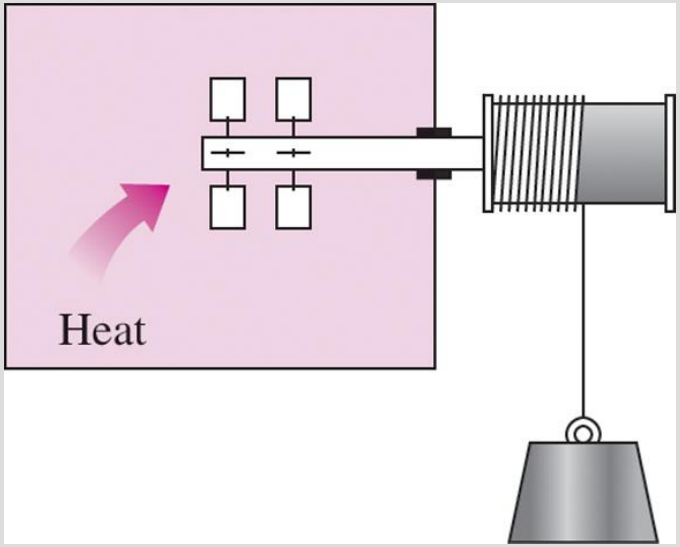
Chapter 6

THE SECOND LAW OF THERMODYNAMICS

Introduction to the Second Law

- Some processes do not violate the first law of thermodynamics, but they still cannot occur in nature.



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

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

Introduction to the Second Law

- Processes occur in a certain direction, and not in the reverse direction.
- The second law can be used to identify the direction of processes.
- A process must satisfy both the first and second laws of thermodynamics to occur.
- The second law also asserts that energy has ***quality*** as well as quantity.
  - **The higher the temperature of a system, the more useful work it can be produce → the quality of its energy is higher.**
- The second law is also used to determine the ***theoretical limits*** for performance of certain engineering systems.

Introduction to the Second Law

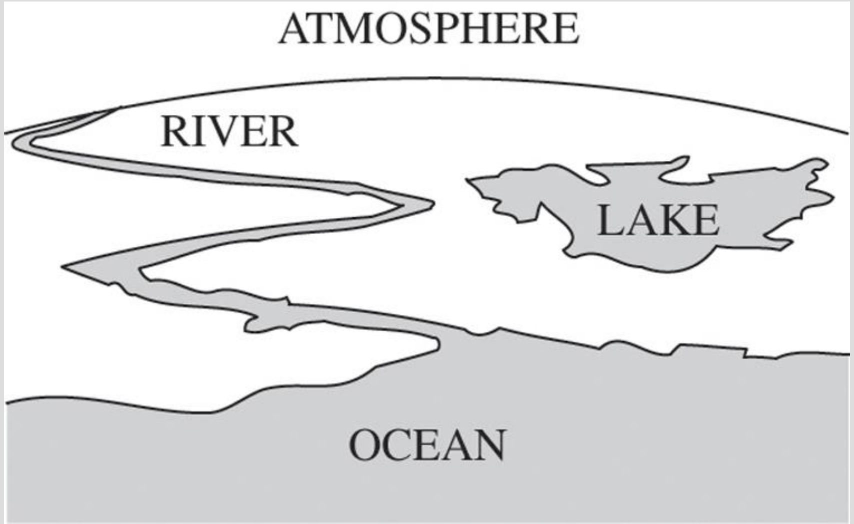
- The second law is not directly expressed in mathematical form like the first law.
- It is expressed by two statements:
  - **Kelvin-Planck Statement**
  - **Clausius Statement**
- The two statements are equivalent even though they appear different.
- To fully understand the two statements, the following concepts need to be introduced:
  - **Thermal Energy Reservoirs**
  - **Heat Engines**
  - **Refrigerators and Heat Pumps**

Thermal Energy Reservoirs

- A ***thermal energy reservoir*** is a body with a relatively large thermal energy capacity.
- It supplies or absorbs finite amounts of heat without an effect on its temperature.

EXAMPLES

oceans, lakes, rivers, the atmosphere, geothermal reservoirs



Thermal Energy Reservoirs

- If a thermal energy reservoir supplies heat, it is called a ***source***.

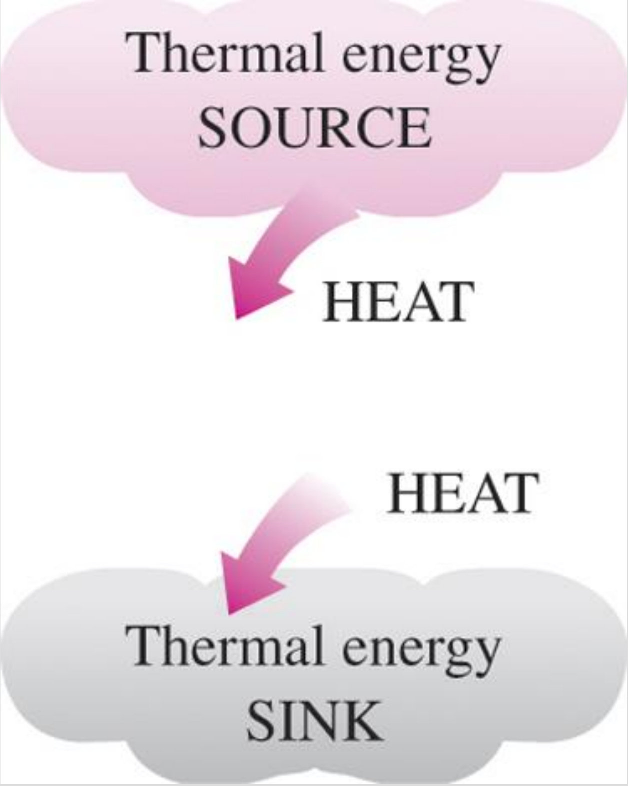
  EXAMPLES

  Geothermal reservoirs, furnaces, combustion chambers

- If a thermal energy reservoir absorbs heat, it is called a ***sink***.

  EXAMPLES

  Oceans, rivers, lakes, the atmosphere



Thermal Energy Reservoirs

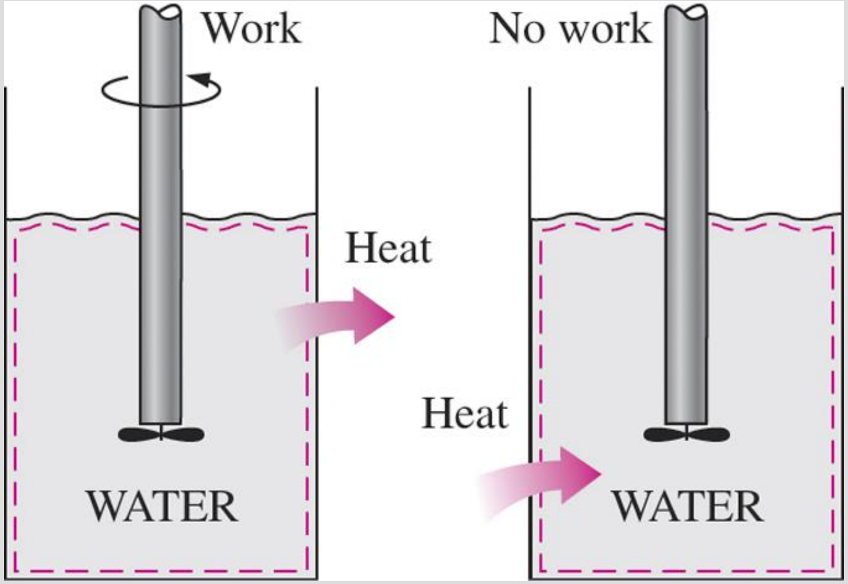
- Some thermal energy reservoirs can be considered sources in some applications and sinks in other applications.

EXAMPLE: The atmosphere

  - In industrial plants where fossil fuels are burned, ***the atmosphere is a sink*** that absorbs the energy contained in the exhaust gases.
  - When a heat pump is used for heating a building, ***the atmosphere is a source of energy.***

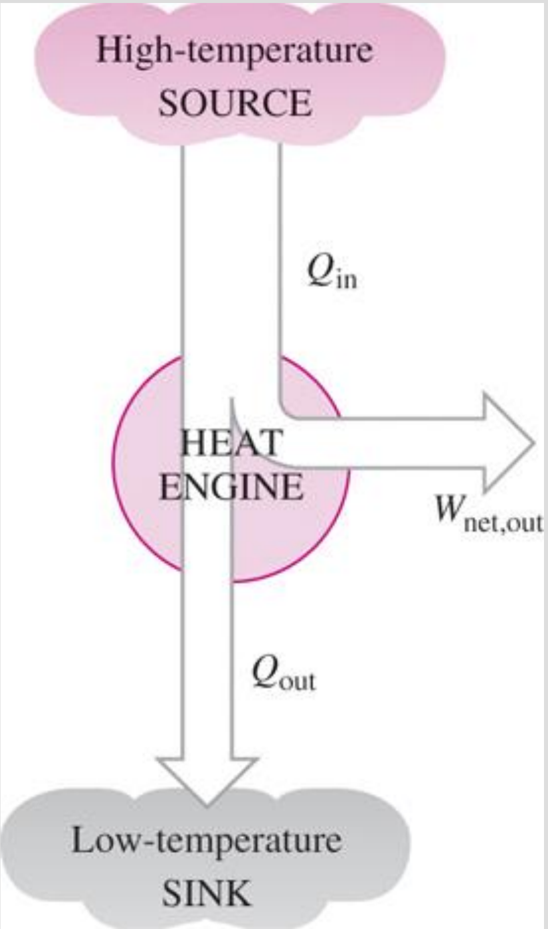
Heat Engines

- Work can always be converted to heat directly and completely, but the reverse is not true.
- Converting heat to work requires engineered devices.
- The type of device that converts part of the heat to work is called a ***heat engine***.



Characteristics of Heat Engines

1. They receive heat from a high-temperature source (solar energy, oil furnace, nuclear reactor, etc.).
2. They convert part of this heat to work (usually in the form of a rotating shaft.)
3. They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).
4. They operate on a cycle.



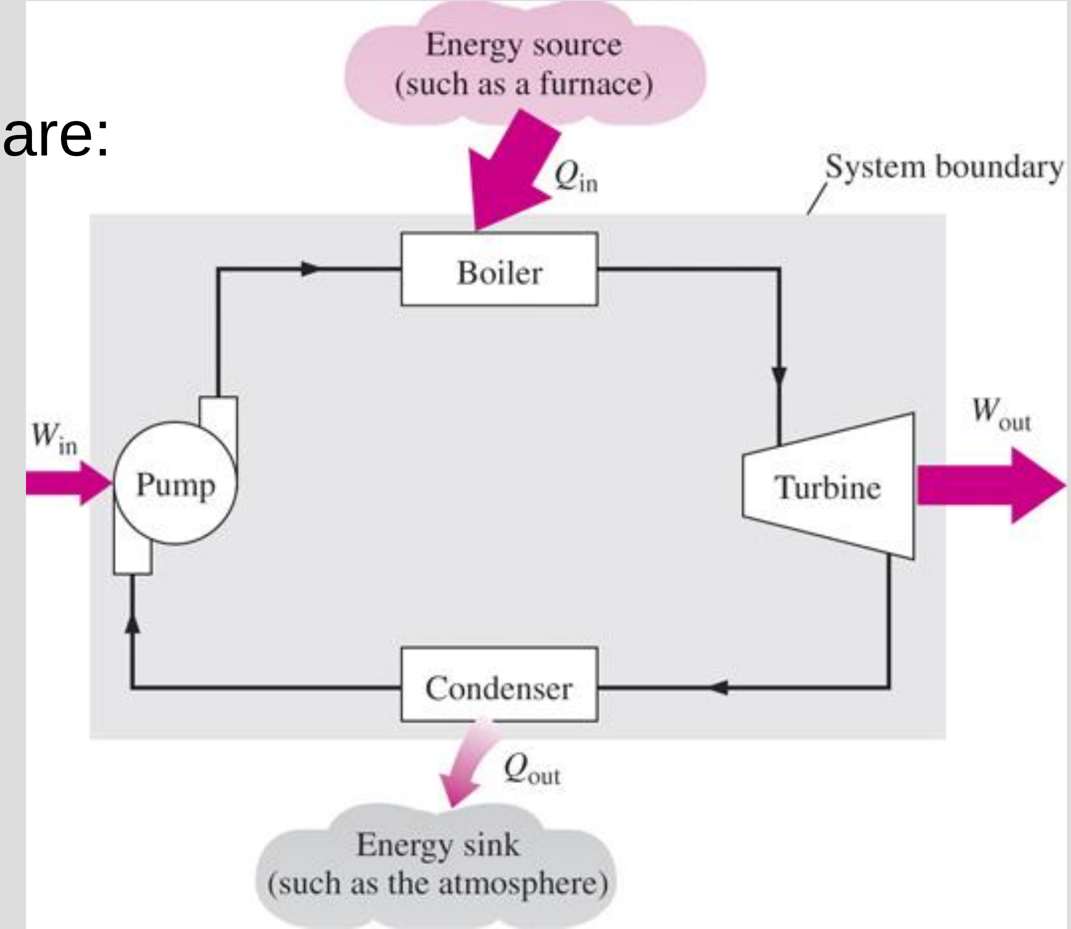
Notes on Heat Engines

- A device cannot be considered a heat engine unless it satisfies **ALL** four conditions.
- Heat engines usually involve a fluid to and from which heat is transferred while undergoing a cycle. This fluid is called the ***working fluid***.

Example: Steam Power Plant

- The working fluid in this system is **water** in its various forms, i.e. compressed liquid, mixture, superheated vapor (steam).

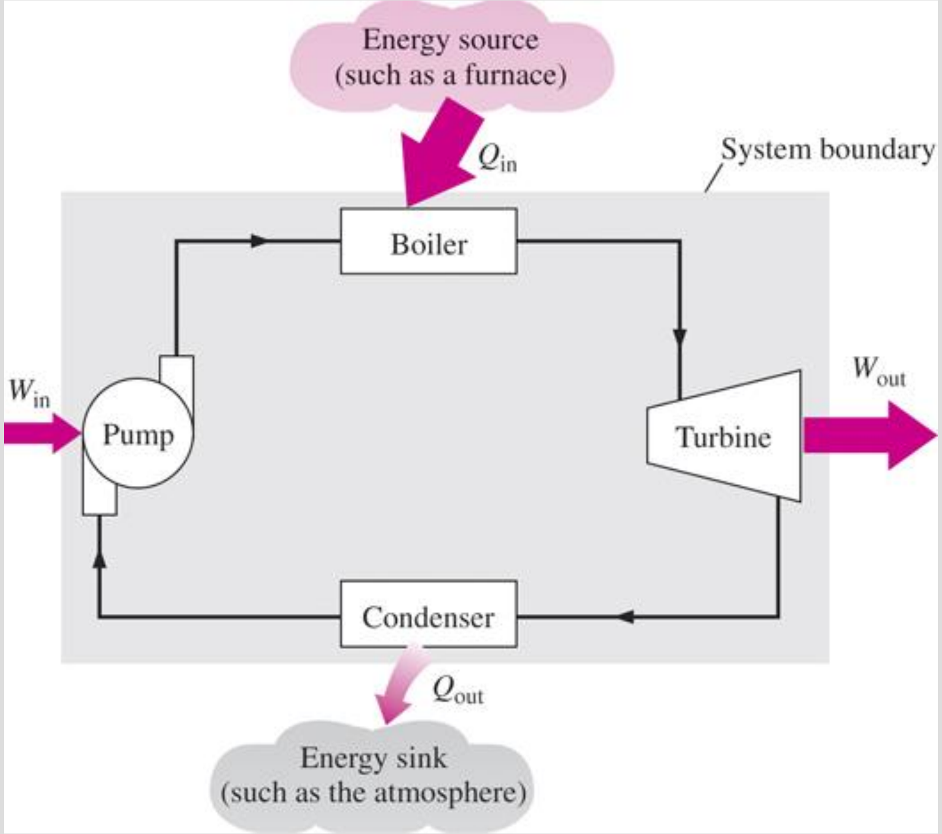
- The main components are:
  - **Boiler**
  - **Turbine**
  - **Condenser**
  - **Pump**



Steam Power Plant

HOW IT WORKS?

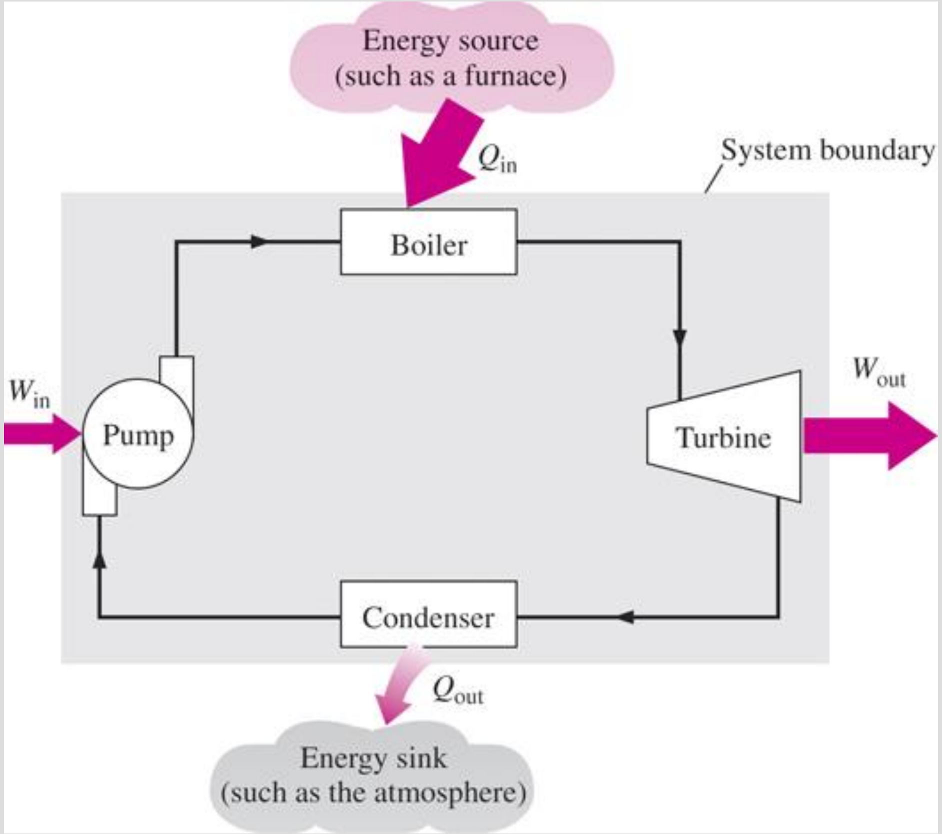
1. The boiler receives heat (Q_{in}) from a high-temperature source (furnace). Water leaves as superheated vapor and at high pressure.



Steam Power Plant

HOW IT WORKS?

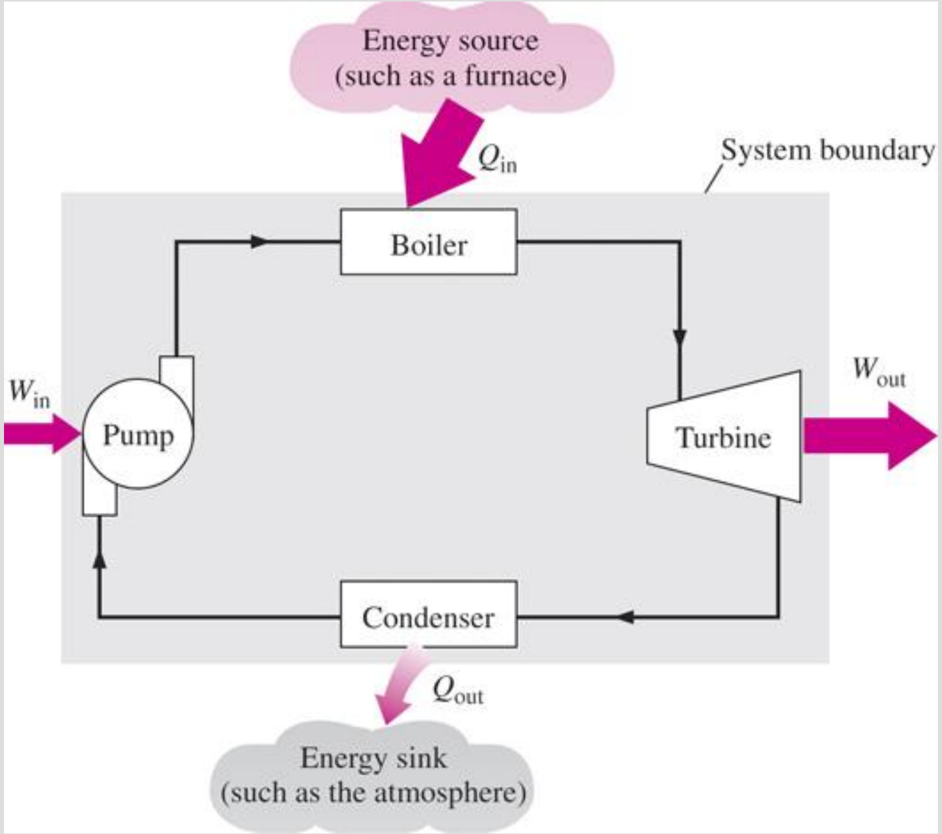
2.The vapor enters the turbine and produces work (W_{out}). Water leaves at low pressure (either slightly superheated or as a high-quality mixture).



Steam Power Plant

HOW IT WORKS?

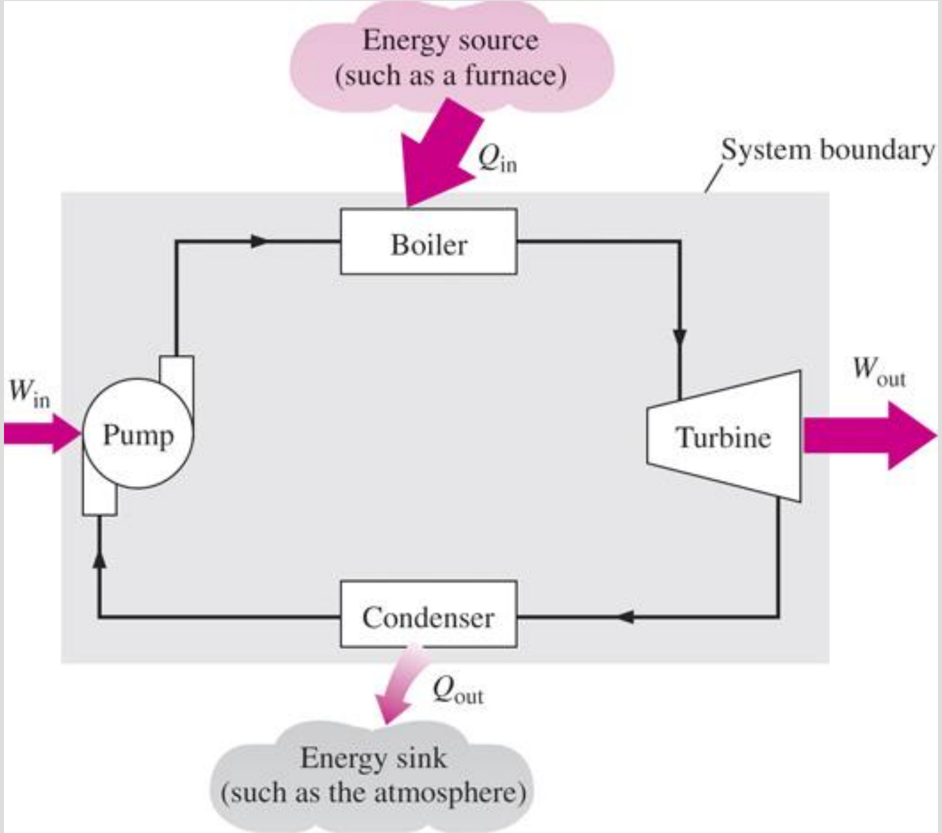
3. The condenser condenses water and rejects heat (Q_{out}) to a low-temperature sink (e.g. atmosphere). Water leaves as a saturated liquid at low pressure.



Steam Power Plant

HOW IT WORKS?

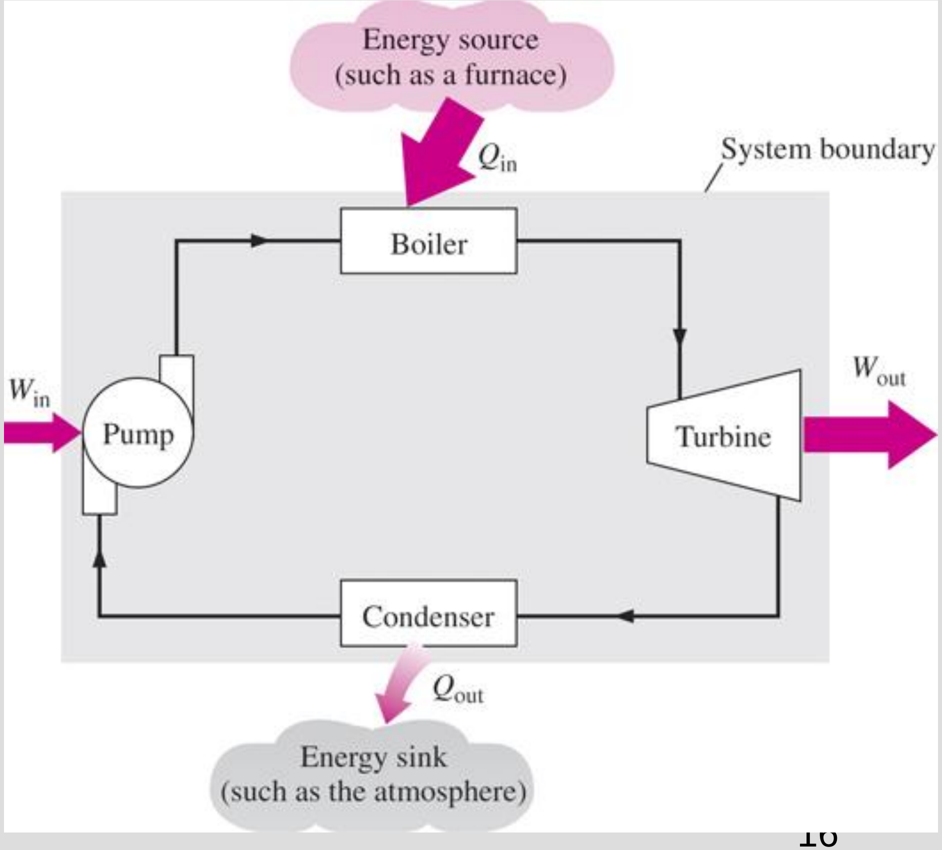
4. The pump increases the pressure of water and requires work input (W_{in}). Water leaves as a compressed liquid at high pressure.



Steam Power Plant

ENERGY BALANCE

$$(Q_{in} + W_{in} + E_{mass,in}) - (Q_{out} + W_{out} + E_{mass,out}) = \Delta E_{system}$$



Simplifying,

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

Pump work is normally extracted from the turbine before electricity is supplied to the grid.

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

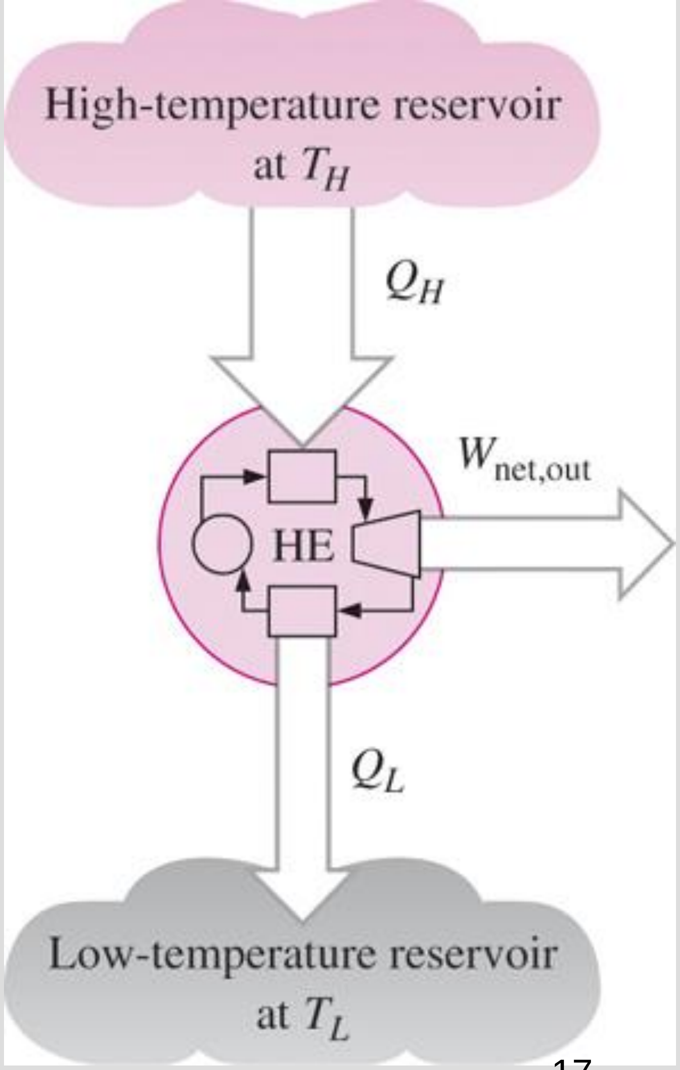
Thermal Efficiency of a Heat Engine

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

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

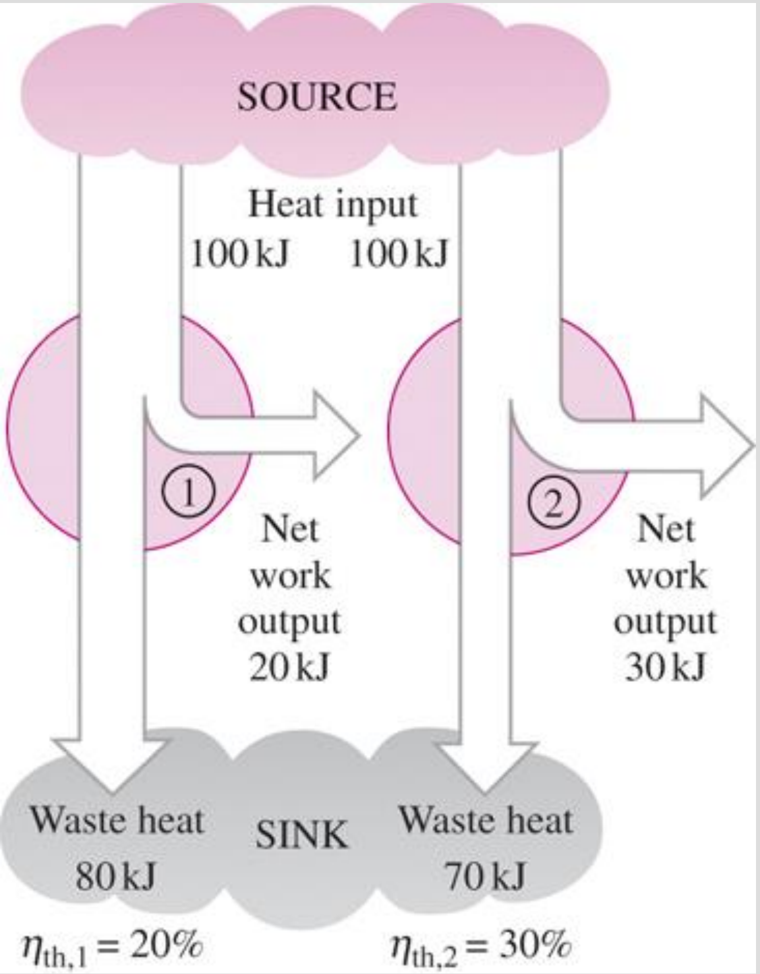
$$W_{\text{net,out}} = Q_H - Q_L$$

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



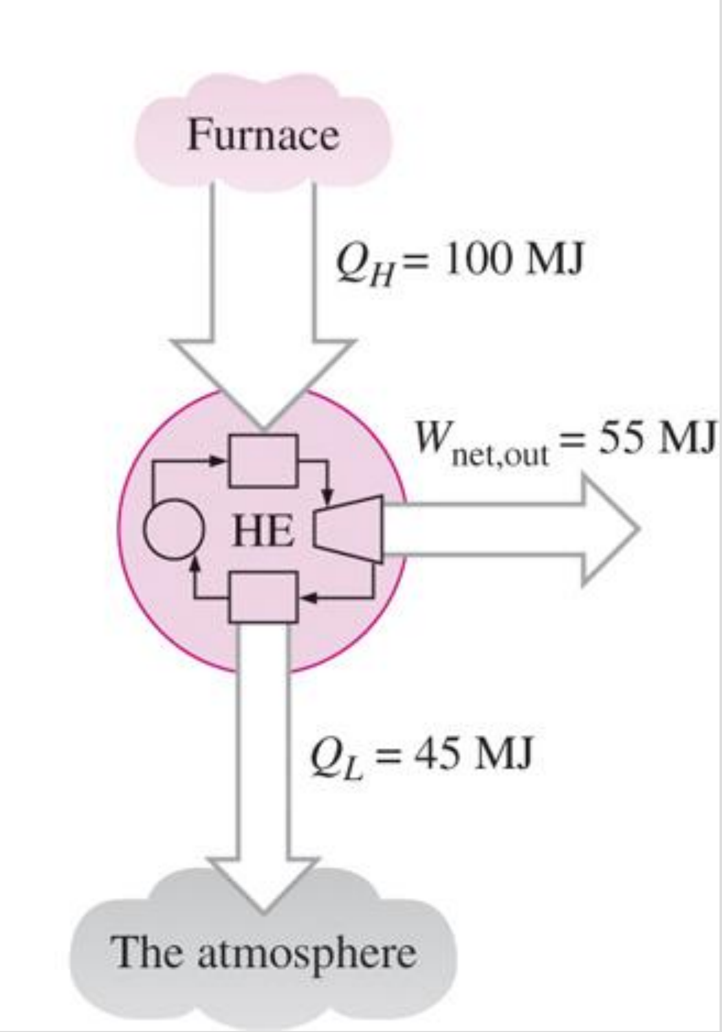
Thermal Efficiency of a Heat Engine

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



Thermal Efficiency of a Heat Engine

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



The Second Law of Thermodynamics

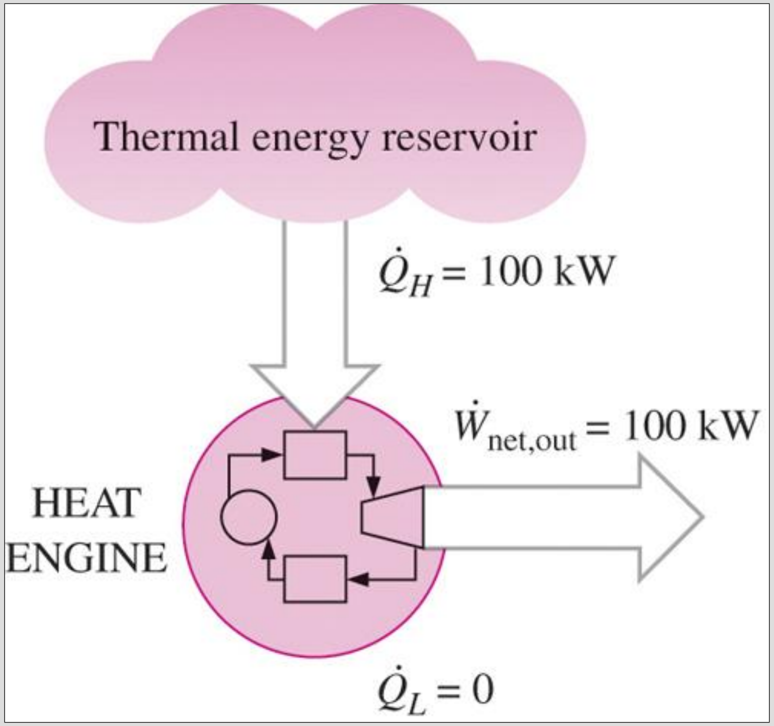
Kelvin-Planck Statement

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.

Implications

- No heat engine can have a thermal efficiency of 100%.
- For a power plant to operate, the working fluid must reject heat to the environment.

An Impossible Heat Engine



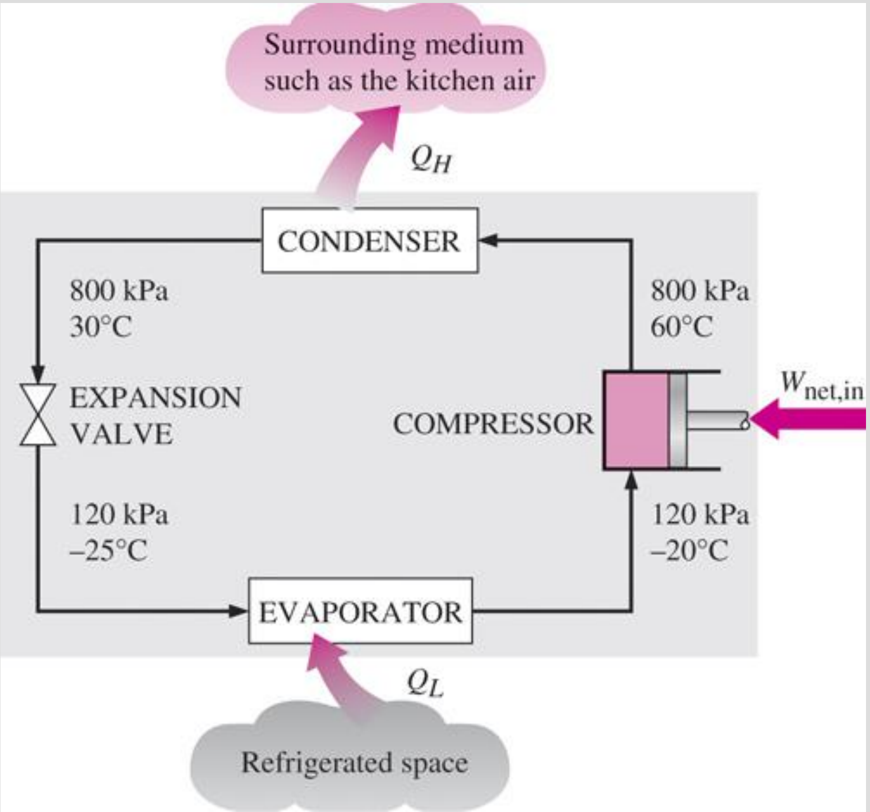
Refrigerators

- Transfer of heat from a low-temperature medium to a high-temperature one does not occur naturally.
- It requires special devices called **refrigerators**.
- Refrigerators 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***.

Vapor-Compression Refrigeration Cycle

HOW IT WORKS?

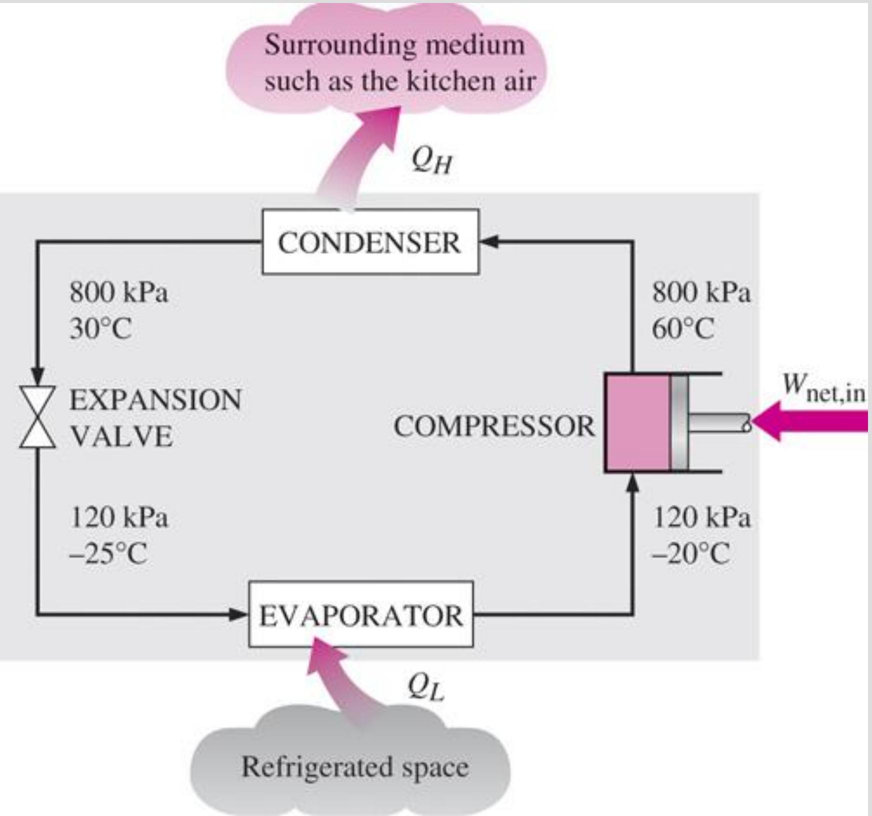
1. The refrigerant enters the evaporator at low pressure and temperature. It absorbs heat from the refrigerated space (Q_L) and evaporates. The refrigerant leaves as a saturated vapor or superheated vapor.



Vapor-Compression Refrigeration Cycle

HOW IT WORKS?

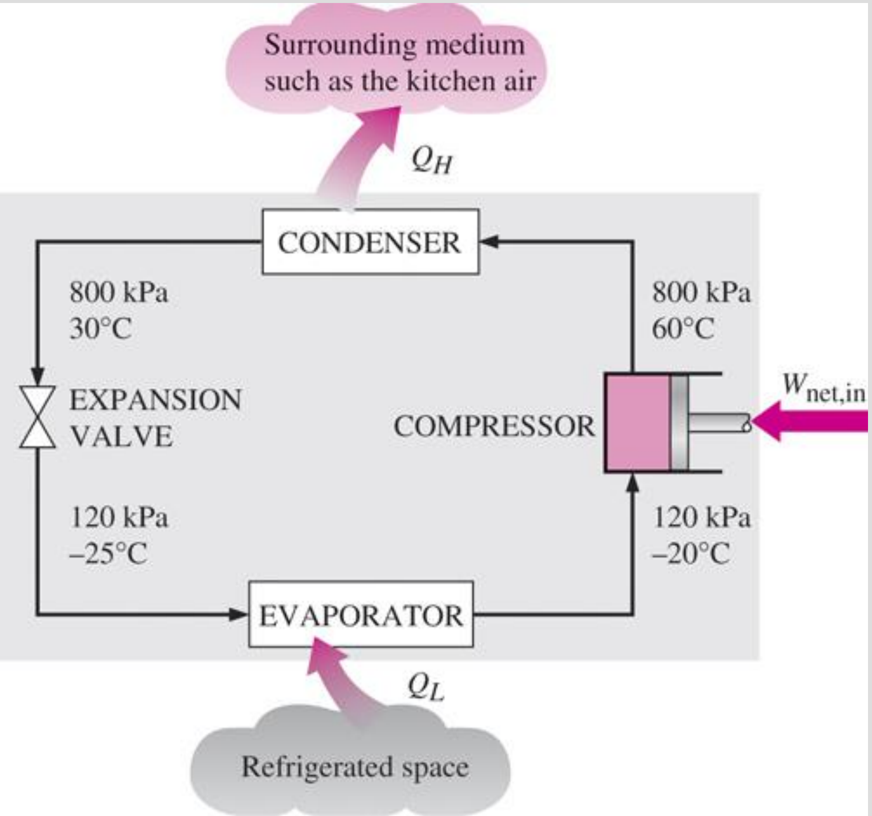
2.The refrigerant is compressed in the compressor to high pressure and temperature. The refrigerant leaves as a superheated vapor. This process requires work input ($W_{net,in}$)



Vapor-Compression Refrigeration Cycle

HOW IT WORKS?

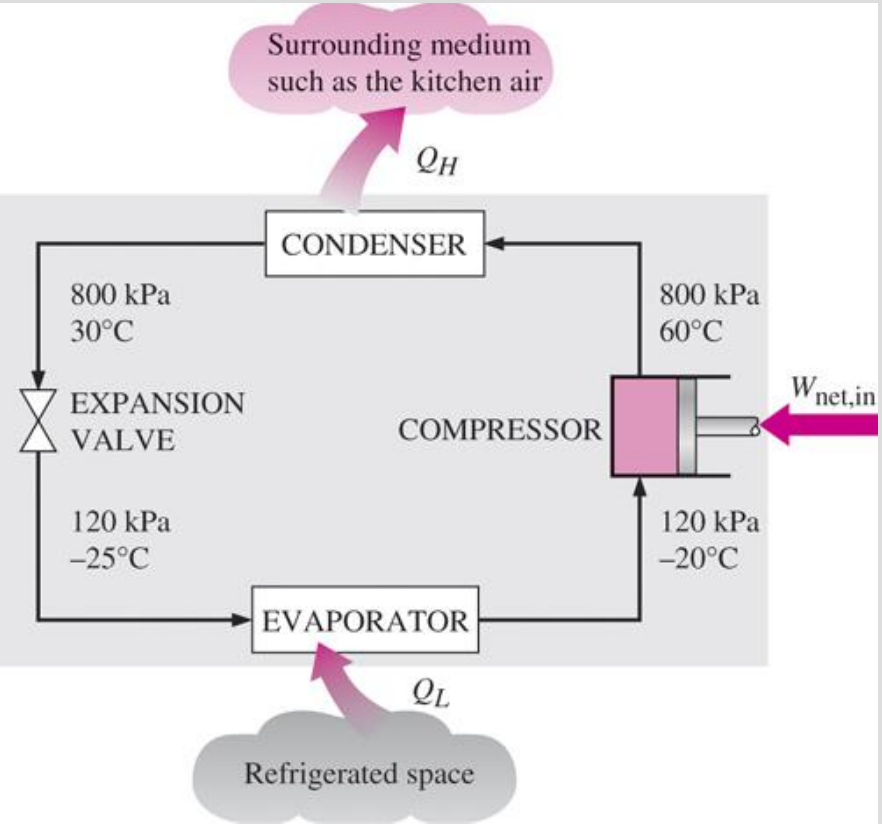
3. The refrigerant condenses in the condenser and rejects heat (Q_H) to the surroundings. The refrigerant leaves as a saturated liquid at high pressure and temperature.



Vapor-Compression Refrigeration Cycle

HOW IT WORKS?

4.The refrigerant goes through an expansion valve where its pressure and temperature decrease, going back to its original state.



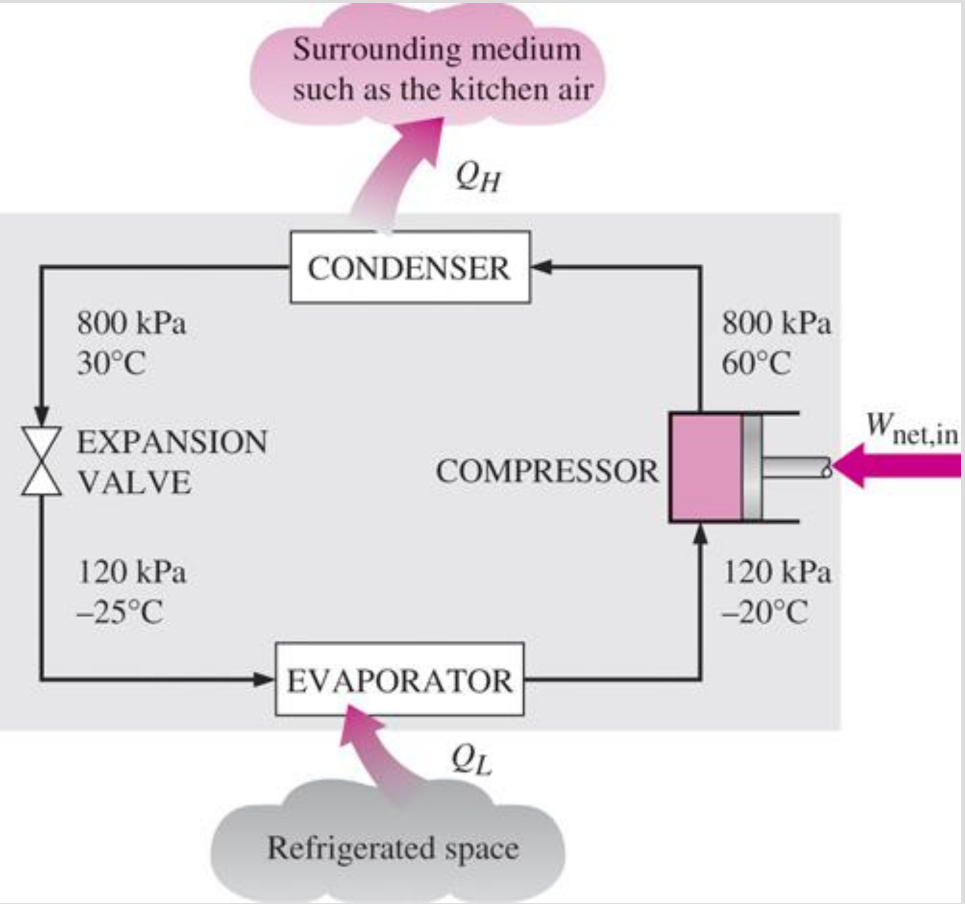
Vapor-Compression Refrigeration Cycle

ENERGY BALANCE

$$(Q_{in} + W_{in} + E_{mass,in}) - (Q_{out} + W_{out} + E_{mass,out}) = \Delta E_{system}$$

Simplifying,

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



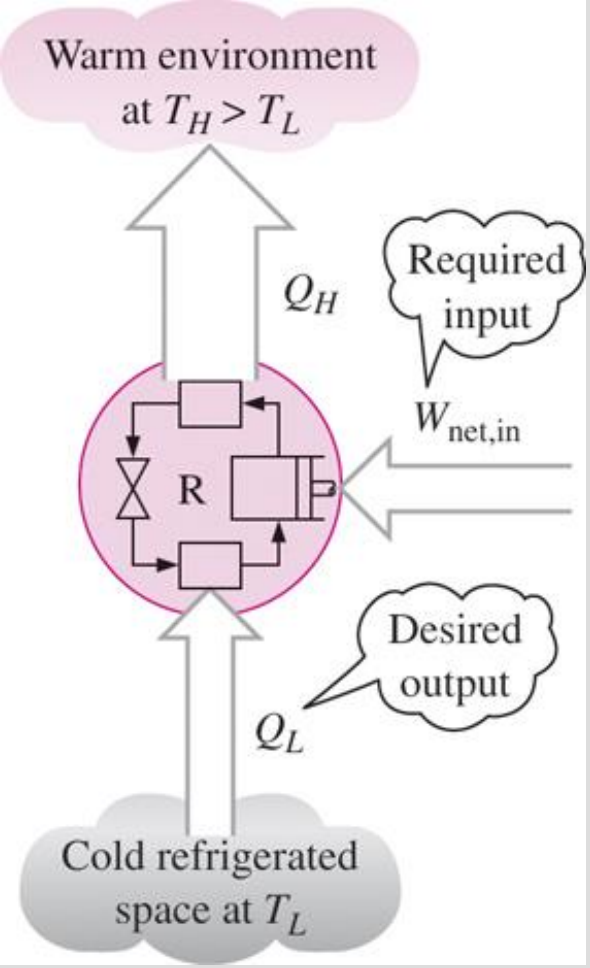
Coefficient of Performance

- 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.

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

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

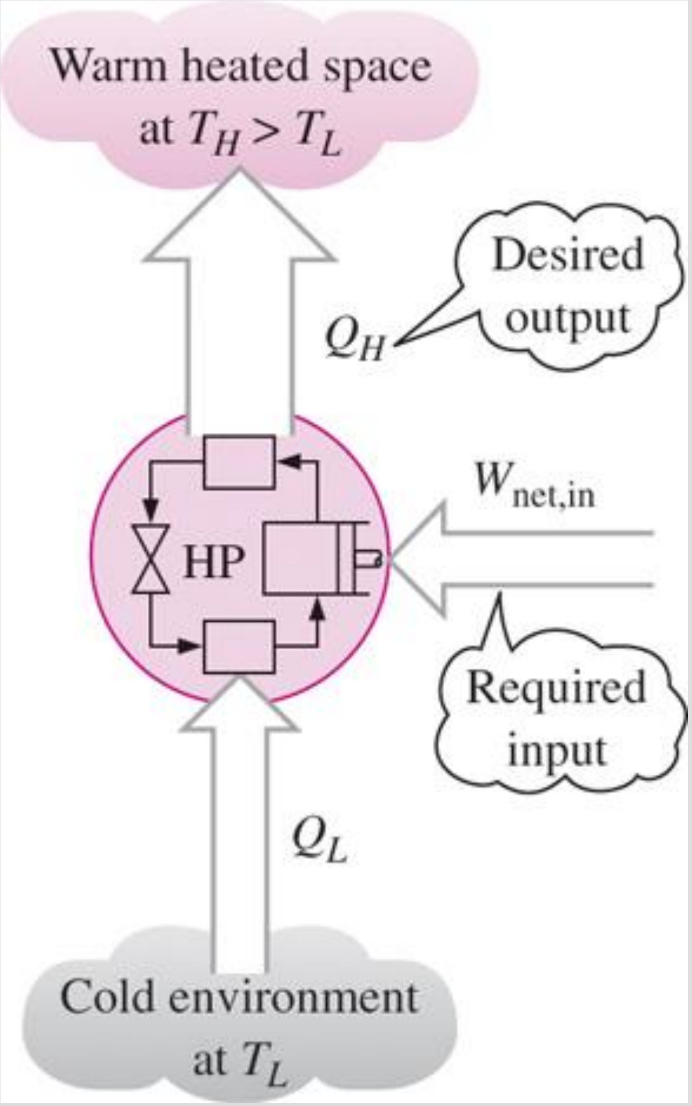
$$\mathrm{COP_R} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1}$$



NOTE: $\mathrm{COP_R}$ can be higher than 1. This does not contradict the first law.

Heat Pumps

- Heat pumps are very similar to refrigerators.
- The cycle components and their functions are the same.
- The difference is in the objective.
- The work supplied to a heat pump is used to extract energy from the cold outdoors (Q_L) and carry it into the warm indoors (Q_H).

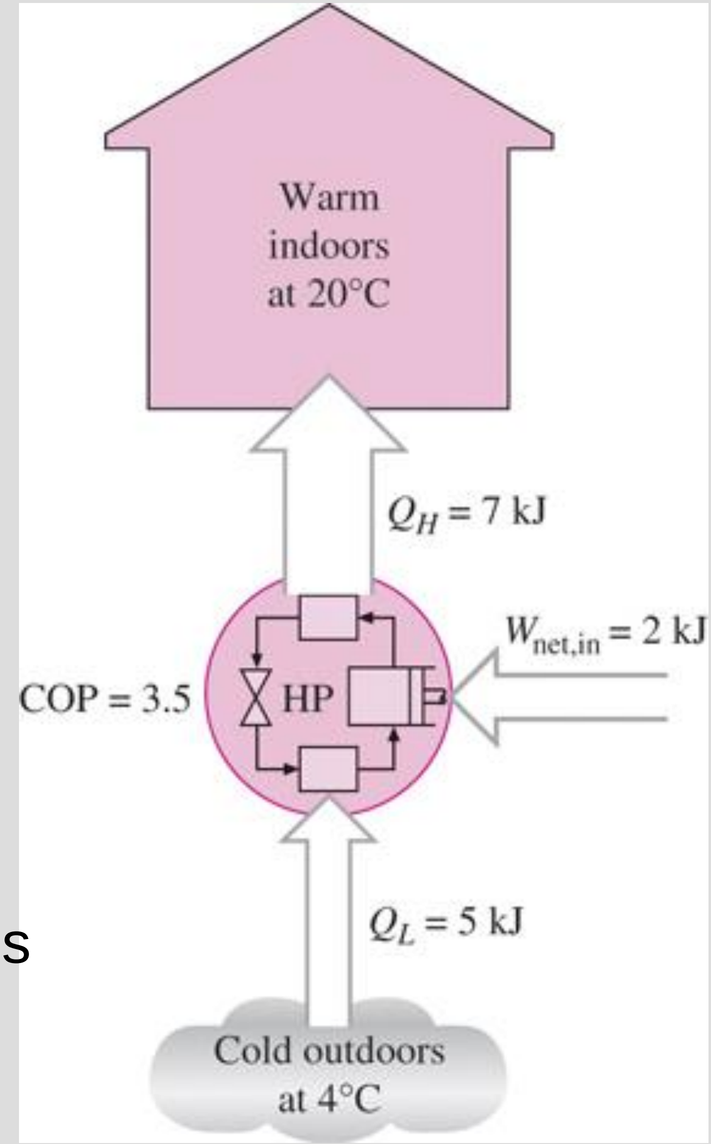


COP of Heat Pumps

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

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

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



- The minimum value of $\mathrm{COP_{HP}}$ is 1.
- It represents a case where the heat supplied to the warm indoors only comes from work input (e.g. an electric heater).
- This is a very inefficient process.

The Second Law of Thermodynamics

Clausius Statement

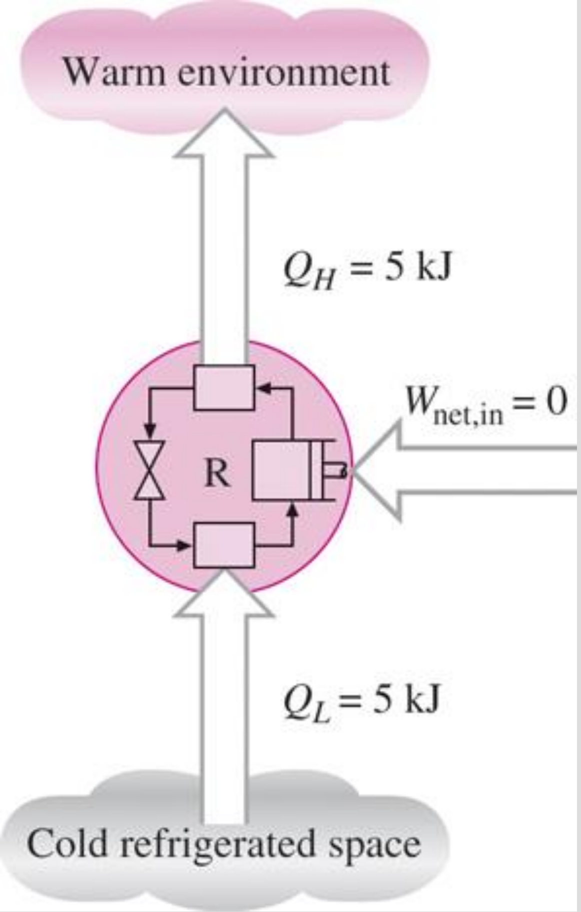
It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.

Implications

- A refrigerator cannot operate unless its compressor is driven by an external power source.

The Second Law of Thermodynamics

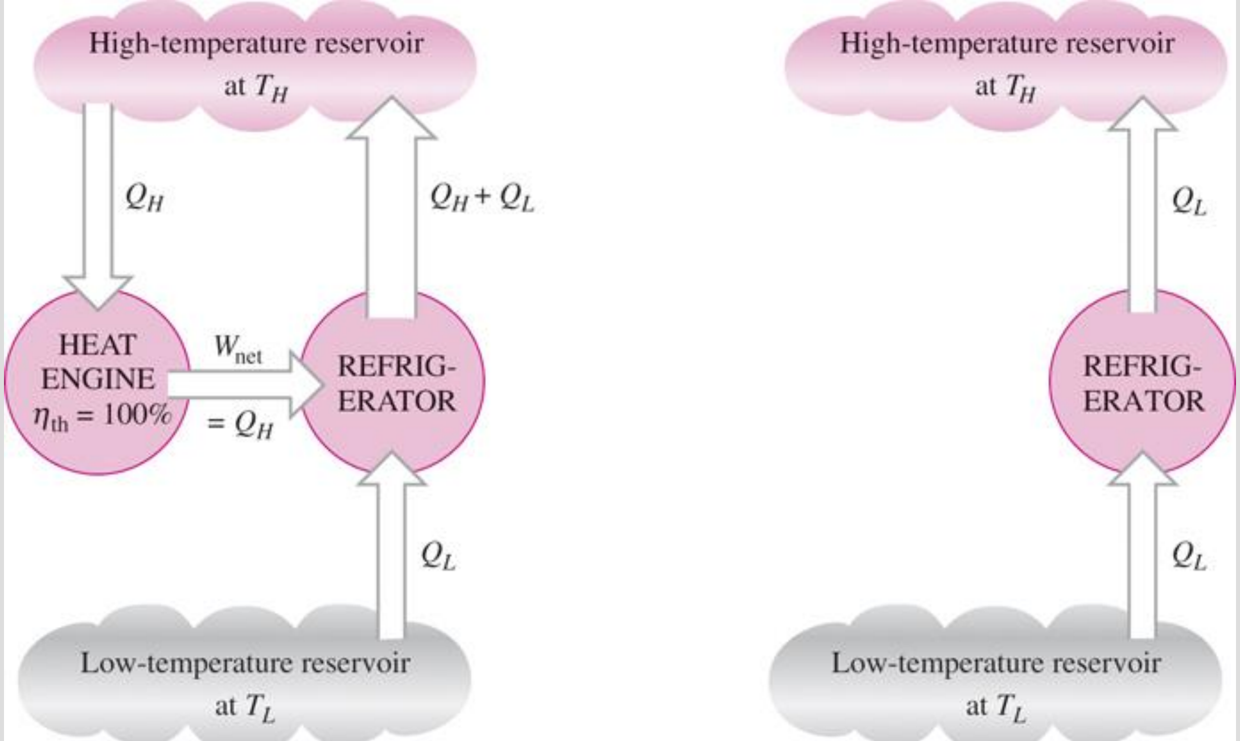
An Impossible Refrigerator



This refrigerator is impossible according to the Clausius Statement of the Second Law.

Equivalence of the Two Statements

- The Kelvin–Planck and the Clausius statements are equivalent in their consequences.
- Any device that violates the Kelvin–Planck statement also violates the Clausius statement, and vice versa.



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

(*b*) The equivalent refrigerator

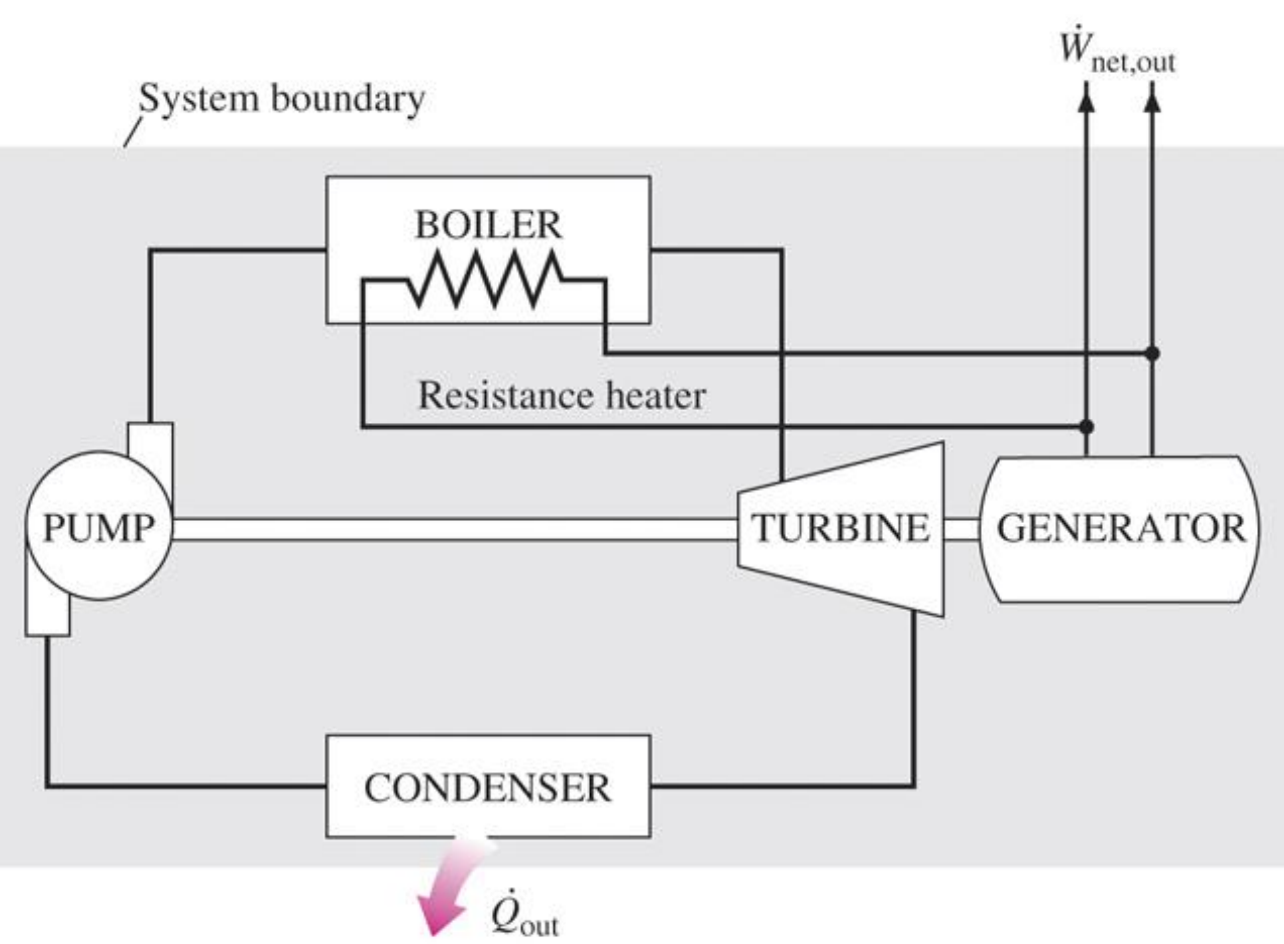
Perpetual Motion Machines

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.

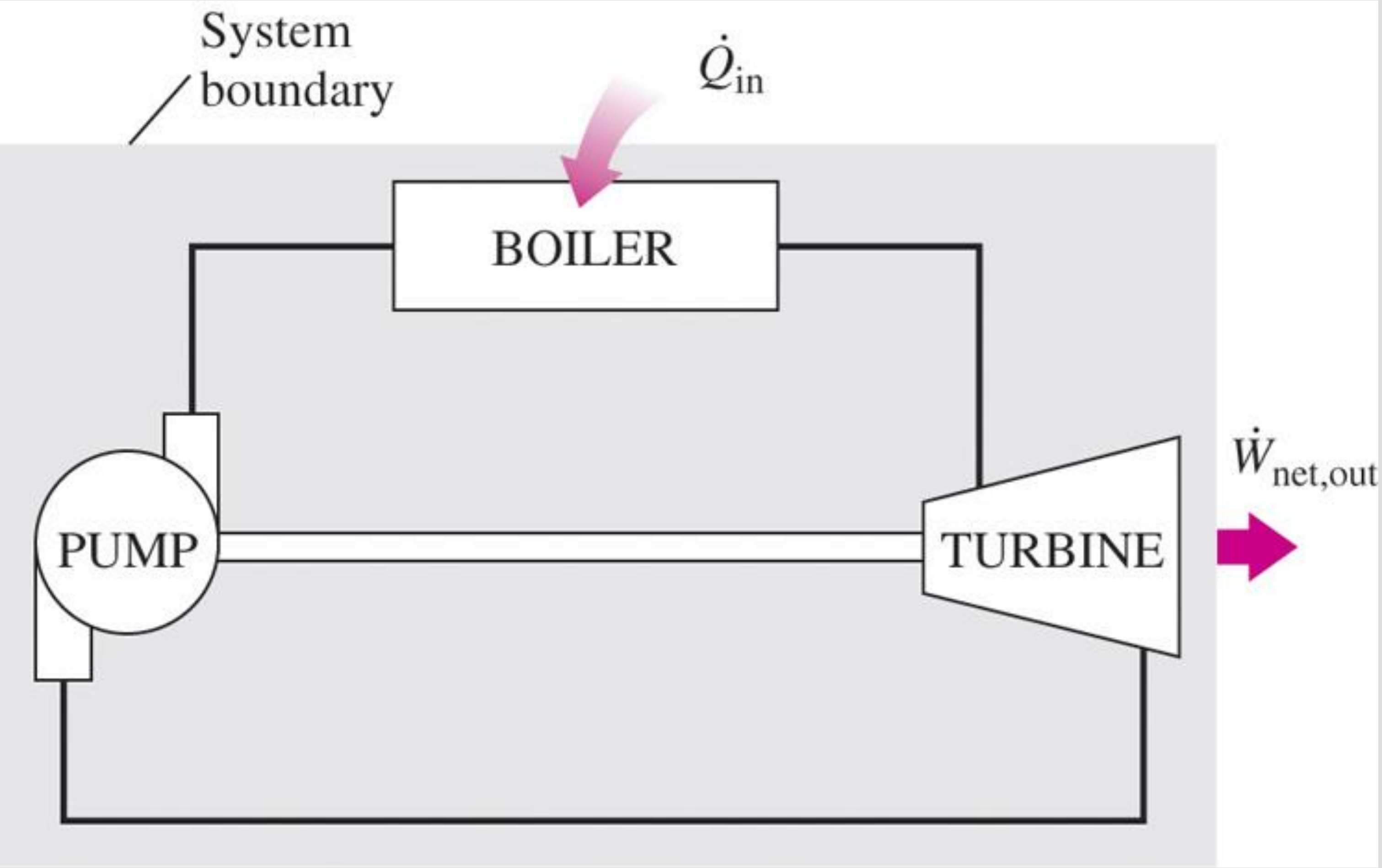
A device that violates the second law is called a PMM2.

Perpetual Motion Machines



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

Perpetual Motion Machines

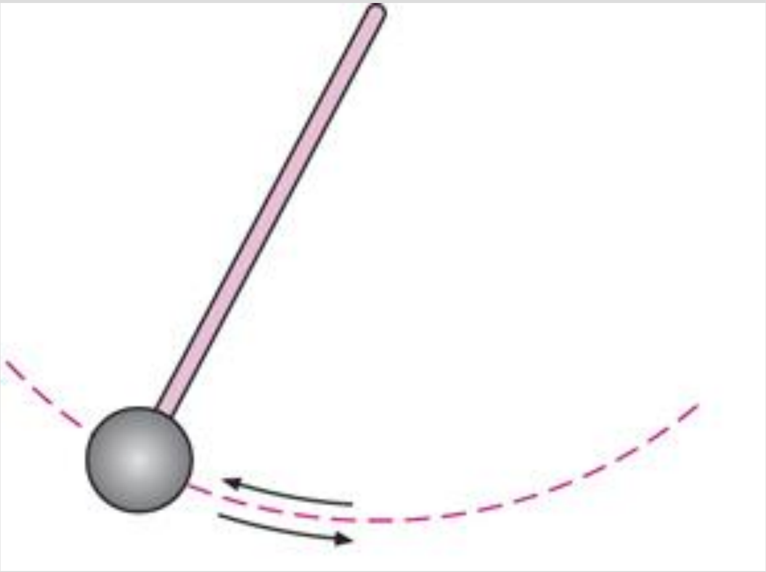


A perpetual-motion machine that violates the second law of thermodynamics (PMM2).

Reversible Processes

- A ***reversible process*** is a process that can be reversed without leaving any trace on the surroundings.

EXAMPLE

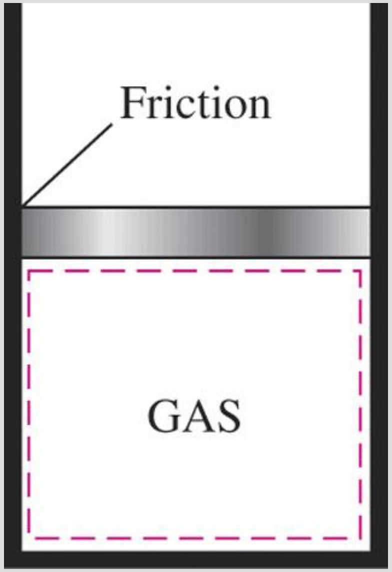


Frictionless Pendulum

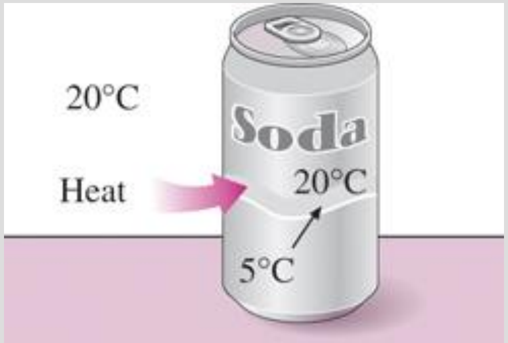
Irreversible Processes

- An ***irreversible process*** is a process that is not reversible, i.e. it leaves a trace on the surroundings.

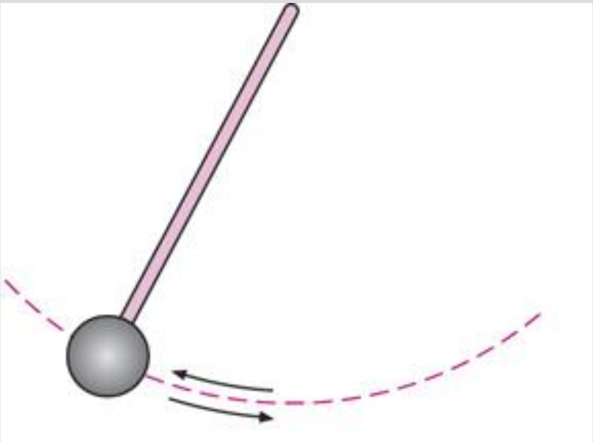
EXAMPLES



Reversing the expansion of a gas will require additional work to overcome friction



Cooling a soda after it gets warm requires work



Returning a real pendulum to its original position requires work to overcome friction

Reversible vs. Irreversible Processes

- All processes occurring in nature are irreversible.
- Some processes are more irreversible than others.

Examples:

  - **Processes with large friction forces.**
  - **Processes with large temperature difference between system and surroundings.**

- Reversible processes deliver the most work if they are work-producing processes, e.g. expansion.
- Reversible processes consume the least work if they are work-consuming processes, e.g. compression.
- We try to approach reversible processes.
- Reversible processes serve as idealized models to which irreversible (actual) processes can be compared.

Types of Irreversibilities

- The factors that cause a process to be irreversible are called ***irreversibilities***.

Examples:

- Friction.
- Heat transfer across a finite temperature difference.
- Mixing of two fluids.
- Chemical reactions.

Internally and Externally Reversible Processes

- ***Internally reversible process:*** If no irreversibilities occur within the boundaries of the system during the process.

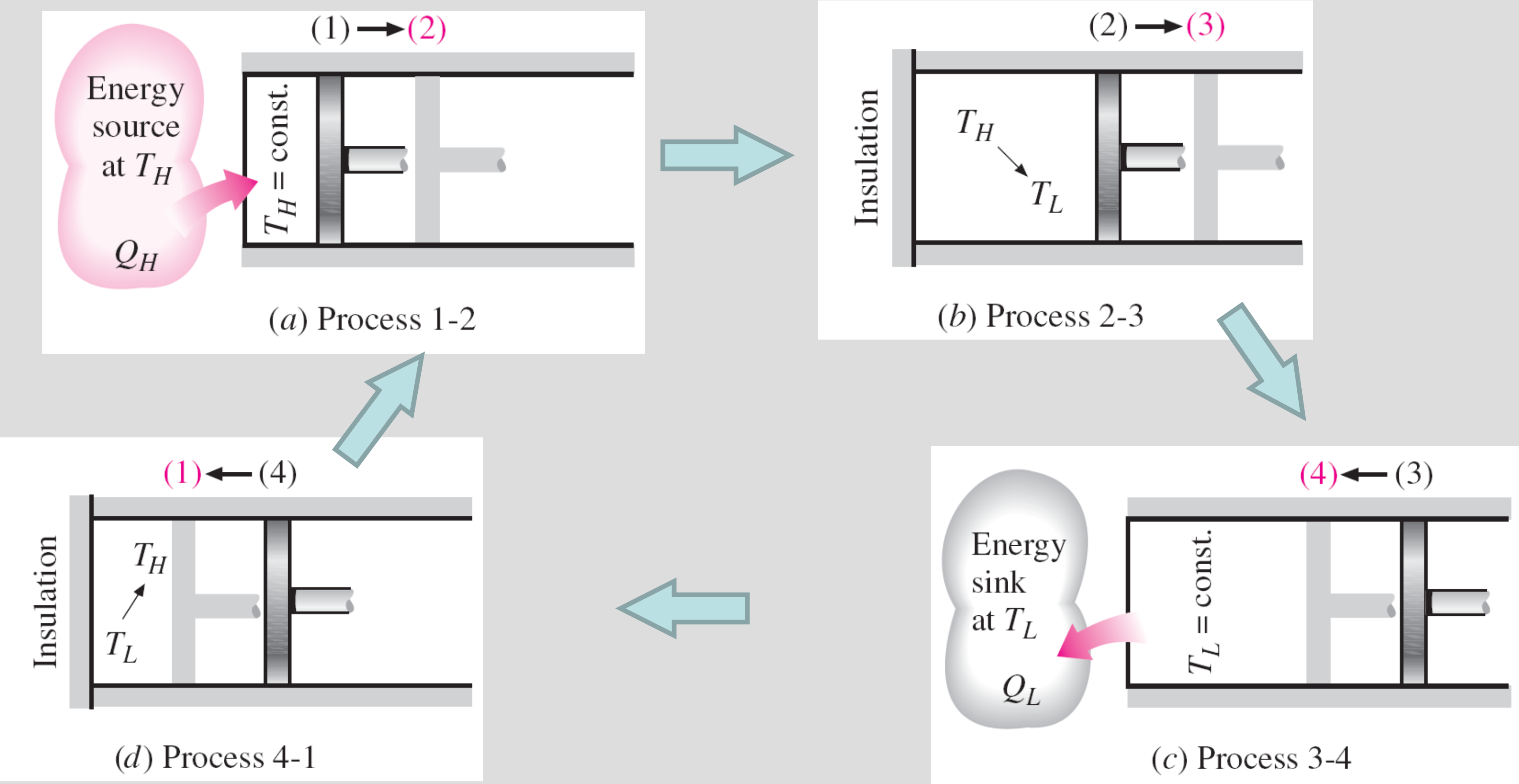
  Example: a process with no friction (can be approached by use of lubrication or high-efficiency ball bearings).

- ***Externally reversible process:*** If no irreversibilities occur outside the system boundaries.

  Example: a process with no heat transfer, or with heat transfer but with a very small temperature difference between the system and surroundings.

- ***Totally reversible process:*** It involves no irreversibilities within the system or its surroundings.

Example of a Reversible System: Carnot Cycle



(*a*) Process 1-2

(*b*) Process 2-3

(*c*) Process 3-4

(*d*) Process 4-1

Process 1-2: Reversible Isothermal Expansion (T_H = constant)

Process 2-3: Reversible Adiabatic Expansion (temperature drops from T_H to T_L)

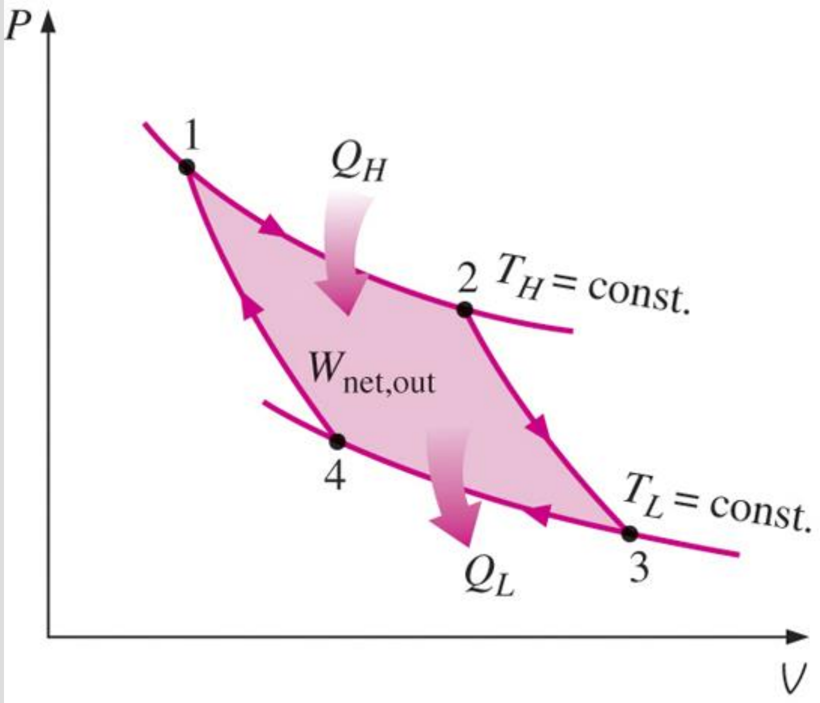
Process 3-4: Reversible Isothermal Compression (T_L = constant)

Process 4-1: Reversible Adiabatic Compression (temperature rises from T_L to T_H)

Carnot Heat Engine

- The Carnot cycle satisfies all the conditions of a heat engine

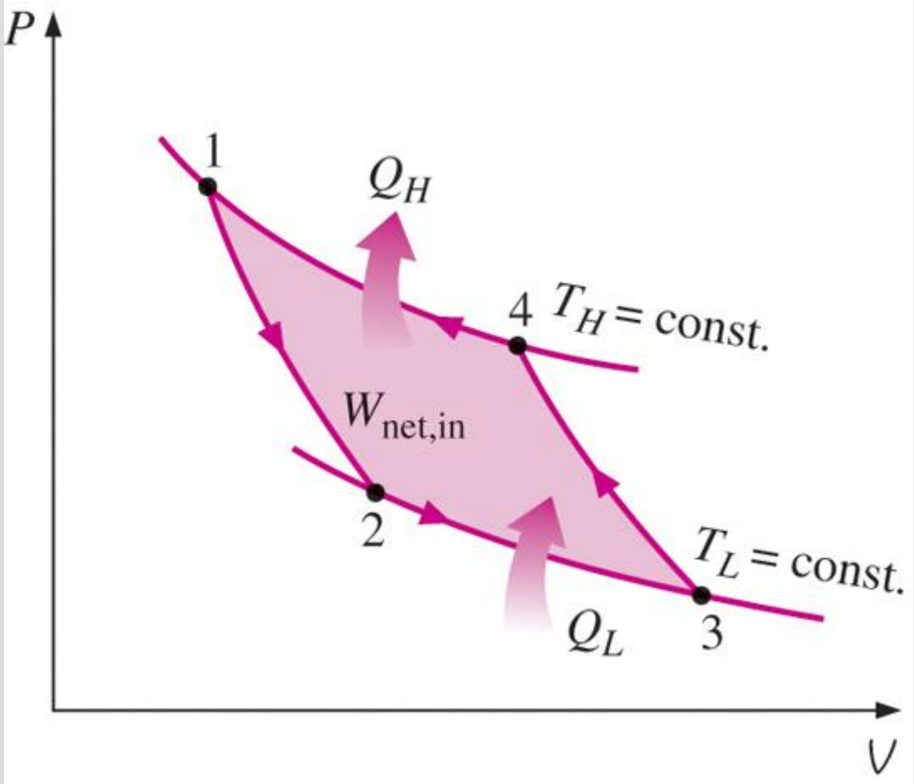
  → It is also called a ***Carnot heat engine***.
- The net result is the conversion of part of Q_H to net work output.
- The Carnot heat engine is unique → it is totally reversible.



Reversed Carnot Cycle

- All the processes that comprise the Carnot cycle can be reversed.
- The reversed Carnot cycle receives heat from a low-temperature source, adds net work input, and supplies heat to a high-temperature sink.

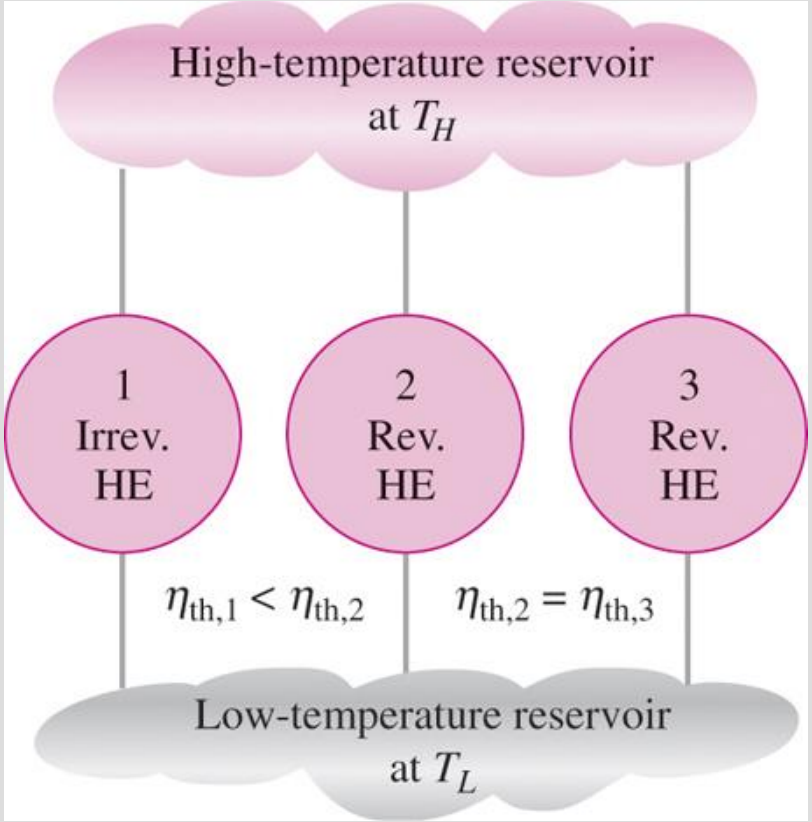
→ The reversed Carnot cycle is a refrigeration cycle.



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 efficiency of a Carnot heat engine is the maximum possible efficiency

Carnot Efficiency

- As shown earlier, the efficiency of any heat engine is given by:

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

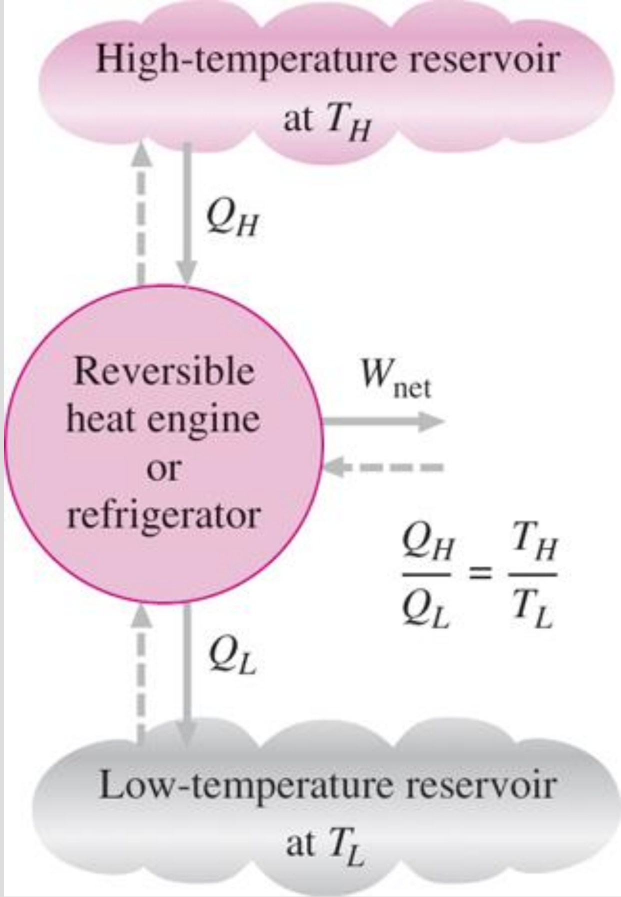
- It can be shown that, for a reversible cycle (e.g. Carnot heat engine):

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

  where T_H and T_L ***must*** be absolute temperature (i.e. in Kelvin or Rankine).

- The efficiency of a reversible heat engine is a special case, which can be expressed as:

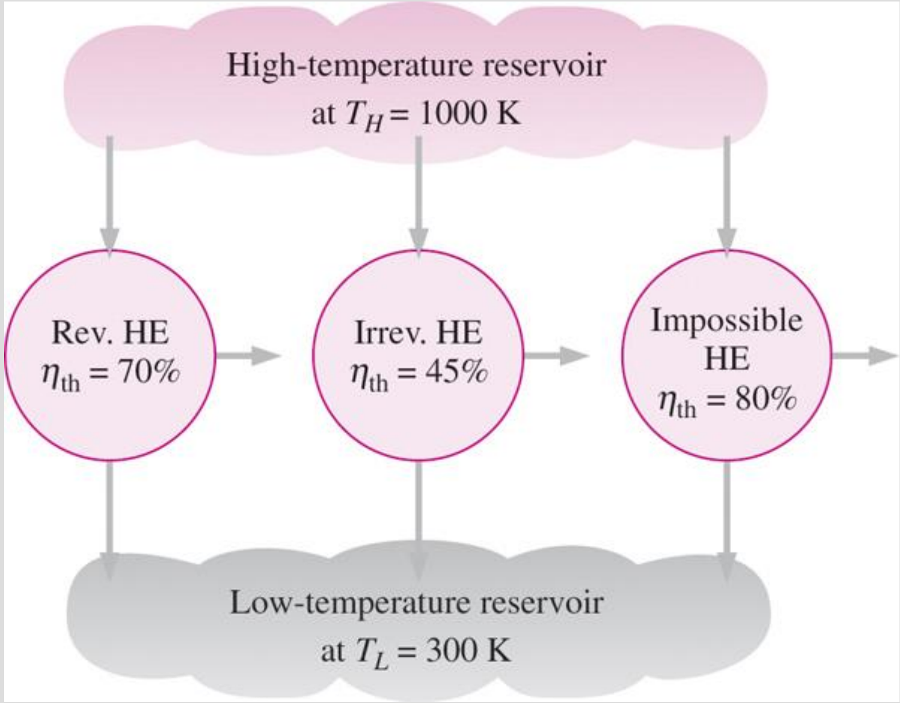
$$\eta_{\text{th,rev}} = 1 - \frac{T_L}{T_H}$$



Carnot Efficiency

- A reversible (e.g. 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 higher efficiency than a reversible heat engine operating between the same temperature limits.

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



Carnot Refrigerator and Heat Pump

- It has been shown earlier that:

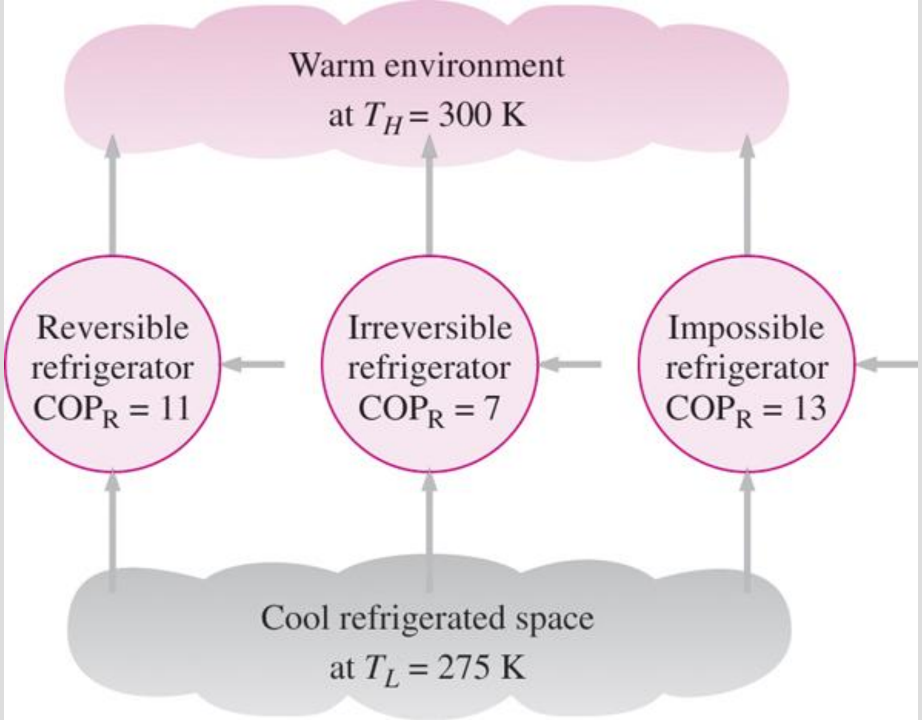
$$\text{COP}_\text{R} = \frac{1}{Q_H/Q_L - 1}$$

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

- Since $Q_H / Q_L = T_H / T_L$ for a reversible cycle, the COP for a Carnot refrigerator or heat pump can be given by:

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

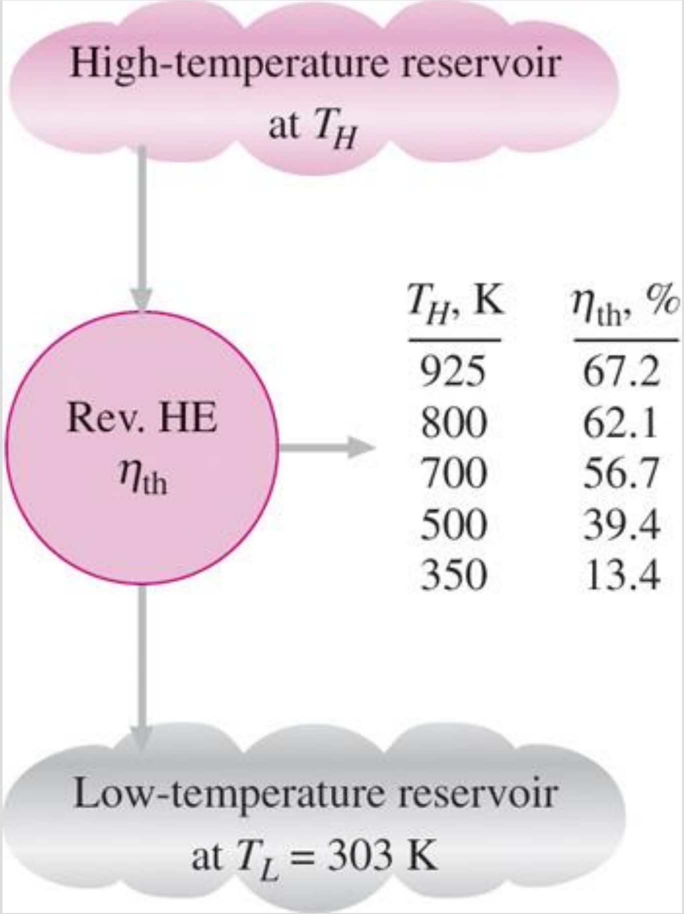
$$\text{COP}_\text{R,rev} = \frac{1}{T_H/T_L - 1}$$



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

Quality of Energy

- The fraction of heat that can be converted to work is a function of source temperature.
- The higher the temperature of the thermal energy, the higher its quality.
- Even though efficiencies of actual heat engines are lower than reversible heat engines, the same principle still applies.



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