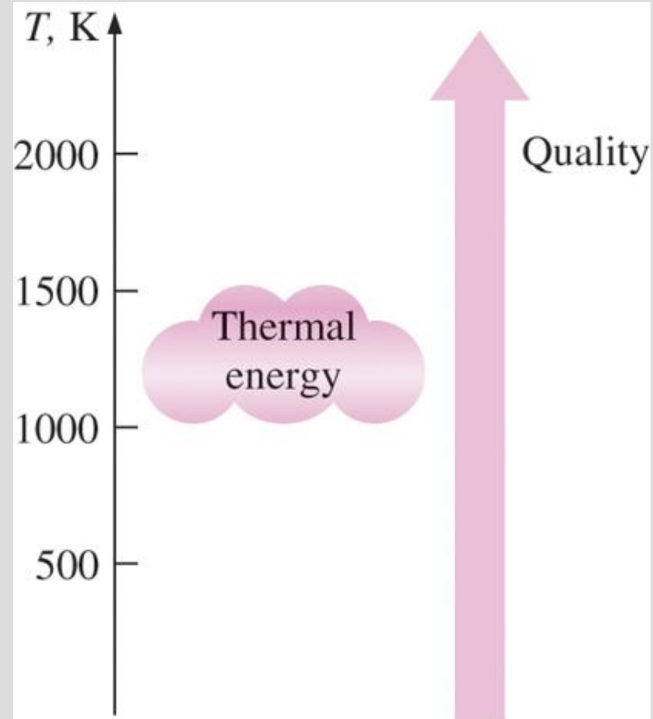
The Quality of Energy



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

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

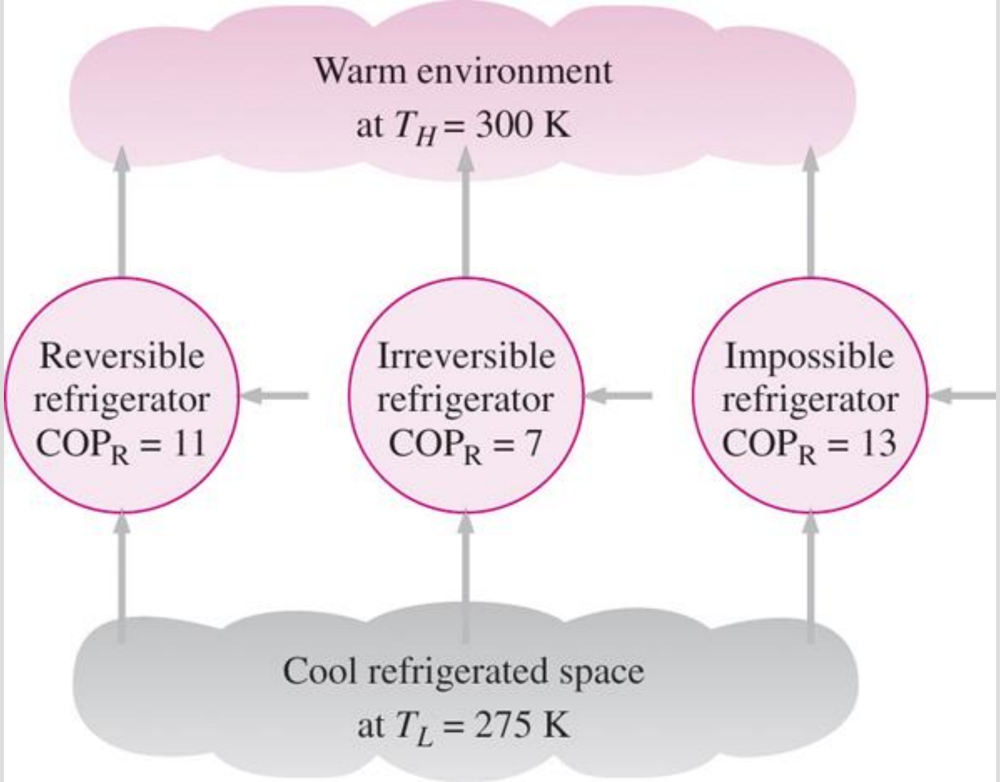
Can we use °C unit for temperature here?



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

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

THE CARNOT REFRIGERATOR AND 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

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

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

How do you increase the COP of a Carnot refrigerator or heat pump? How about for actual ones?