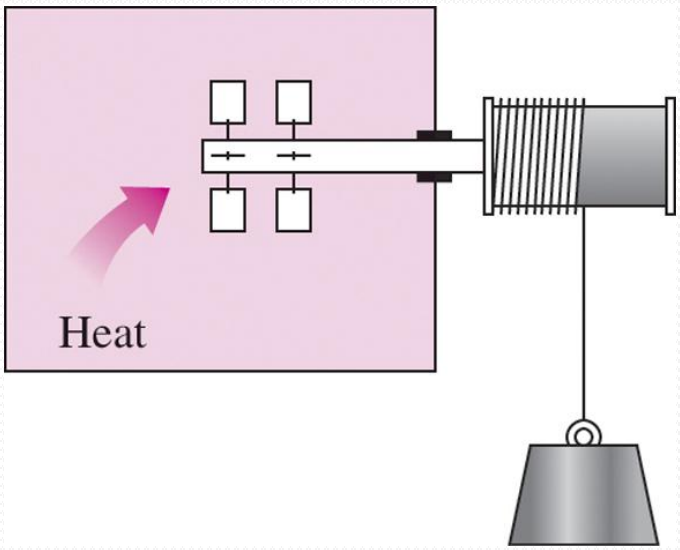
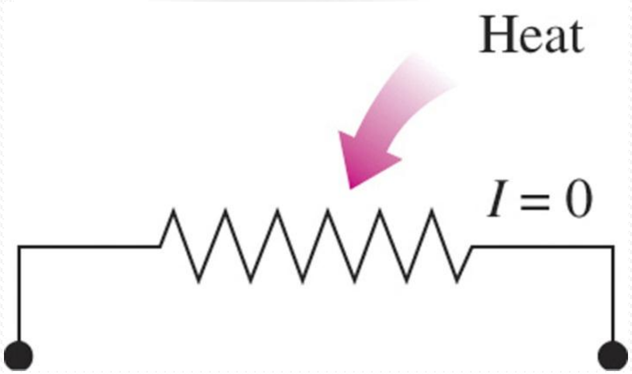
Chapter 7 The Classical Second Law of Thermodynamics

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



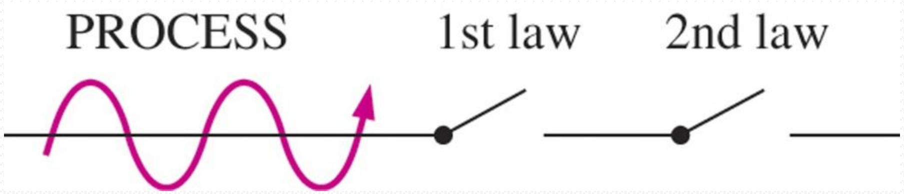
Transferring heat to a paddle wheel will not cause it to rotate.



Transferring heat to a wire will not generate electricity.

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

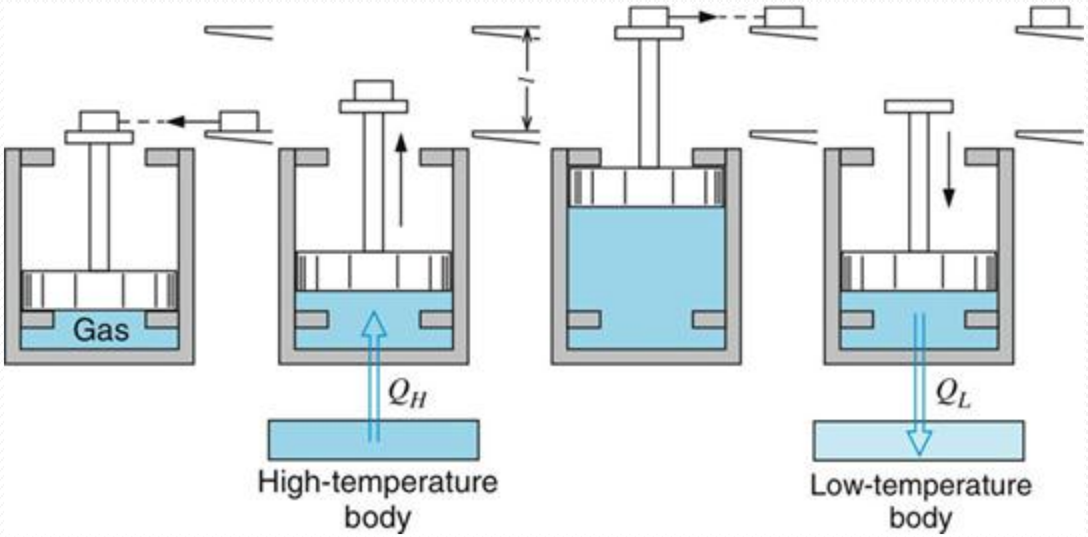
Processes occur in a certain direction, and not in the reverse direction.



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

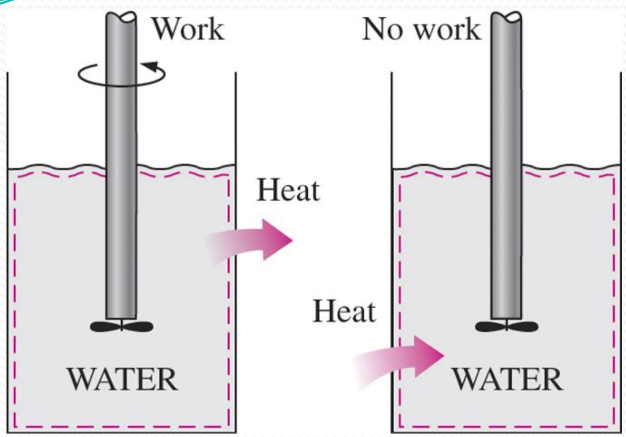
MAJOR USES OF THE SECOND LAW

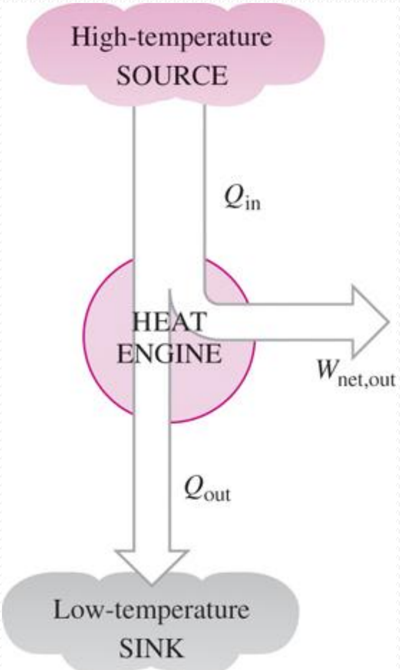
1. The second law may be used to identify the direction of processes.
2. The second law also asserts that energy has *quality* as well as quantity. The first law is concerned with the quantity of energy and the transformations of energy from one form to another with no regard to its quality. The second 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.



A simple heat engine

HEAT ENGINES





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

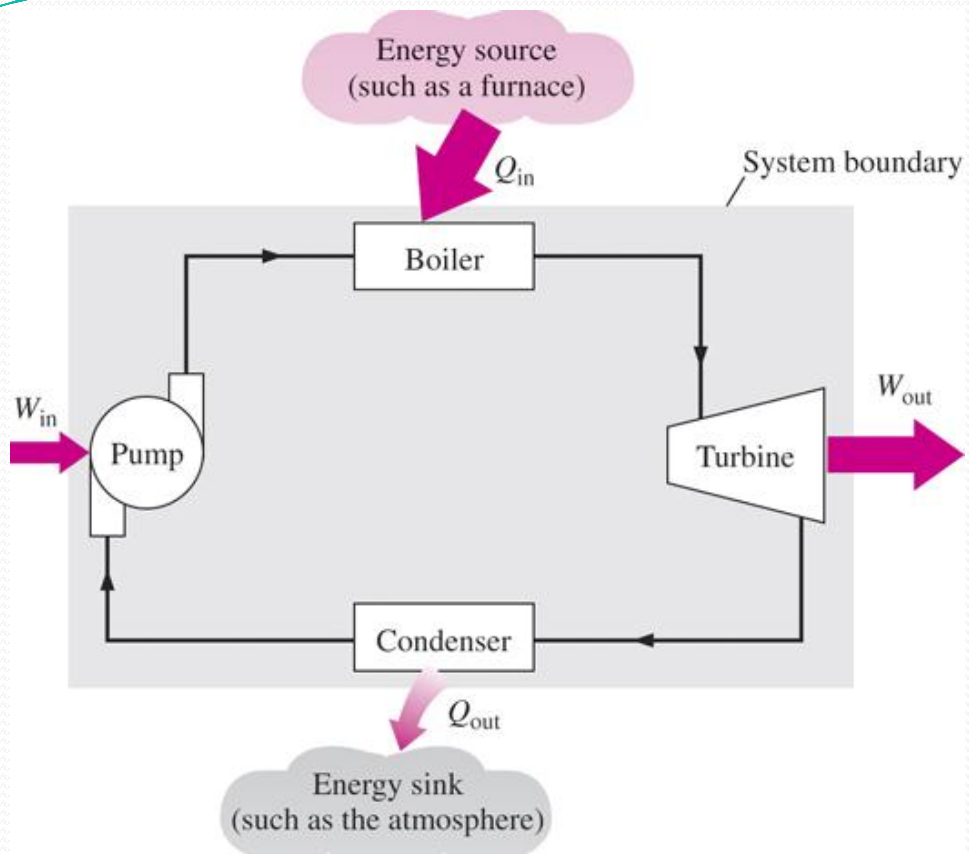
Part of the heat received by a heat engine is converted to work, while the rest is rejected to a sink.

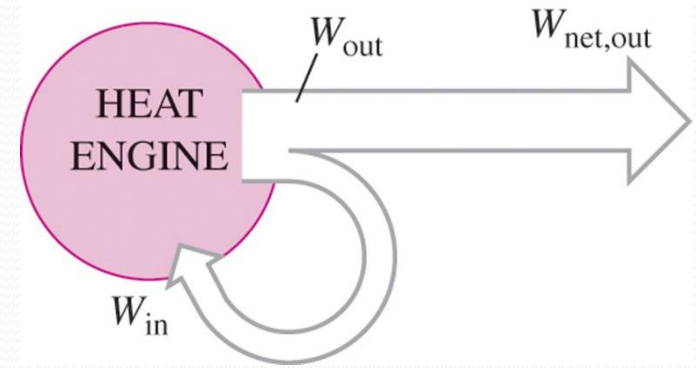
The devices that convert heat to work.

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**.

A steam power plant





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

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

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

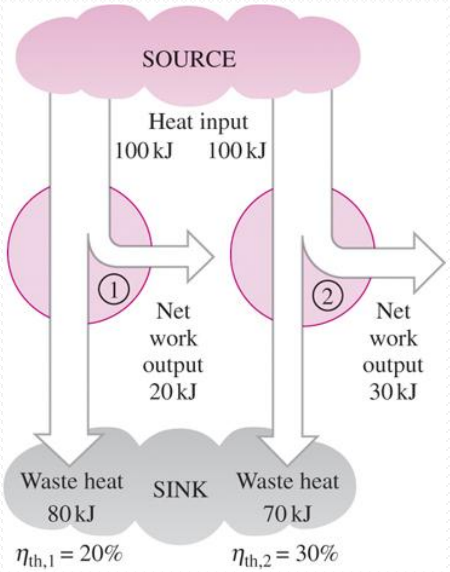
Q_{in} = amount of heat supplied to steam in boiler from a high-temperature source (furnace)

Q_{out} = amount of heat rejected from steam in condenser to a low-temperature sink (the atmosphere, a river, etc.)

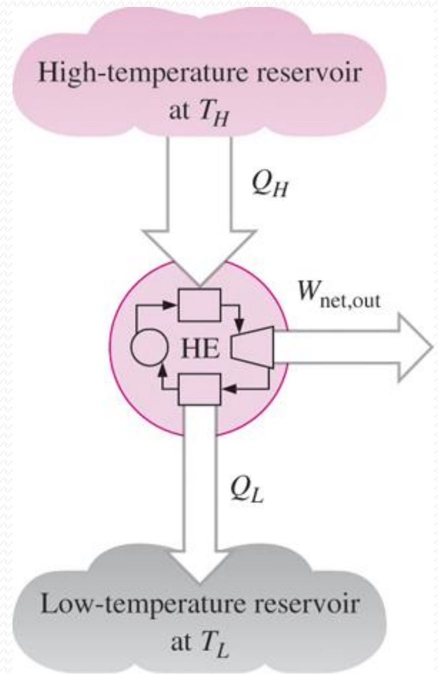
W_{out} = amount of work delivered by steam as it expands in turbine

W_{in} = amount of work required to compress water to boiler pressure

Thermal efficiency



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



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

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

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

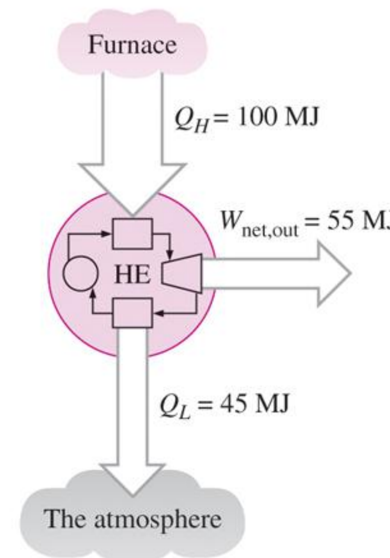
Schematic of a heat engine.

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

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

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

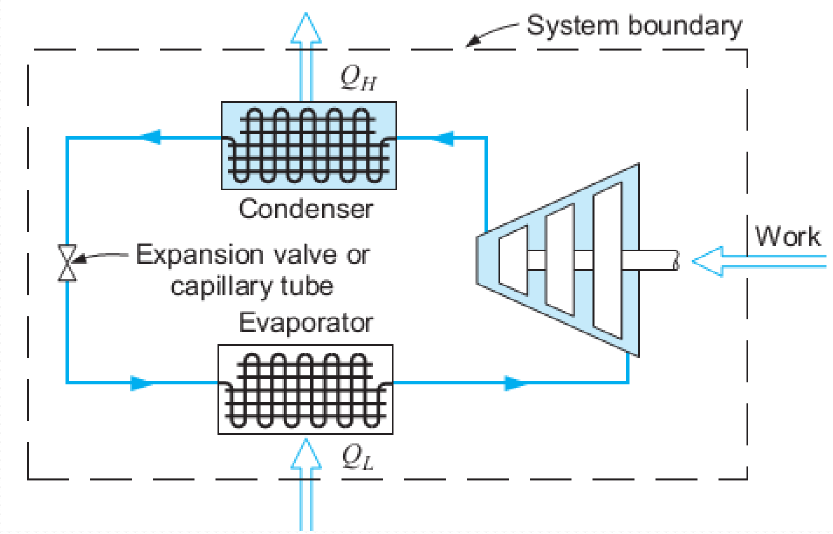
Even the most efficient heat engines reject almost one-half of the energy they receive as waste heat.



The transfer of heat from a low-temperature medium to a high-temperature one requires special devices called refrigerators. Another device that transfers heat from a low-temperature medium to a high-temperature one is the heat pump

The "efficiency" of a refrigerator or heat pump is expressed in terms of the coefficient of performance (COP) or β.

$$COP = \frac{\text{Desired Result}}{\text{Required Input}}$$



For a refrigerator

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

For a heat pump

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

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

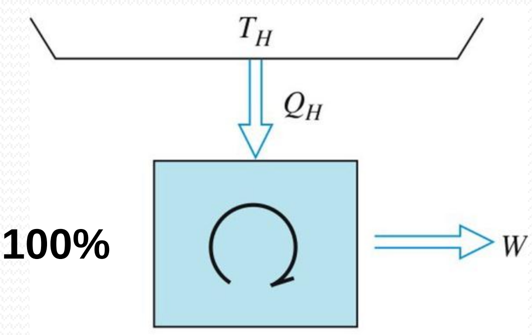
The Second Law of Thermodynamics

There are two classical statements of the second law, known as the Kelvin–Planck statement and the Clausius statement.

The Kelvin–Planck statement: it is impossible to construct a heat engine that operates in a cycle, receives a given amount of heat from a high temperature body, and does an equal amount of work.

It is impossible to build a heat engine that has a thermal efficiency of 100%

η_{th} < 100%



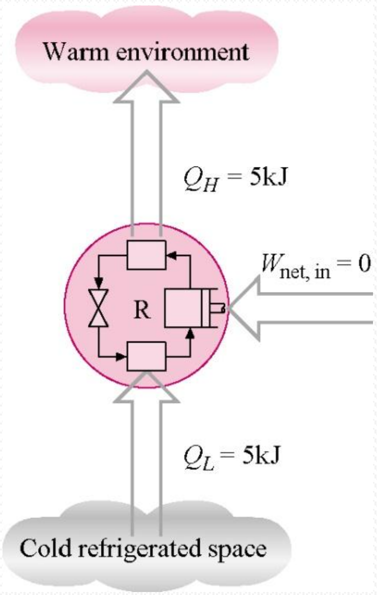
Impossible

The 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 cooler body to a hotter body.

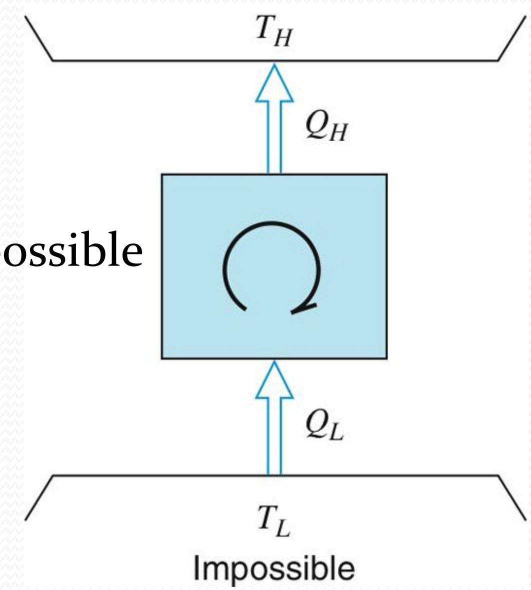
It states that it is impossible to construct a refrigerator that operates without an input of work. This statement is related to the refrigerator or heat pump.

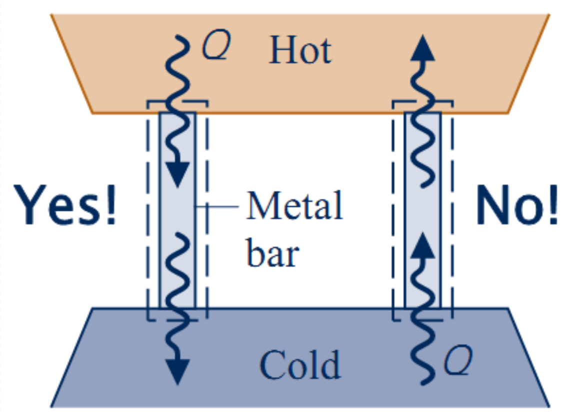
This also implies that the coefficient of performance is always less than infinity.

$COP < \infty$

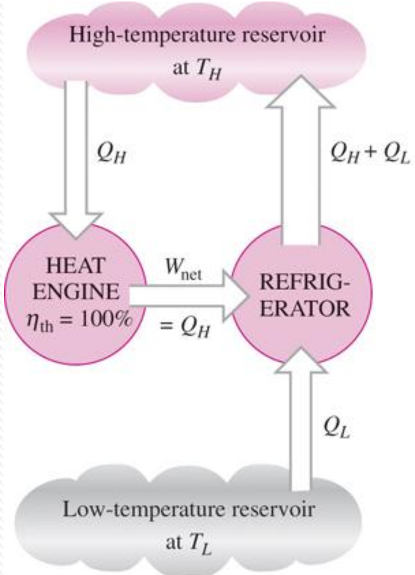


impossible



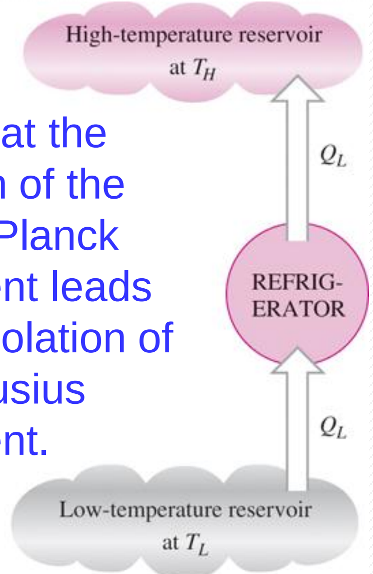


Equivalence of the Two Statements

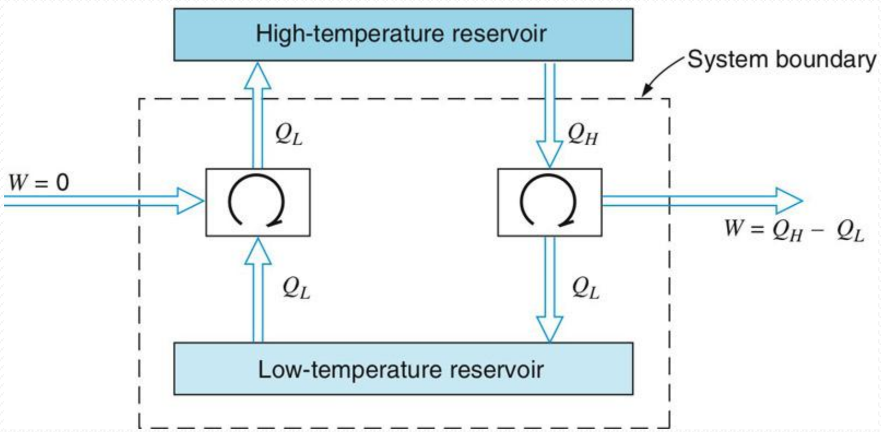


(*a*) A refrigerator that is powered by a 100 percent efficient heat engine

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

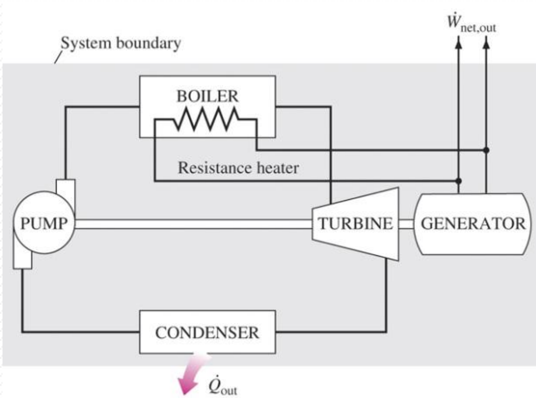


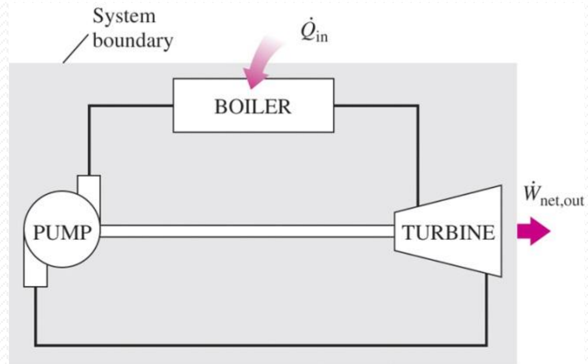
(*b*) The equivalent refrigerator



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.





Any device that violates the first or second law of thermodynamics is called a **perpetual-motion machine**.

A perpetual–motion machine of the **first kind** would create work from nothing or create mass or energy, thus violating the first law.

A perpetual–motion machine of the **second kind** would extract heat from a source and then convert this heat completely into other forms of energy, thus violating the second law.

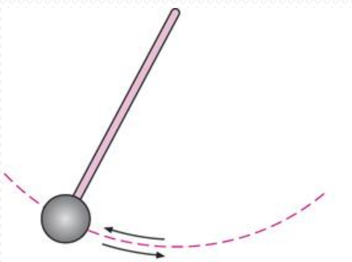
A perpetual–motion machine of the **third kind** would have no friction, and thus would run indefinitely but produce no work.

The Reversible and Irreversible Process

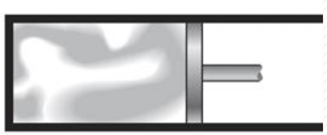
Reversible process: *A process that can be reversed without leaving any trace on the surroundings.*

Irreversible process: A process that is not reversible.

- 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.
- We try to approximate reversible processes. **Why?**

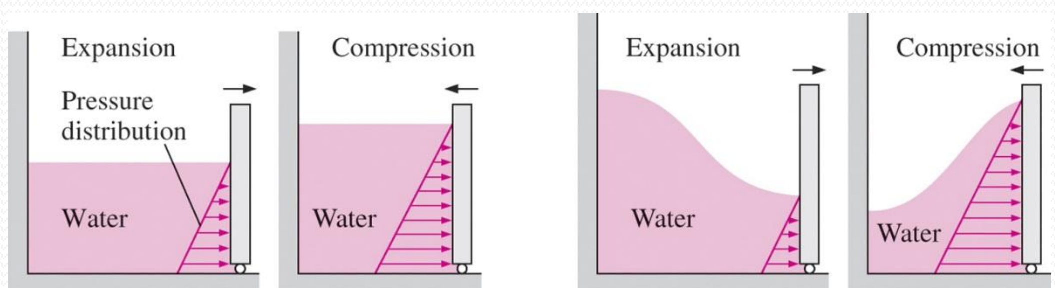


(*a*) Frictionless pendulum



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

Two familiar reversible processes.



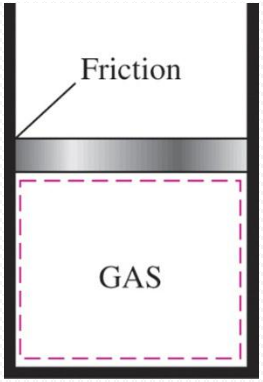
(*a*) Slow (reversible) process

(*b*) Fast (irreversible) process

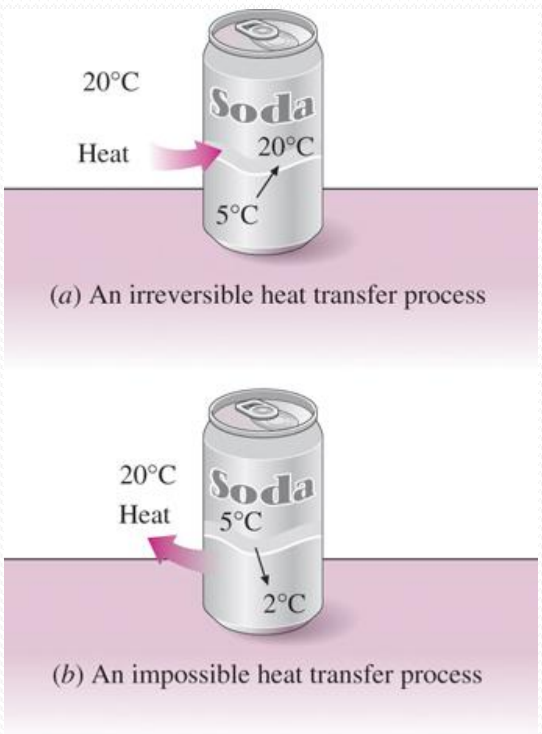
Reversible processes deliver the most and consume the least work.

Irreversibilities

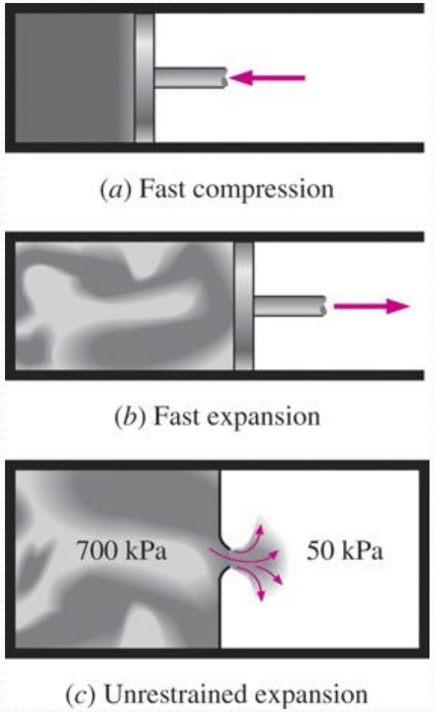
- The factors that cause a process to be irreversible are called **irreversibilities**.
- They include friction, unrestrained expansion, mixing of two fluids, heat transfer across a finite temperature difference, electric resistance, inelastic deformation of solids, and chemical reactions.
- The presence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



Friction renders a process irreversible.



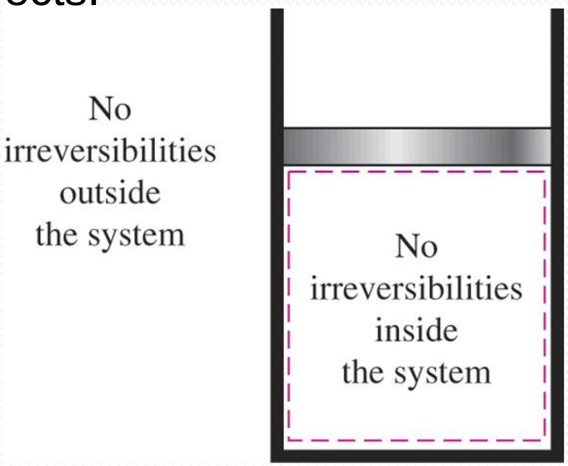
(*a*) Heat transfer through a temperature difference is irreversible, and (*b*) the reverse process is impossible.



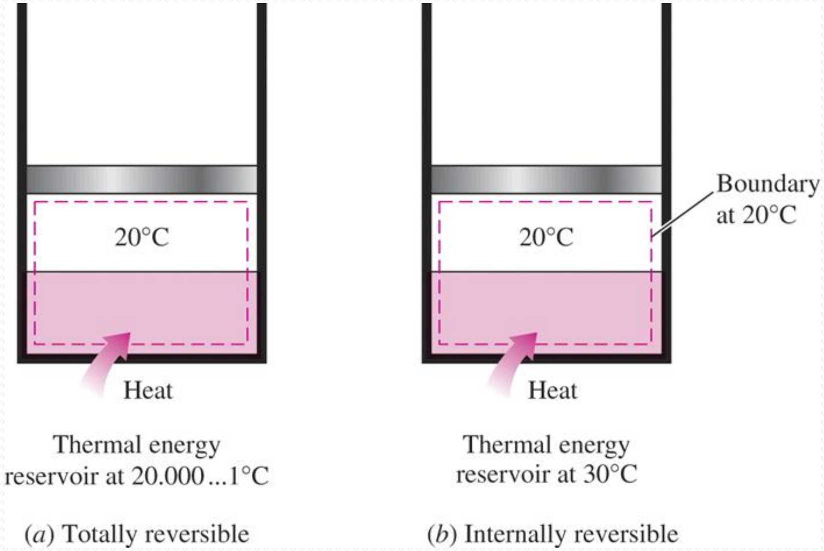
Irreversible compression and expansion processes.

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.

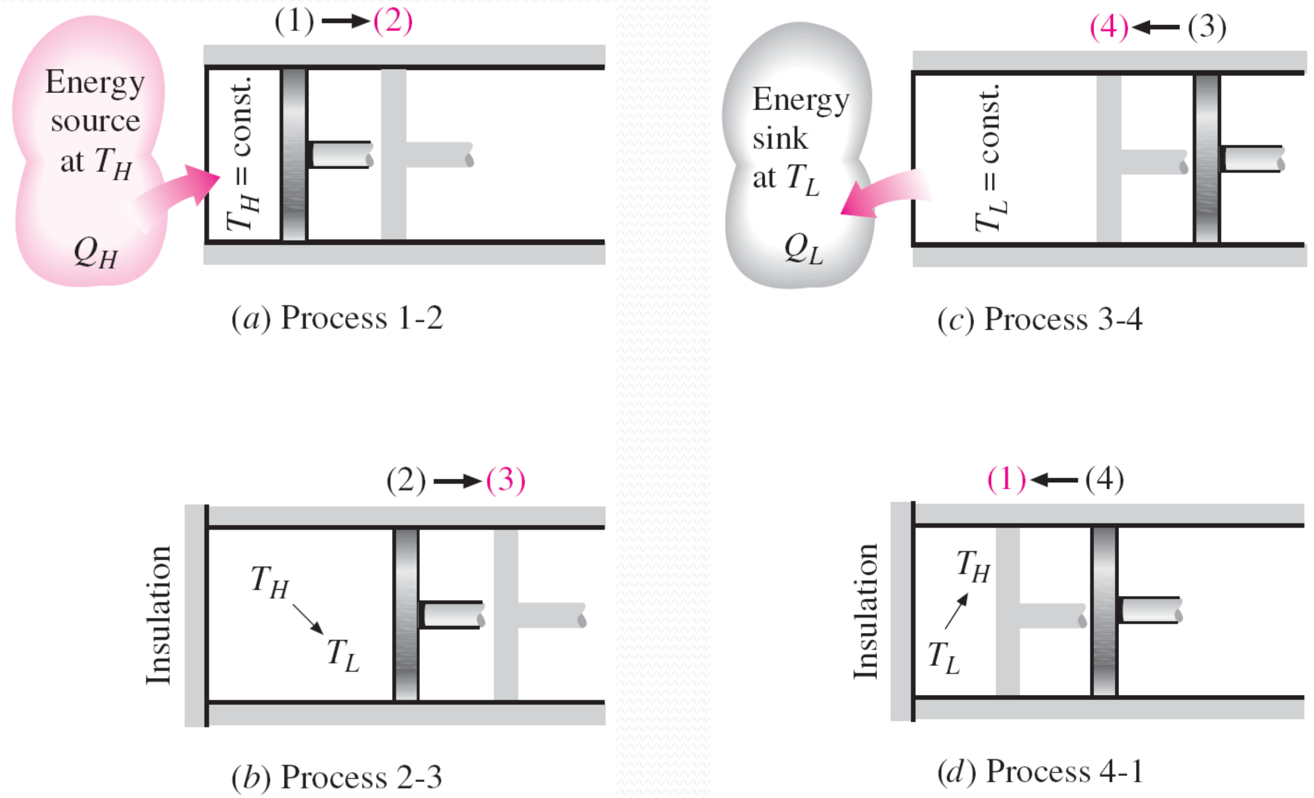


A reversible process involves no internal and external irreversibilities.



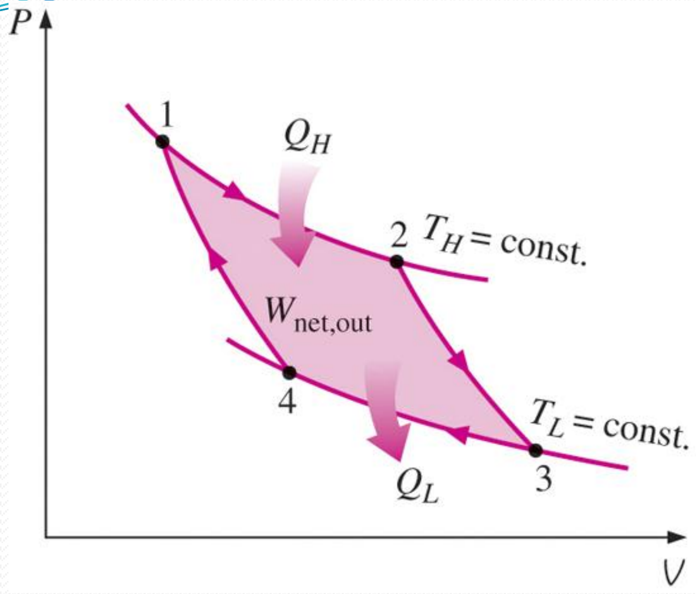
Totally and internally reversible heat transfer processes.

The Carnot Cycle

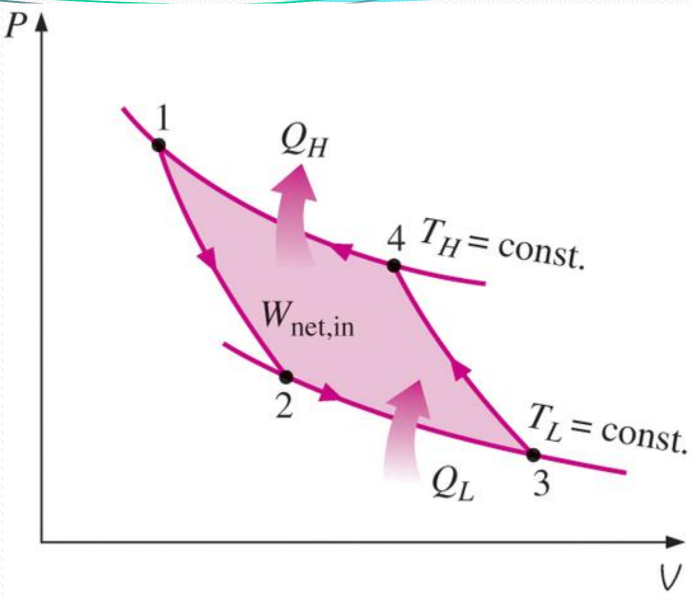


Execution of the Carnot cycle in a closed system.

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)



P-V diagram of the Carnot cycle.



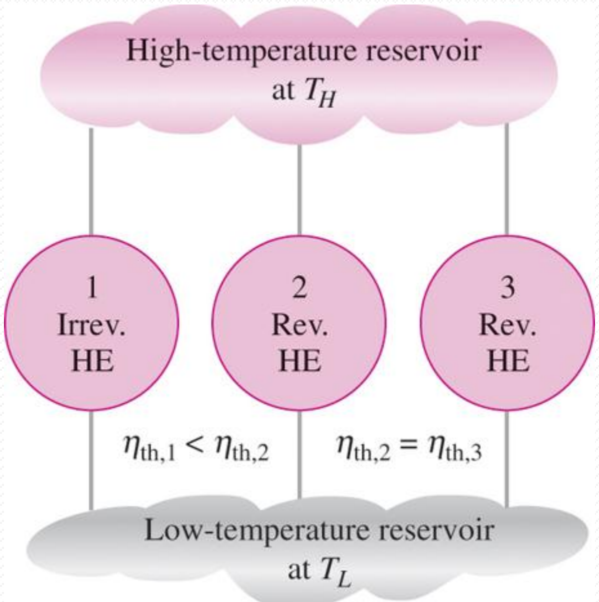
P-V diagram of the reversed Carnot cycle.

The Reversed Carnot Cycle

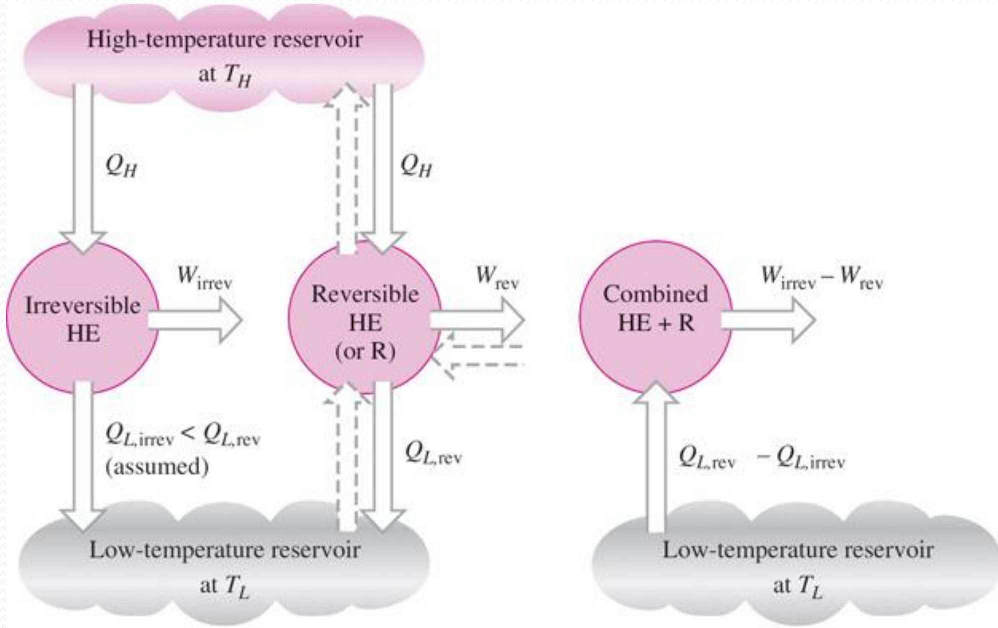
The Carnot heat-engine cycle is a totally reversible cycle.

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.



(*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.

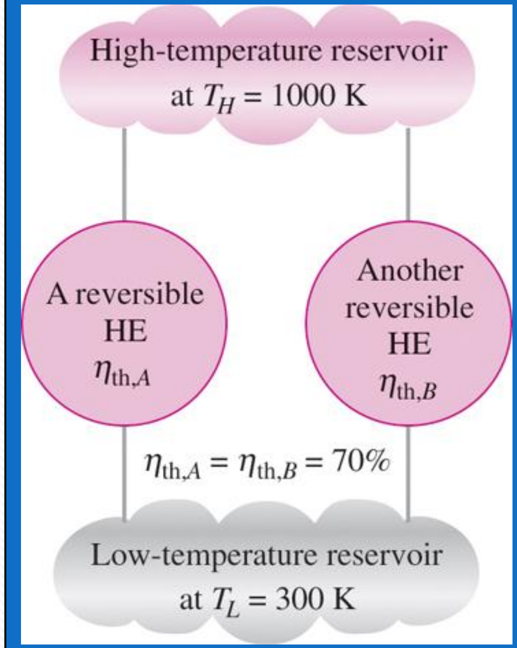
1. It is impossible to construct an engine that operates between two given reservoirs and is more efficient than a reversible engine operating between the same two reservoirs.
2. All engines that operate on the Carnot cycle between two given constant–temperature reservoirs have the same efficiency.

Thermodynamic Temperature Scale

The zeroth law of thermodynamics provides a basis for temperature measurement, but that a temperature scale must be defined in terms of a particular thermometer substance and device.

A temperature scale that is independent of any particular substance, which might be called an **absolute temperature scale**

The efficiency of a Carnot cycle is independent of the working substance and depends only on the reservoir temperatures.

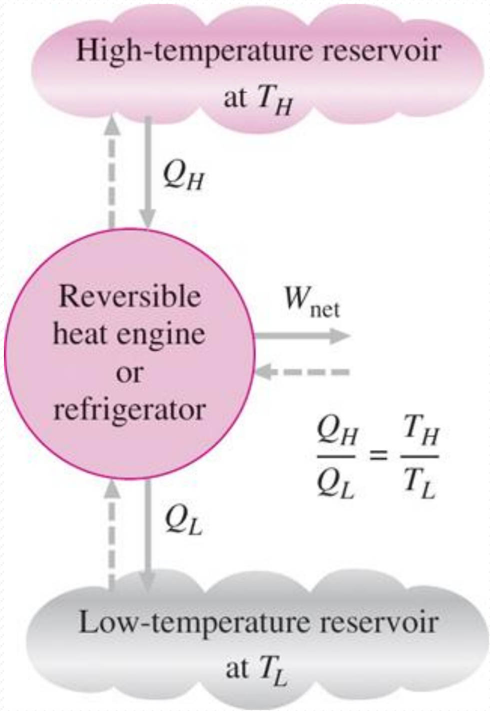


All reversible heat engines operating between the same two reservoirs have the same efficiency.

Since the efficiency of a Carnot cycle is a function only of the temperature, it follows that

$$\eta_{thermal} = 1 - \frac{Q_L}{Q_H} = 1 - \psi(T_L, T_H)$$

For simplicity, the thermodynamic scale is defined as $$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$$



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

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

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

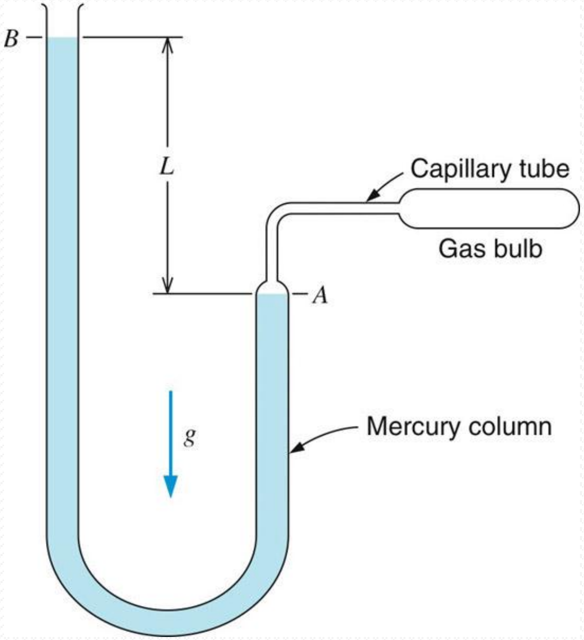
Then the efficiency of a Carnot engine, or any reversible heat engine, becomes

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

The Ideal–Gas Temperature Scale

The pressure of a real gas approaches zero, its equation of state approaches that of an ideal gas

$$Pv = RT$$

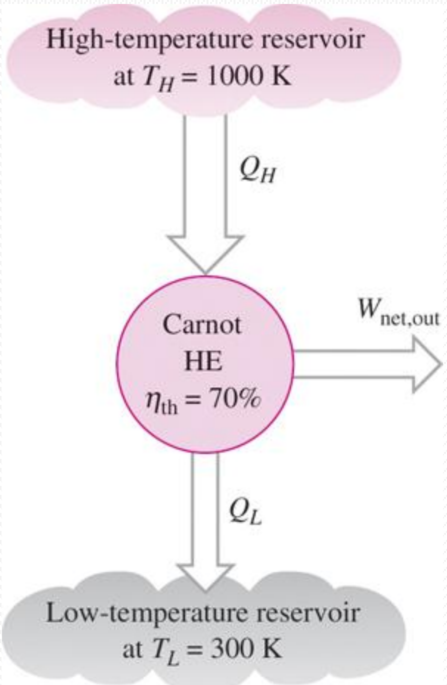


A constant–volume gas thermometer is shown schematically in Figure. Let the gas bulb be placed in the location where the temperature is to be measured, and let the mercury column be adjusted so that the level of mercury stands at the reference mark *A*, Thus, the volume of the gas remains constant. Assume that the gas in the capillary tube is at the same temperature as the gas in the bulb. Then the pressure of the gas, which is indicated by the height *L* of the mercury column, is a measure of the temperature.

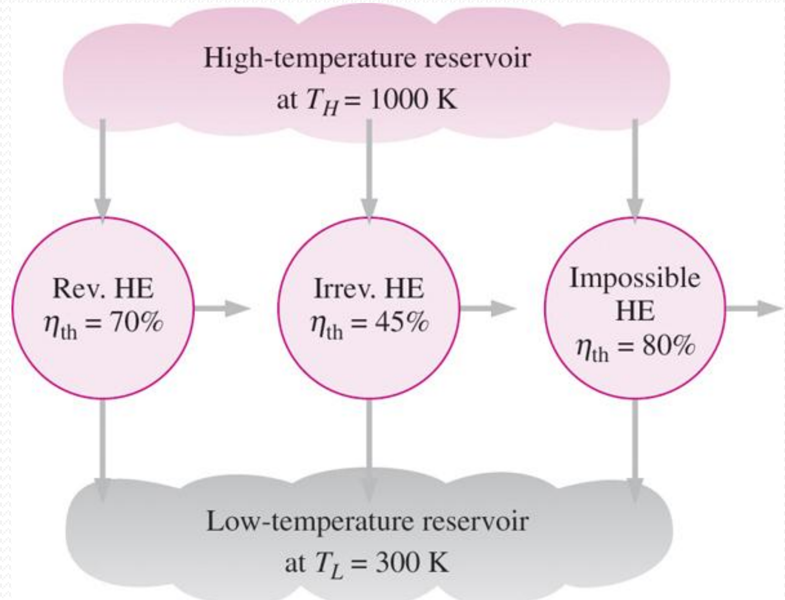
Temperature *T* could be determined from a pressure measurement *P* by using temperature and pressure of the triple point

$$T = 273.16\left(\frac{P}{P_{tp}}\right)$$

Ideal versus Real Machines



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

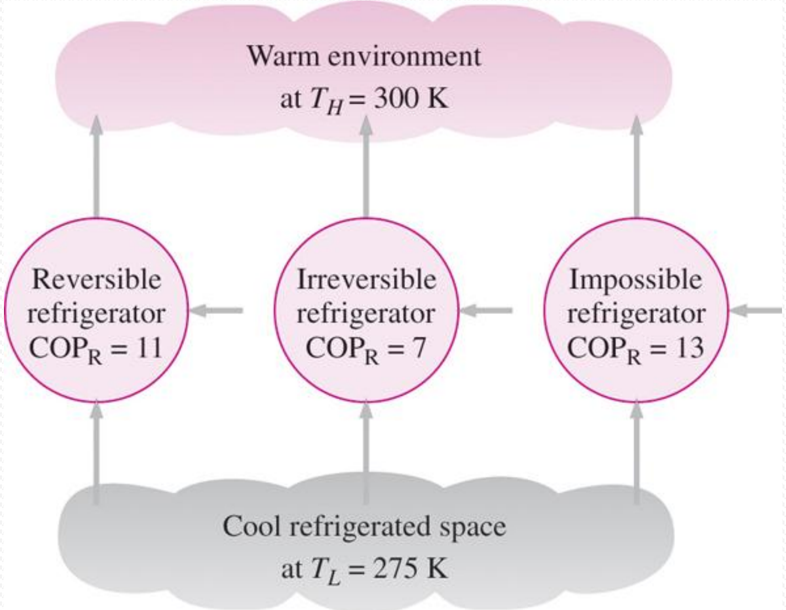
$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

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 CARNOT REFRIGERATOR AND HEAT PUMP



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

$$COP_R \begin{cases} < COP_{R,\,rev} & \text{irreversible refrigerator} \\ = COP_{R,\,rev} & \text{reversible refrigerator} \\ > COP_{R,\,rev} & \text{impossible refrigerator} \end{cases}$$

Any refrigerator or heat pump

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

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

Carnot refrigerator or heat pump

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

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

$$\beta = \frac{Q_L}{Q_H - Q_L} \underset{carnot}{=} \frac{T_L}{T_H - T_L}$$

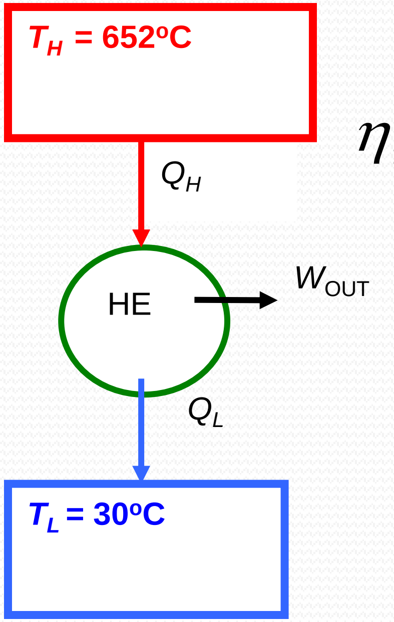
$$\beta' = \frac{Q_H}{Q_H - Q_L} \underset{carnot}{=} \frac{T_H}{T_H - T_L}$$

Example 6-2

A Carnot heat engine receives 500 kJ of heat per cycle from a high-temperature heat reservoir at 652°C and rejects heat to a low-temperature heat reservoir at 30°C. Determine

(a) The thermal efficiency of this Carnot engine.
(b) The amount of heat rejected to the low-temperature heat reservoir.

a.



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

$$= 1 - \frac{(30+273)K}{(652+273)K}$$

$$= 0.672 \quad or \quad 67.2\%$$

b.

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

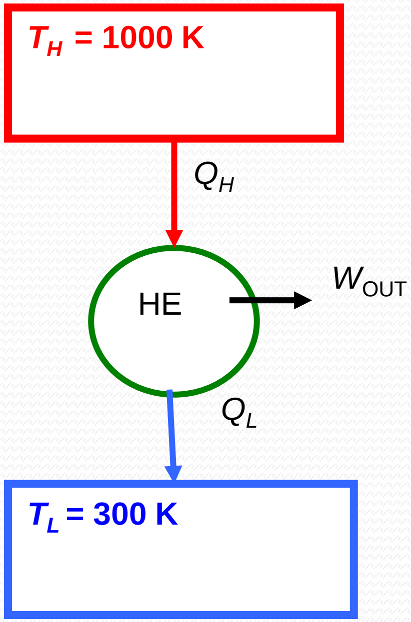
$$= \frac{(30+273)K}{(652+273)K} = 0.328$$

$$Q_L = 500\,kJ(0.328)$$

$$= 164\,kJ$$

Example 6-3

An inventor claims to have invented a heat engine that develops a thermal efficiency of 80 percent when operating between two heat reservoirs at 1000 K and 300 K. Evaluate his claim.



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

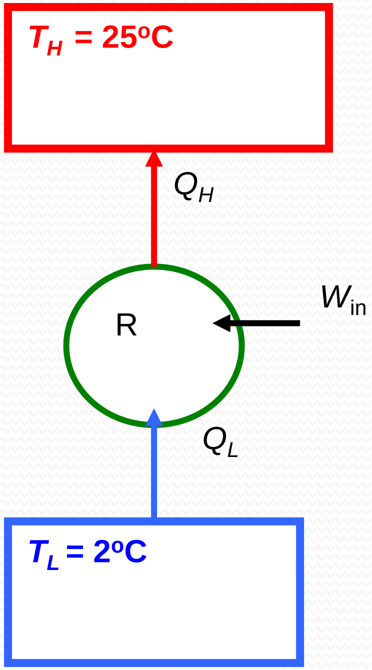
$$= 1 - \frac{300K}{1000K}$$

$$= 0.70 \quad or \quad 70\%$$

The claim is false since no heat engine may be more efficient than a Carnot engine operating between the heat reservoirs.

Example 6-4

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 has a COP of 13.5. Is there any truth to his claim?



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

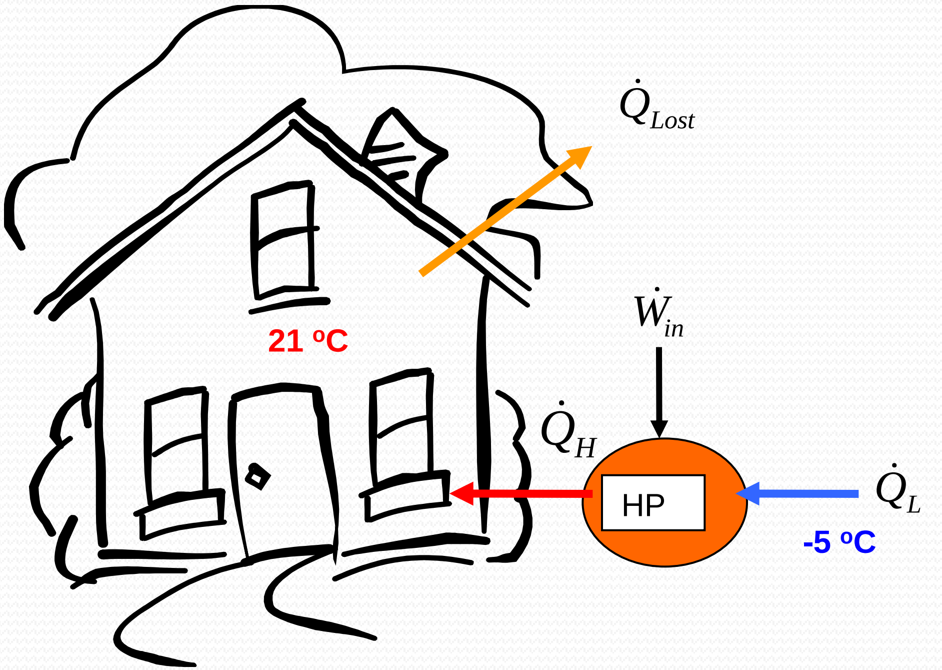
$$= \frac{(2+273)K}{(25-2)K}$$

$$= 11.96$$

The claim is false since no refrigerator may have a COP larger than the COP for the reversed Carnot device.

Example 6-5

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



$$COP_{HP} = \frac{\dot{Q}_H}{\dot{Q}_H - \dot{Q}_L} = \frac{T_H}{T_H - T_L}$$

$$= \frac{(21+273)K}{(21-(-5))K}$$

$$= 11.31$$

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

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

$$= \frac{135{,}000\,kJ/h}{11.31}\frac{1h}{3600s}\frac{1kW}{kJ/s}$$

$$= 3.316\,kW$$

The heat lost by the building has to be supplied by the heat pump.

$$\dot{Q}_H = \dot{Q}_{Lost} = 135000\frac{kJ}{h}$$