CHAPTER 6

THE SECOND LAW OF THERMODYNAMICS

CHAPTER 6 -- The Second Law of Thermodynamics

OUTCOME:

- Identify Valid (possible) Processes as those that satisfy both the first and second laws of Thermodynamics
- Understand concepts of thermal energy reservoirs; reversible and irreversible processes; heat engines; refrigerators; and heat pumps.
- State the Kelvin-Plank and Clausius statements of the Second Law and demonstrate their equivalence
- Apply the Second Law of Thermodynamics to Cycles and cyclic devices
- Describe the Carnot Cycle; Carnot's principles; and idealized Carnot heat engines, refrigerators and heat pumps
- Obtain expressions for the thermal efficiencies and coefficients of performance for reversible heat engines, heat pumps & refrigerators

Why do we need another law??

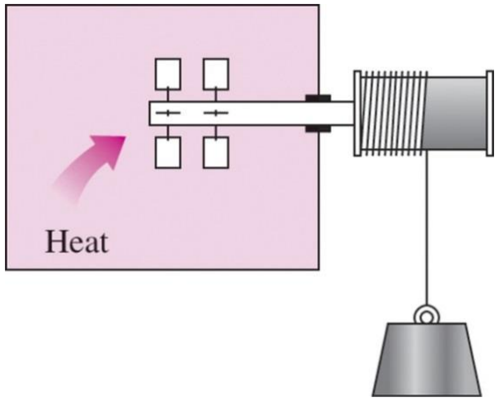
- **The first law is a “book keeping” law**
  - Keeps track of energy in & out of the system to make sure that energy is conserved
  - Does not place any constraints on the direction of processes or the levels of performance of thermodynamic systems

Introduction to the Second Law

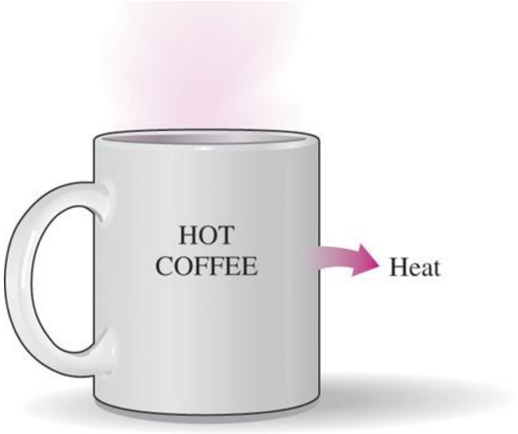
- Empirical observation suggests that some processes can proceed only in certain direction and cannot be reversed
- **Examples:**
  - Heat transfer across a temperature difference
  - Frictional heating (stirrer)

Introduction to the Second Law

Some processes do not violate the first law of thermodynamics, but they 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

- The second law places constraints on the directionality of processes and on the extent by which heat can be continuously converted into work.
- **Where does it come from?**
    - Like all fundamental laws, its truth rests on the fact that in all our experience, no system has ever been found which violates it.

Introduction to the Second Law

- 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 be possible.
- 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*** of performance for certain engineering systems.

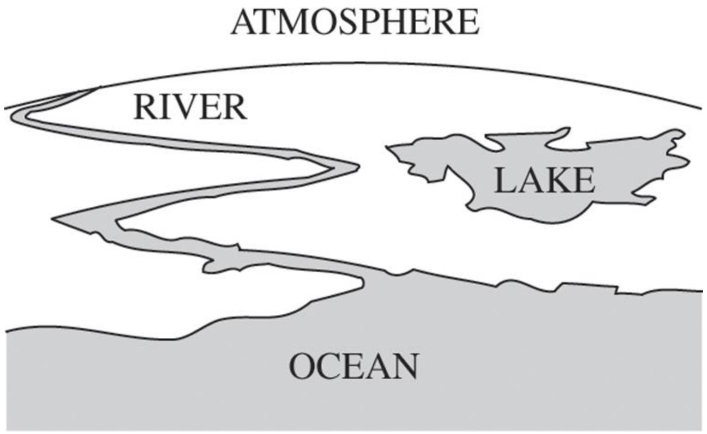
Introduction to the Second Law

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

Thermal Energy Reservoirs

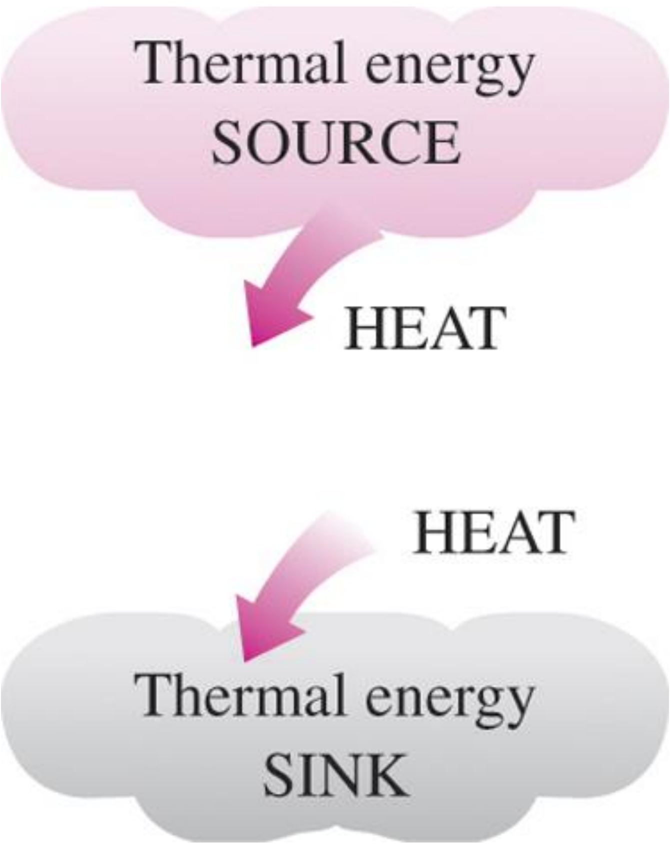
- A ***thermal energy reservoir*** is a body with a relatively large thermal energy capacity.
- It can supply or absorb finite amounts of heat without a measurable change in its temperature.

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

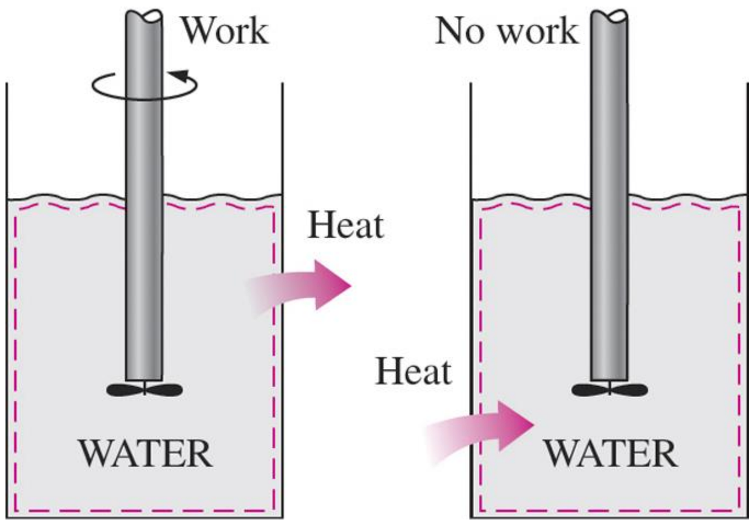
- Some thermal energy reservoirs can be considered sources in some applications and sinks in other applications.

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.***
- When a window air conditioner is used to cool a room, ***the atmosphere is a sink*** that absorbs the heat rejected from the room

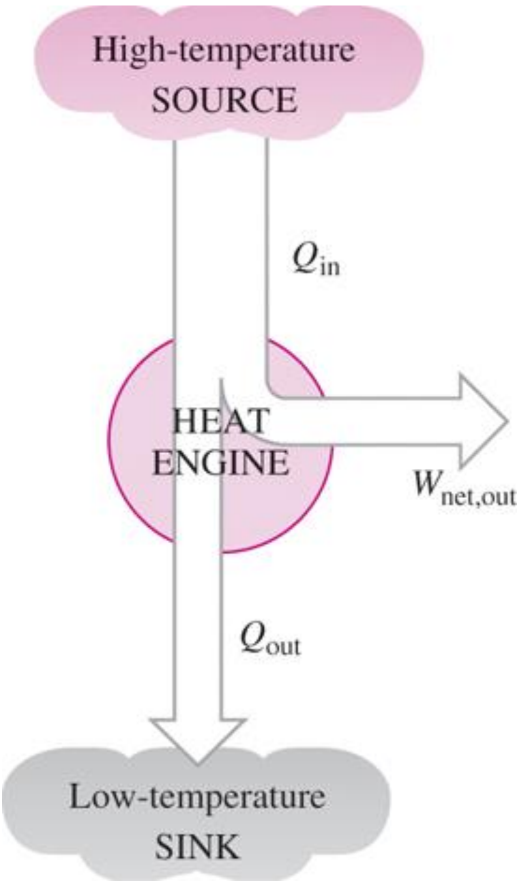
Heat Engines

- Work can always be converted to heat **completely and continuously**, but the reverse is not true.
- Converting heat to work requires engineered devices.
- The type of device that can continuously convert 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.



HEAT ENGINES

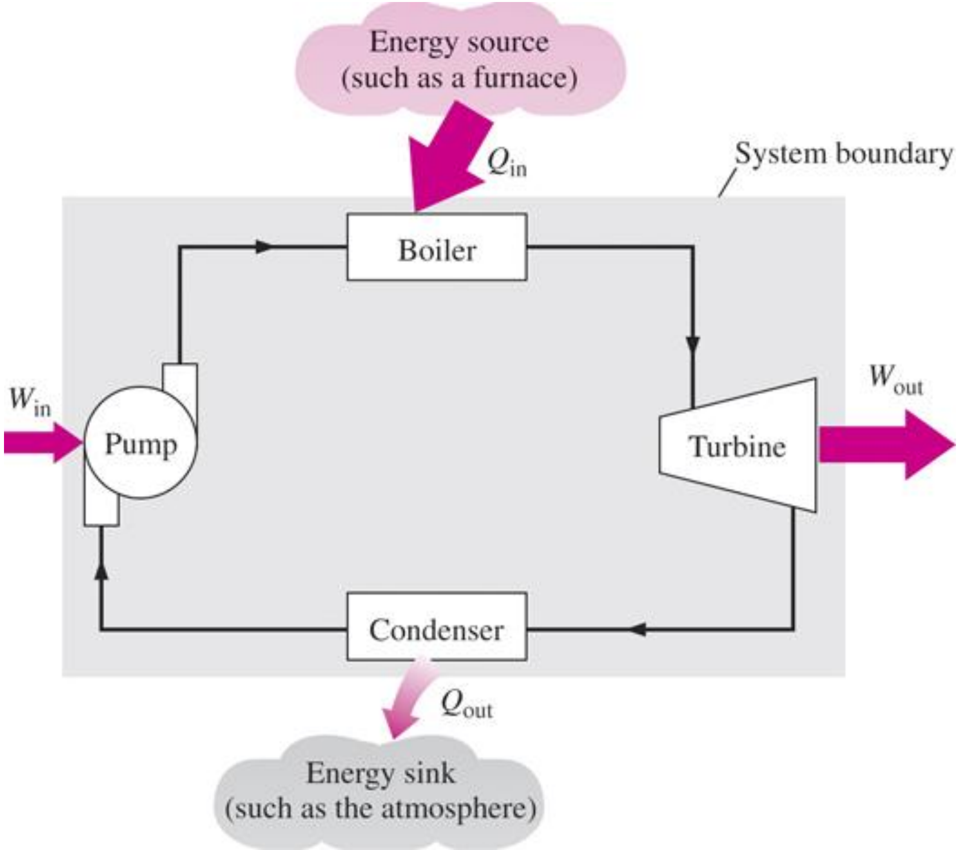
- A "Heat Engine" is a device that operates in a thermodynamic cycle and produces a certain amount of **net positive work** as a result of net heat transfer from a high temperature body to a low temperature body

HEAT ENGINES

- **There are two invariable characteristics of heat engines:**
  - Heat addition process at a relatively high temperature
  - Heat rejection process at a relatively low temperature
- Since the devices operate in a cycle, the first law dictates that the net work produced is equal to the net heat added (i.e. the difference between the amount of heat added and the amount of heat rejected)
- The fluid to and from which heat is transferred while undergoing a cycleis called the ***working fluid***.

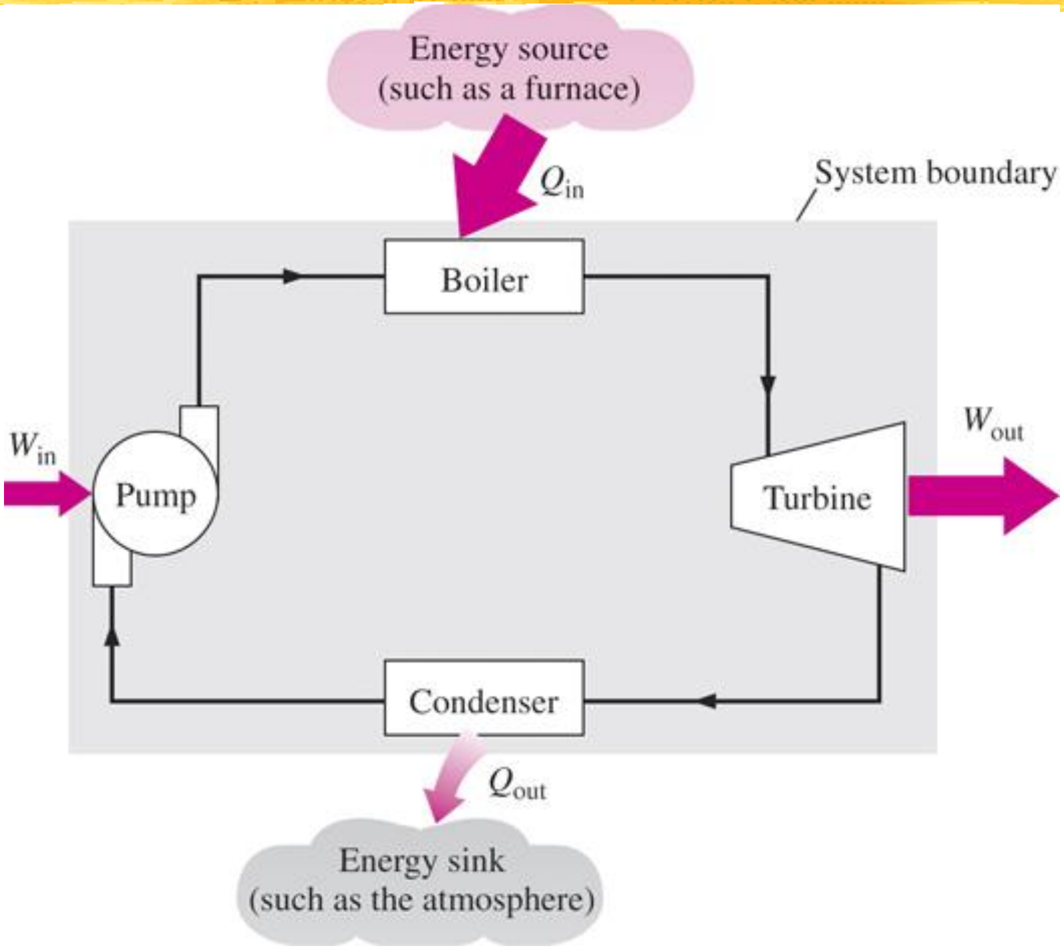
Heat Engines --
Example: Simple Steam Power Plant

- 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**



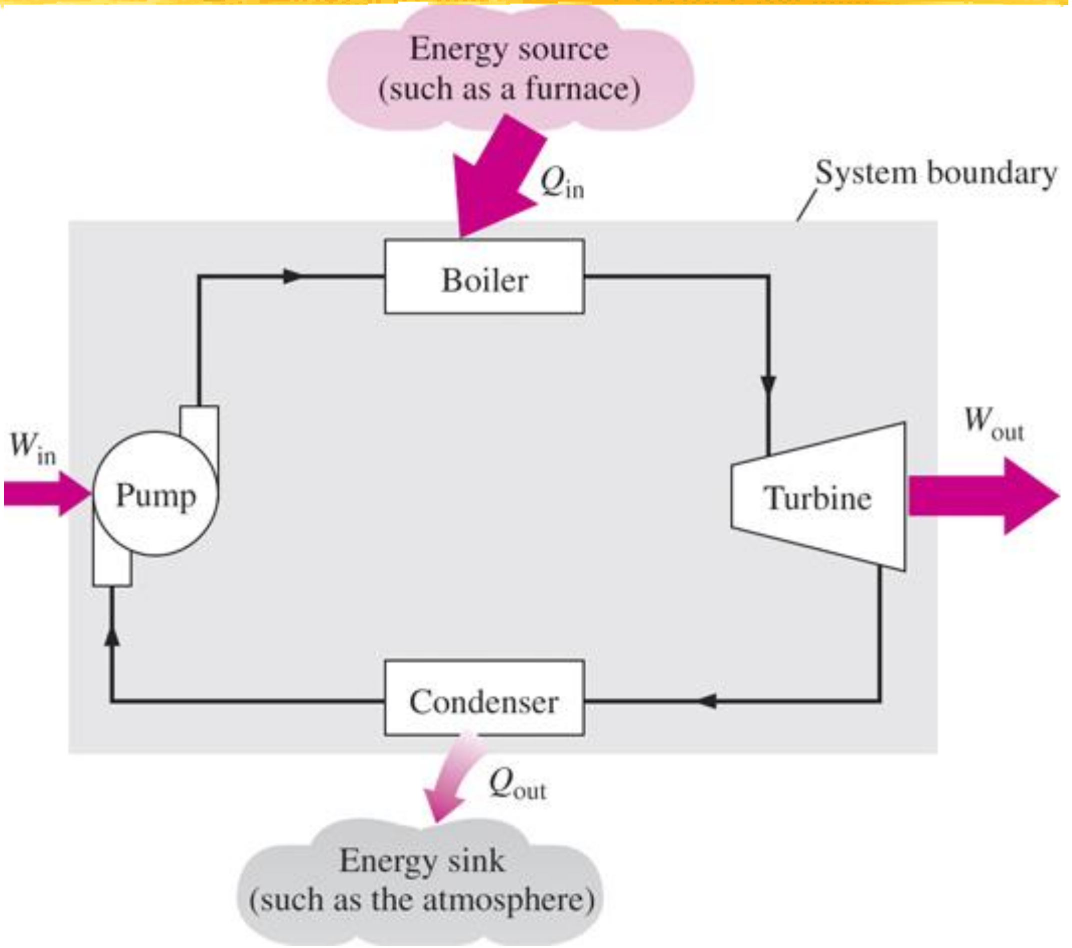
Steam Power Plant –
How does it work?

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



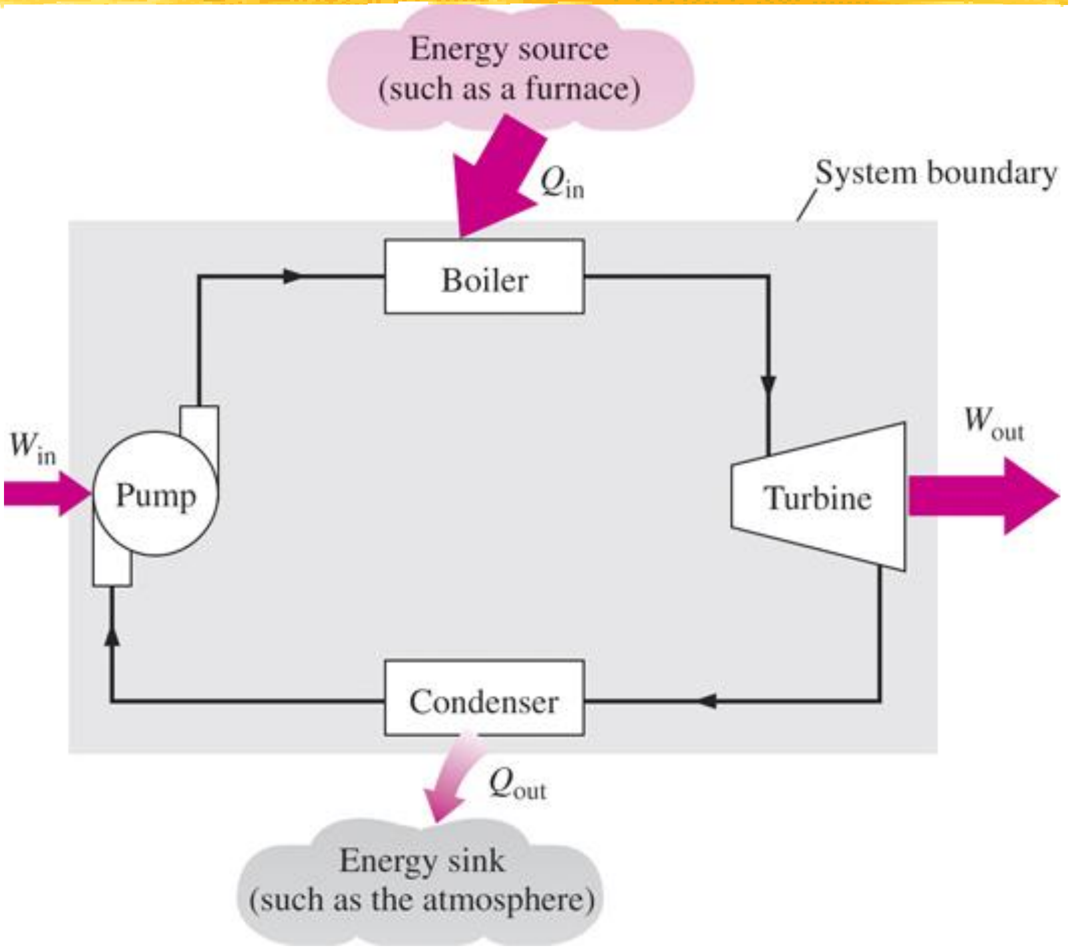
Steam Power Plant –
How does it work?

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).



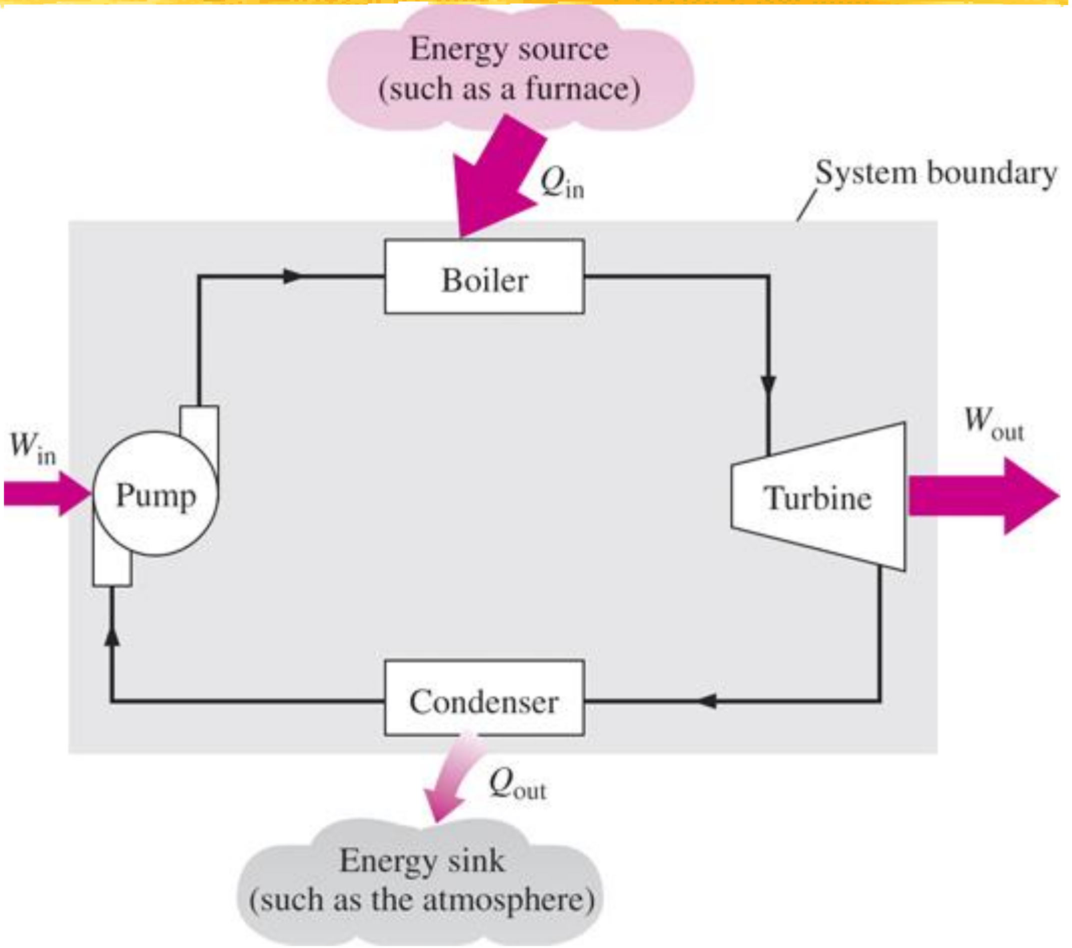
Steam Power Plant –
How does it work?

3. The condenser condenses the 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 does it work?

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



Steam Power Plant – ENERGY BALANCE

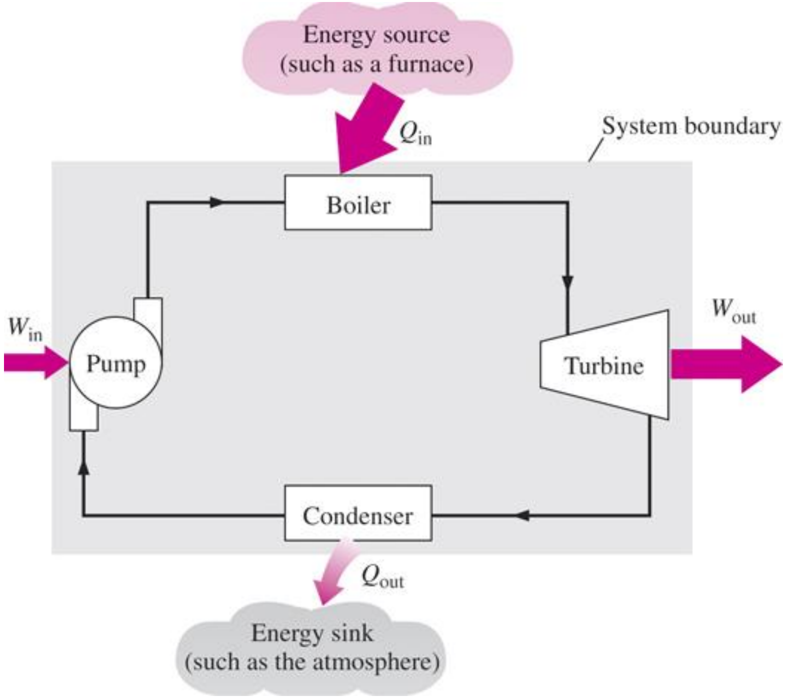
$$(Q_{in} + W_{in} + E_{mass,in}) - (Q_{out} + W_{out} + E_{mass,out}) = \Delta E_{system}$$

- ❑ The plant operates as a **closed system** undergoing a cycle consisting of four processes.
- ❑ Therefore,

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

- ➢ Pump work is extracted from the turbine output before power is supplied to the grid.

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



Thermal Efficiency of a Heat Engine

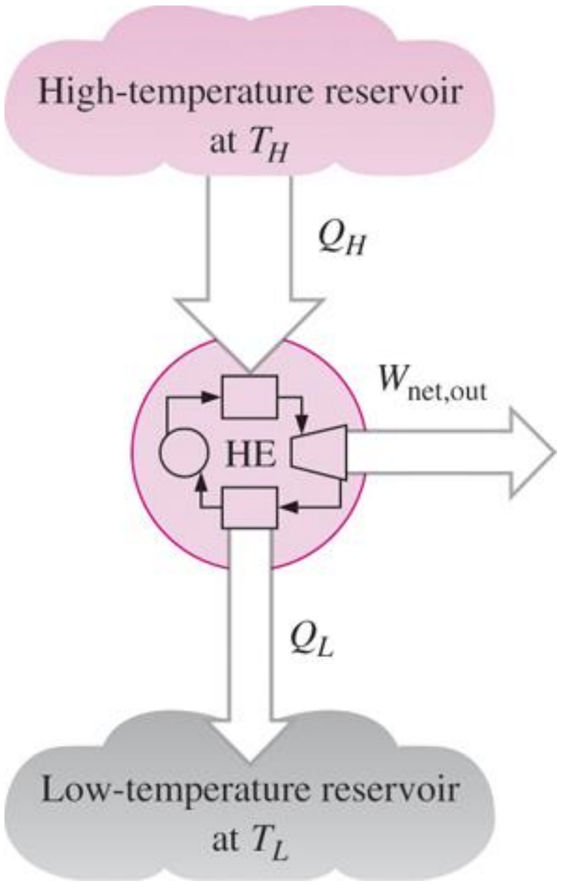
Recall Chapter 2: Performance is measured by comparing the desired output to the required input:

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

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

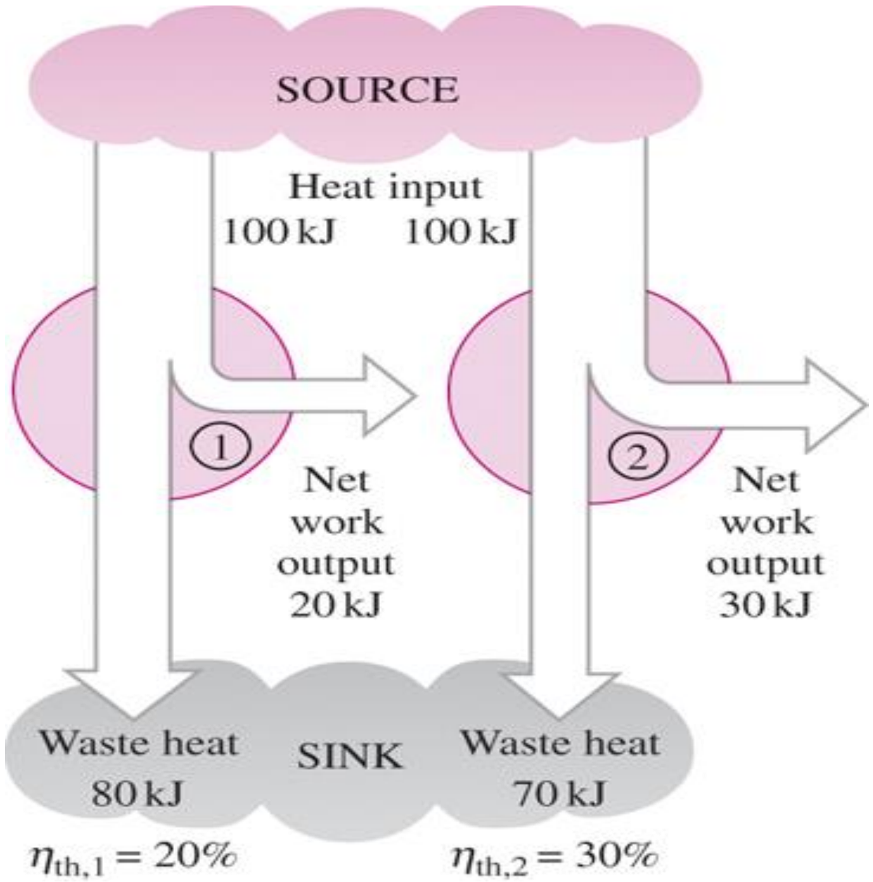
$$W_{net,out} = Q_H - Q_L$$

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



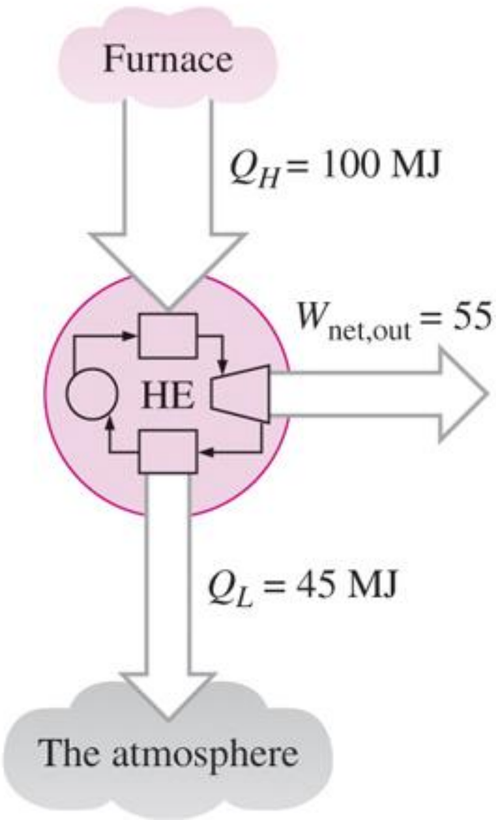
Thermal Efficiency of a Heat Engine

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



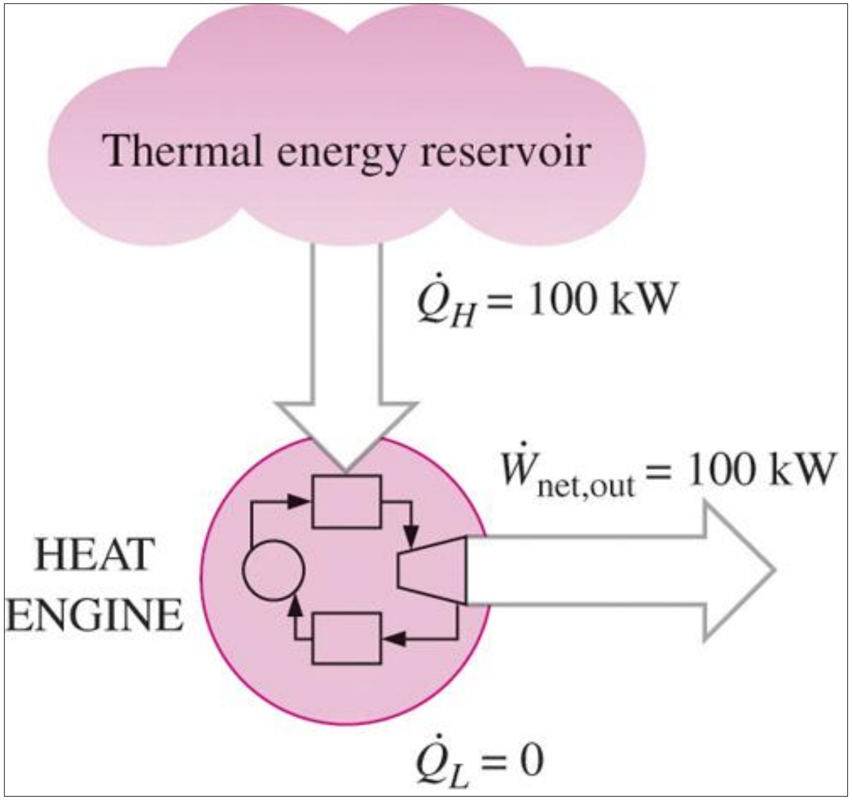
Thermal Efficiency of a Heat Engine

- Even the most efficient heat engines reject nearly one-half of the energy they receive as "waste heat."
- What is the best that can be done?? [More on that later]



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.



An Impossible Heat Engine

Implications of The Kelvin-Planck Statement

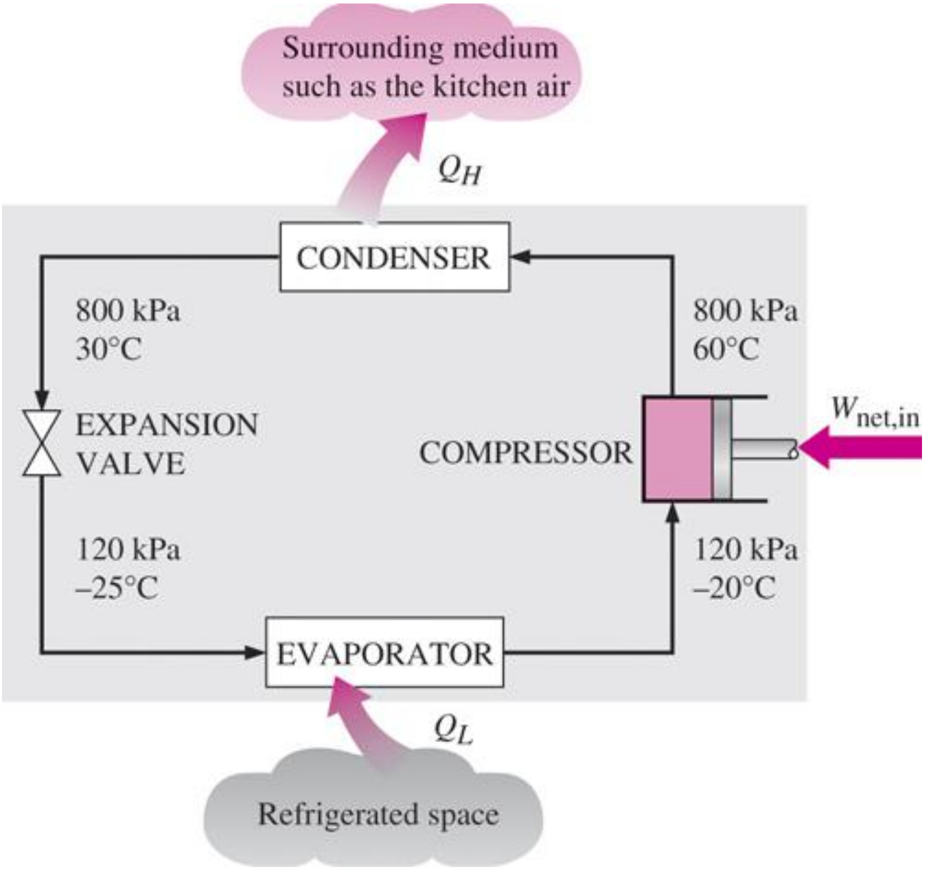
- Heat **cannot** be **completely** and **continuously** converted to work
- All heat engines **MUST** have a heat rejection process to a lower temperature “sink”
- The efficiency of a heat engine **MUST** be less than 100%.
- What is the best that can be done?? **[More on that later]**

Refrigerators & Heat Pumps

- From experience, we know that heat, **by itself**, cannot be transferred from a low temperature body to a higher temperature body.
  - Refrigerators and Heat Pumps are devices that operate in a cycle and allow us to transfer heat from a low temperature source to a higher temperature sink. ***To do so, an amount of work must be expended***
  - The most frequently used refrigeration cycle is the ***vapor-compression refrigeration cycle***.
  - The working fluid used in the refrigeration cycle is called a ***refrigerant***.

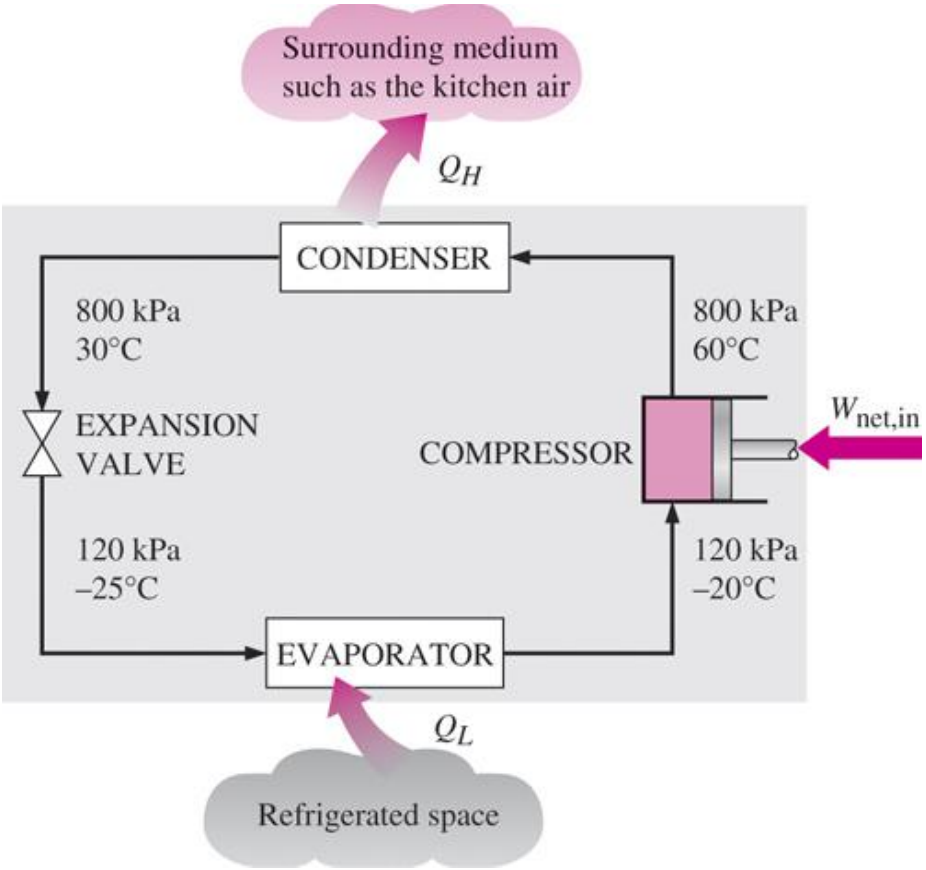
Vapor-Compression Refrigeration Cycle – How does it work?

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.



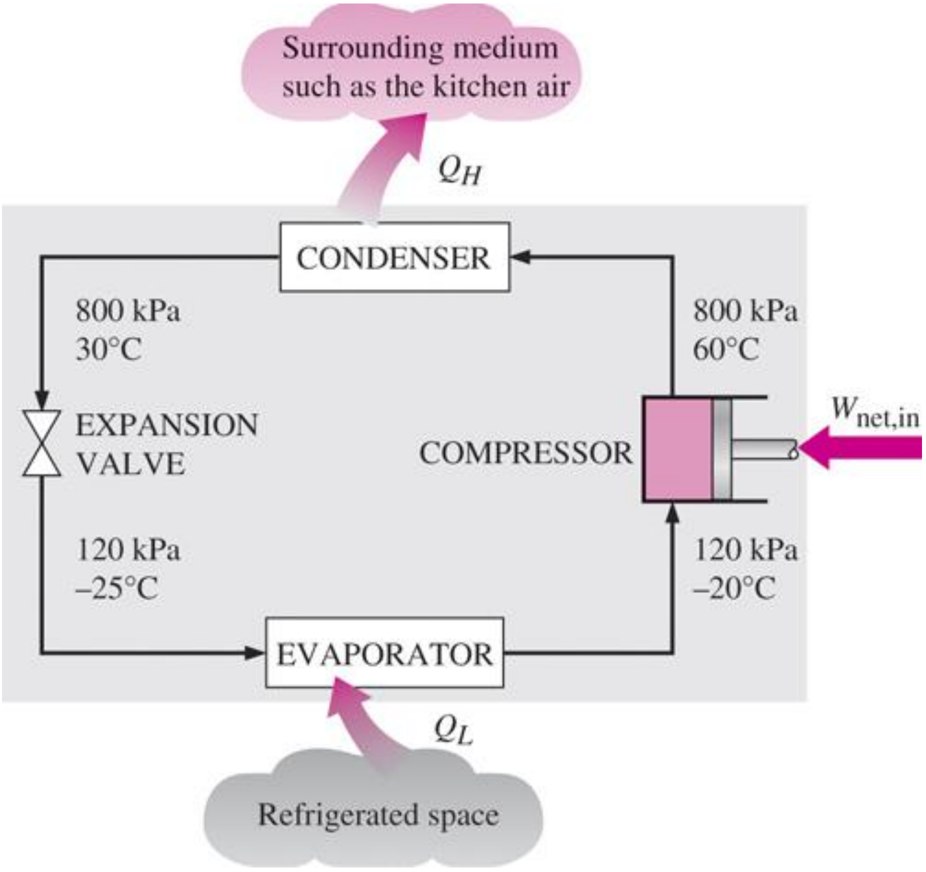
Vapor-Compression Refrigeration Cycle – How does it work?

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 ($W_{net,in}$)



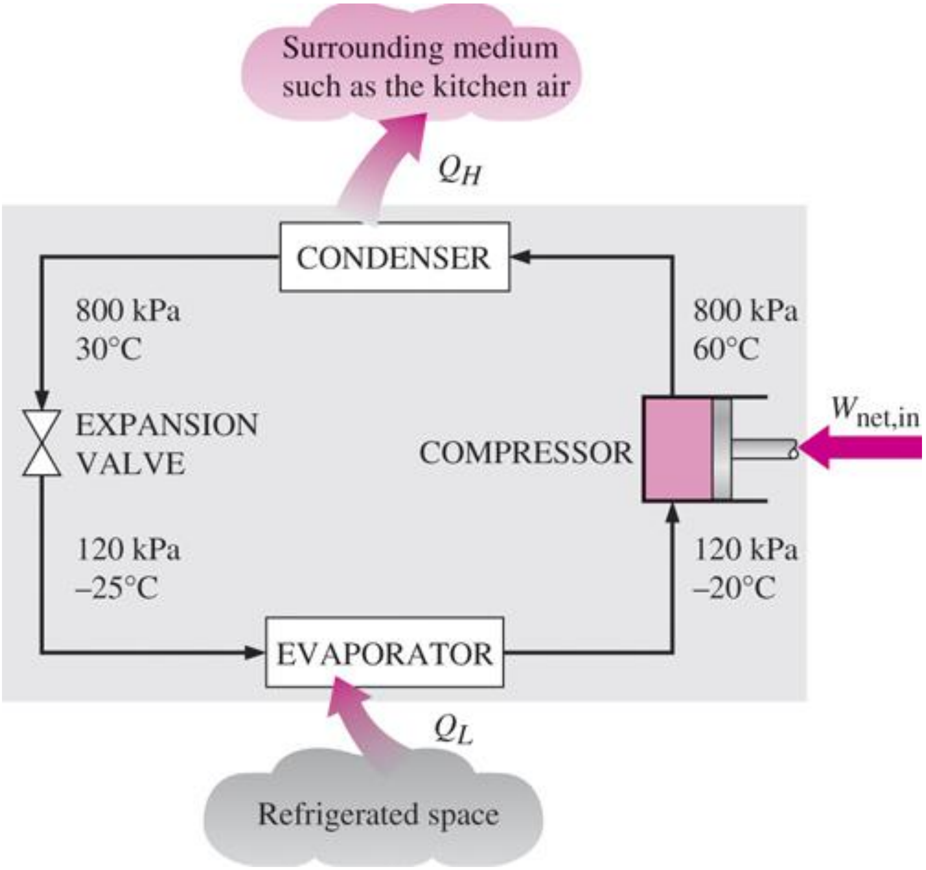
Vapor-Compression Refrigeration Cycle – How does it work?

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 does it work?

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



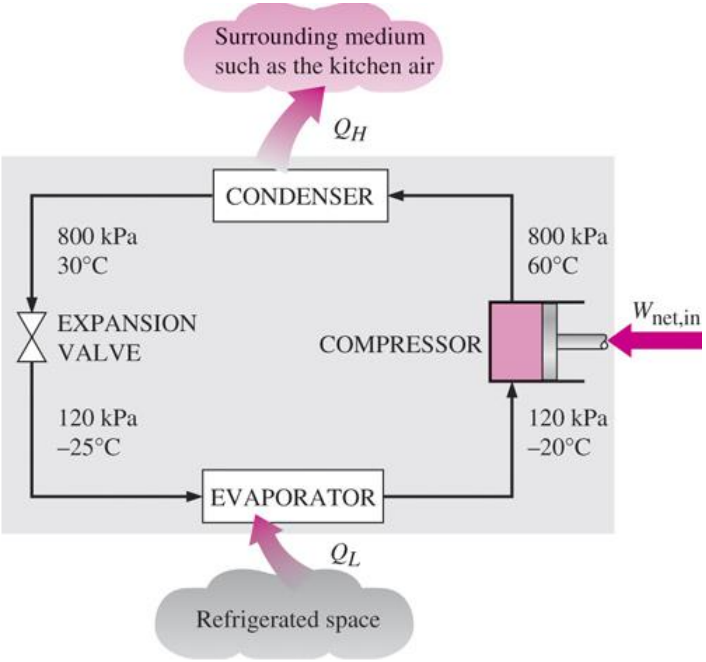
Vapor-Compression Refrigeration Cycle – ENERGY BALANCE

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

- The refrigerator operates as a **closed system** undergoing a cycle consisting of four processes.
- Therefore,

$$\Delta E_{system} = 0$$

$$E_{mass,\ in} \text{ and } E_{mass,\ out} = 0$$



Vapor-Compression Refrigeration Cycle – ENERGY BALANCE

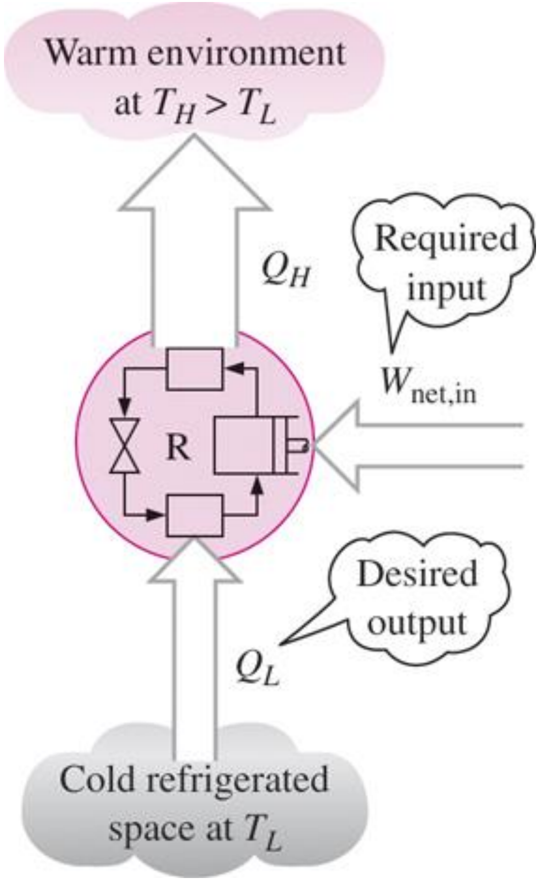
- $Q_{in} = Q_L = Q_{evaporator}$
  - Heat added from the refrigerated space at low temperature
- $Q_{out} = Q_H = Q_{condenser}$
  - Heat rejected to the surroundings at higher temperature
- $W_{net,in} = W_{compressor}$
  - Work supplied to operate compressor

❑ By First Law: $W_{net,in} = Q_{out} - Q_{in} = Q_H - Q_L$

Coefficient of Performance for a Refrigerator

- The *effectiveness* 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 cold refrigerated space.

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

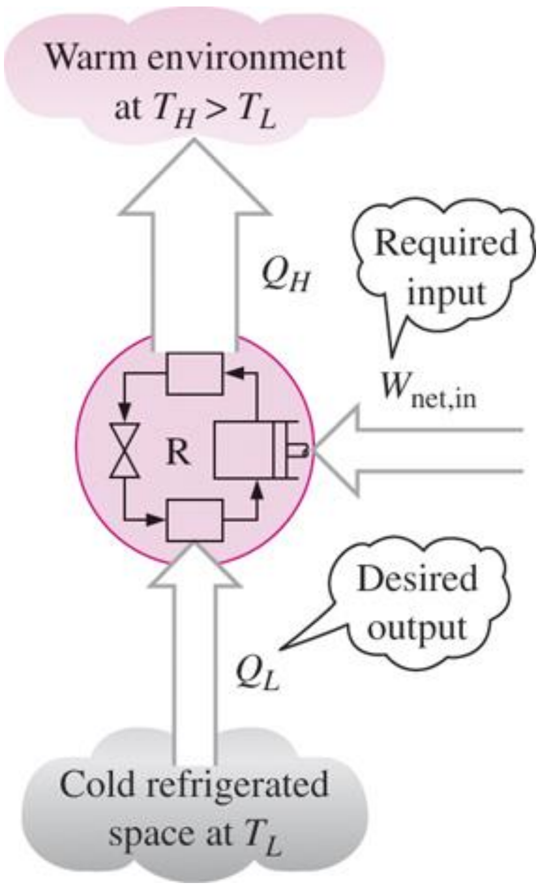


Coefficient of Performance for a Refrigerator

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

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

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



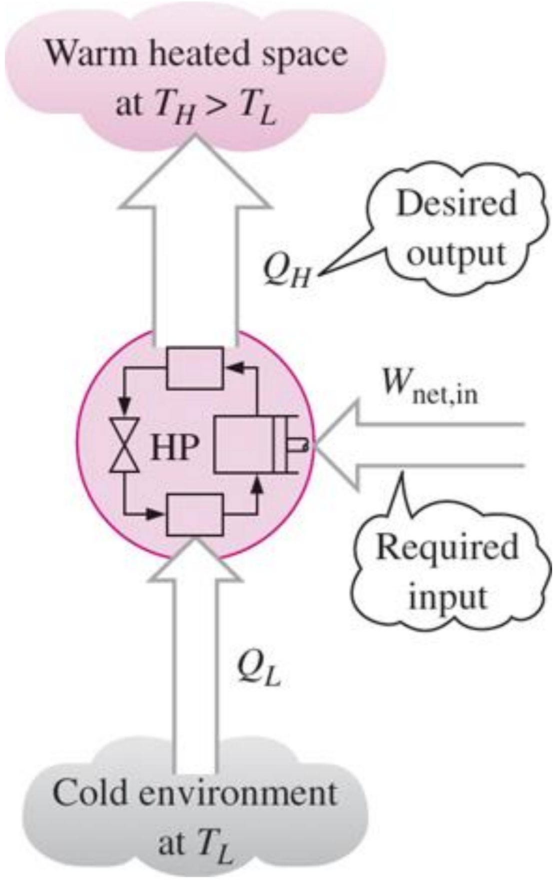
- ❑ $\mathrm{COP_R}$ can be > 1 (hence, term "COP" is used rather than "efficiency").
- ❑ This does not contradict either the first or second laws.

HEAT PUMPS

- A heat pump operates exactly as a refrigerator except, in this case, the desired output is to maintain a heated space at a higher temperature
  - Heat is transferred from the outside (low temperature) to the living space (higher temperature); to do so, a net amount of work must be expended (work input)

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 deliver it to the warm indoors (Q_H).



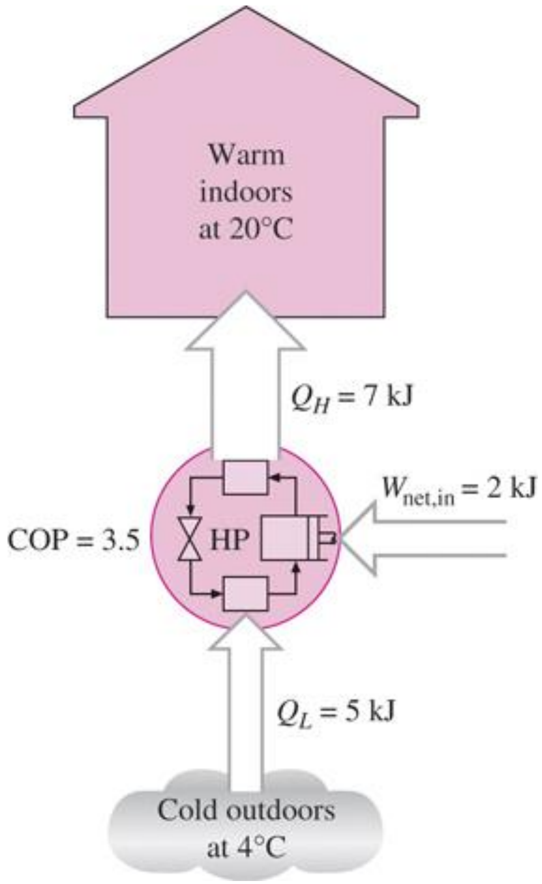
Coefficient of Performance for a Heat Pump

- The objective of a heat pump is to deliver heat (Q_H) to the warm indoor space.

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

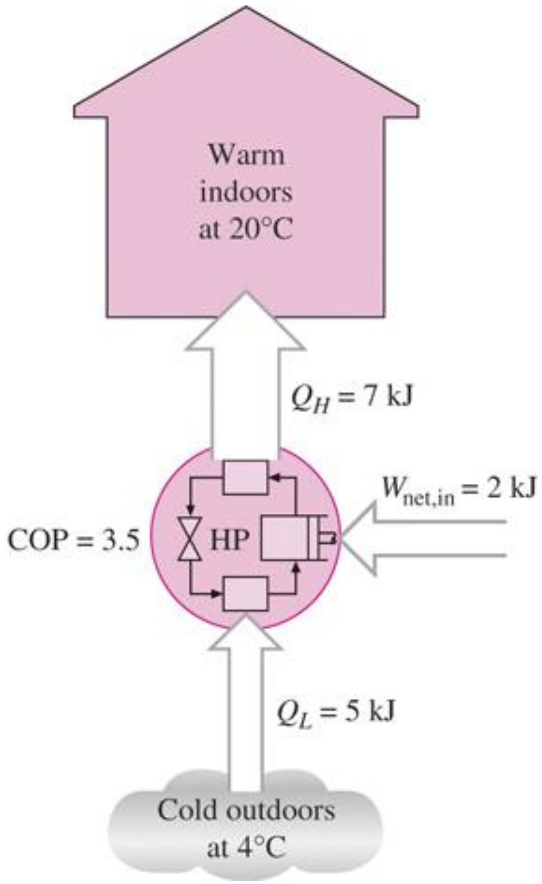
$$\mathrm{COP_{HP}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$

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



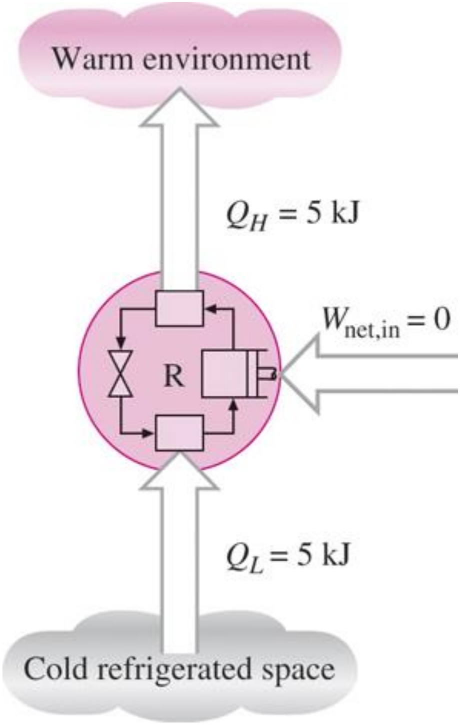
Coefficient of Performance for a Heat Pump

- COP_{HP} must be >1.
- A COP_{HP} = 1 means that the heat supplied to the warm indoors only comes from the work input.
- This is the same as an electric heater -- 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.*



An Impossible Refrigerator

Implications of the **Clausius Statement**

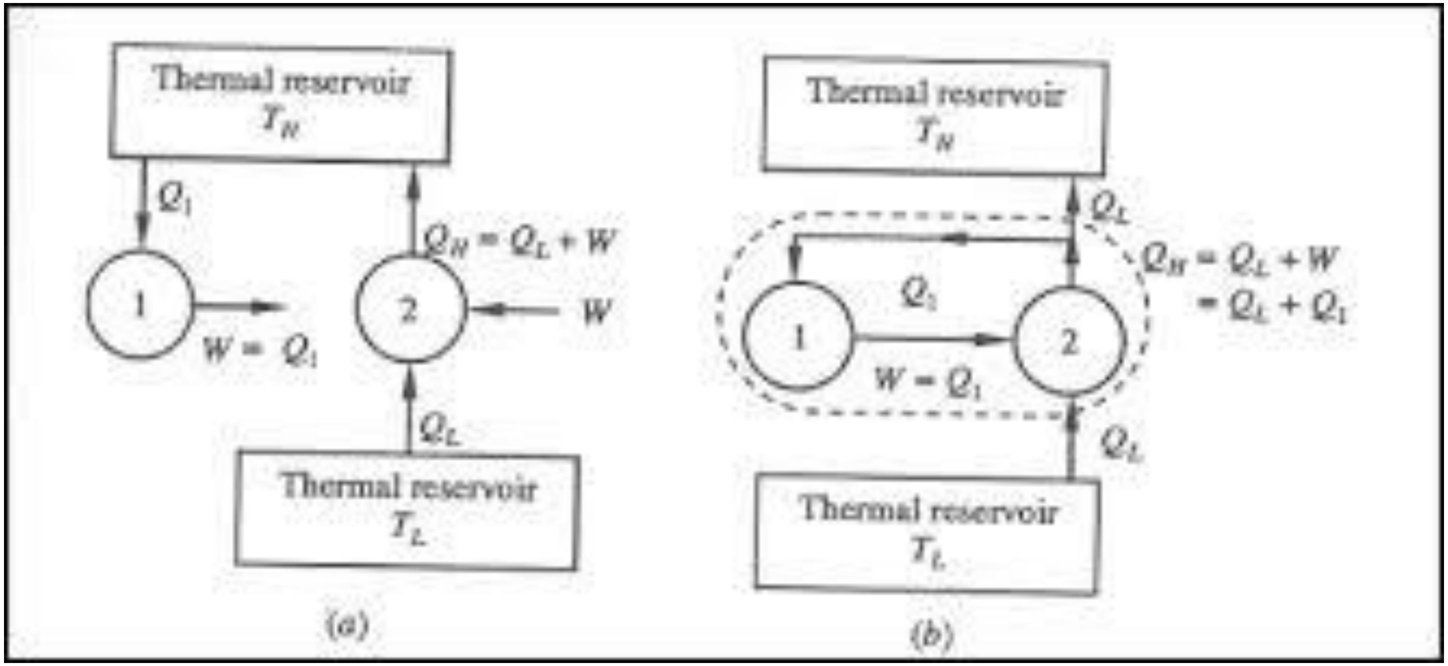
- Heat **by itself** cannot be transferred from a lower temperature body to a higher temperature body.
- All Refrigerators/Heat Pumps **MUST** have a net work input.
- COP_R and COP_{HP} **must be finite** ($< \infty$)
- What is the best that can be done? **[More on that later]**

Refrigerators & Heat Pumps

- **There are three invariable characteristics of refrigerators/heat pumps:**
  - Heat addition process at a relatively low temperature (refrigerated space)
  - Heat rejection process at a higher temperature (kitchen air)
  - A net amount of work must be supplied to the cycle (compressor)

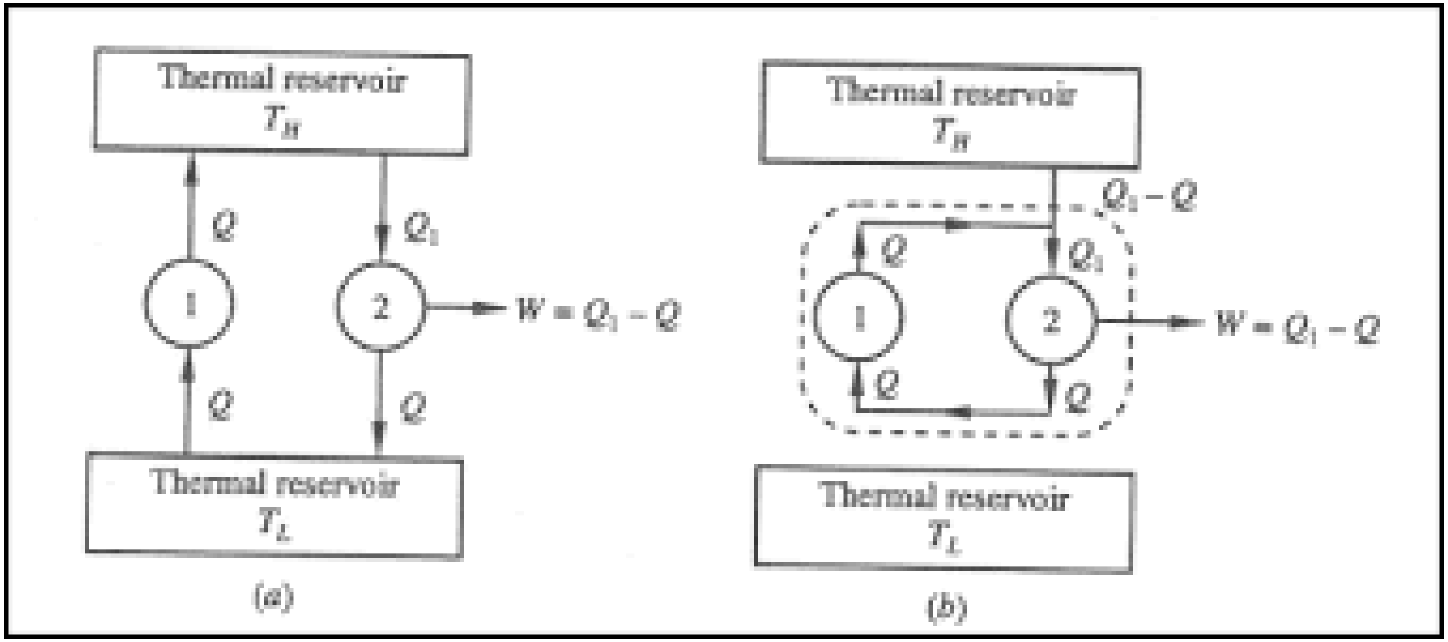
Equivalence of the Kelvin-Planck and Clausius Statements

- Any device that violates the Kelvin–Planck statement (Engine 1) also violates the Clausius statement (Refrigerator 1+2), and vice versa.



Equivalence of the Kelvin-Planck and Clausius Statements

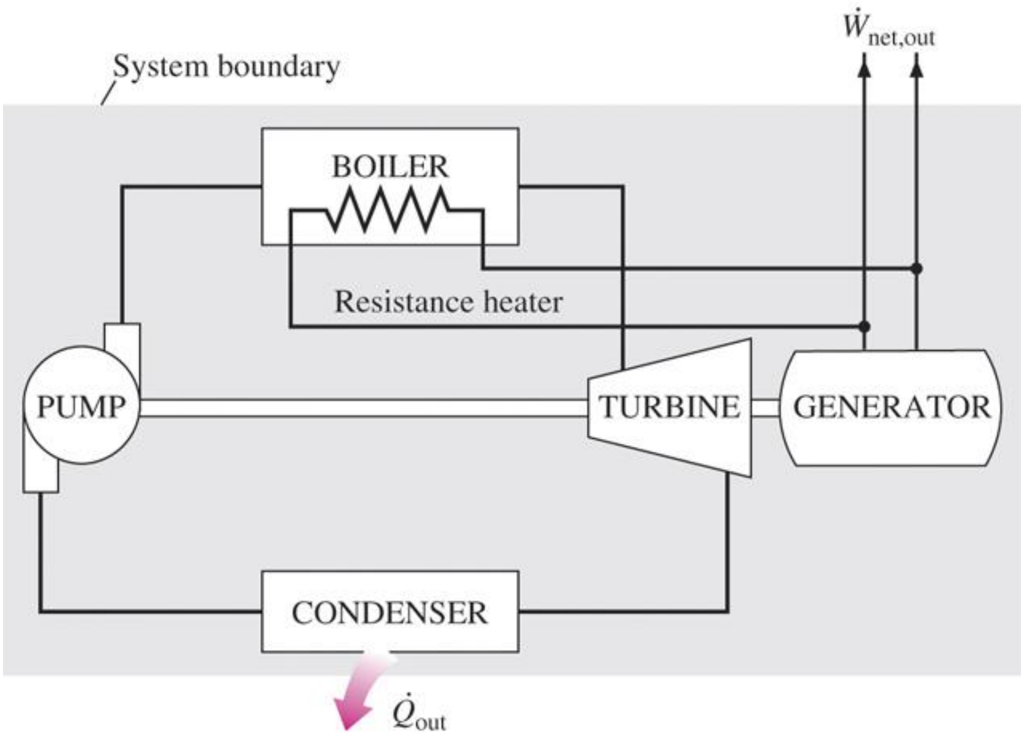
- ❑ Any device that violates the Clausius statement (Refrigerator 1) also violates the Kelvin-Planck statement (Engine 1+2).



Perpetual Motion Machines

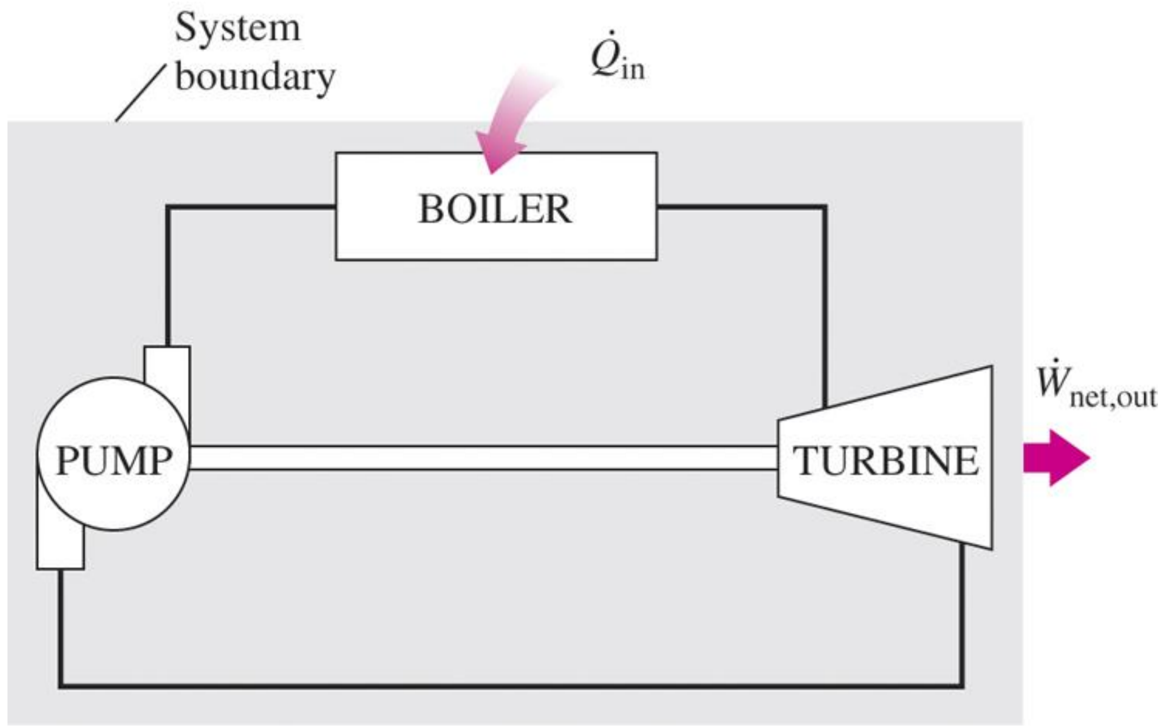
- A perpetual motion machine of the first kind (PMM1) is a device which violates the first law (i.e. it creates energy)
- A perpetual motion machines of the second kind (PMM2) produces work by cooling "freely" available sources of energy such as the oceans or the atmosphere. The Second Law declares the impossibility of 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).

QUESTION

- If $\eta_{thermal}$ must be < 100%, **what is the maximum efficiency** one can achieve for a heat engine operating between two specified temperatures T_H & T_L?
  - Before we can answer this question, we need to introduce the concept of **"reversibility."**

REVERSIBILITY

- A **reversible process** for a system is defined as a process, which once having taken place, can be reversed and in so doing **leaves no change in either the system or the surroundings.**
  - A ***reversible process*** is a process that can be reversed without leaving any trace on the surroundings.
  - All real processes are "irreversible"

Reversible versus Irreversible Processes

- All real processes occurring in nature are irreversible.
- Some processes are more irreversible than others (e.g. more friction or higher ΔT for heat transfer)
- Reversible processes serve as idealized models to which irreversible (actual) processes can be compared.
  - 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.

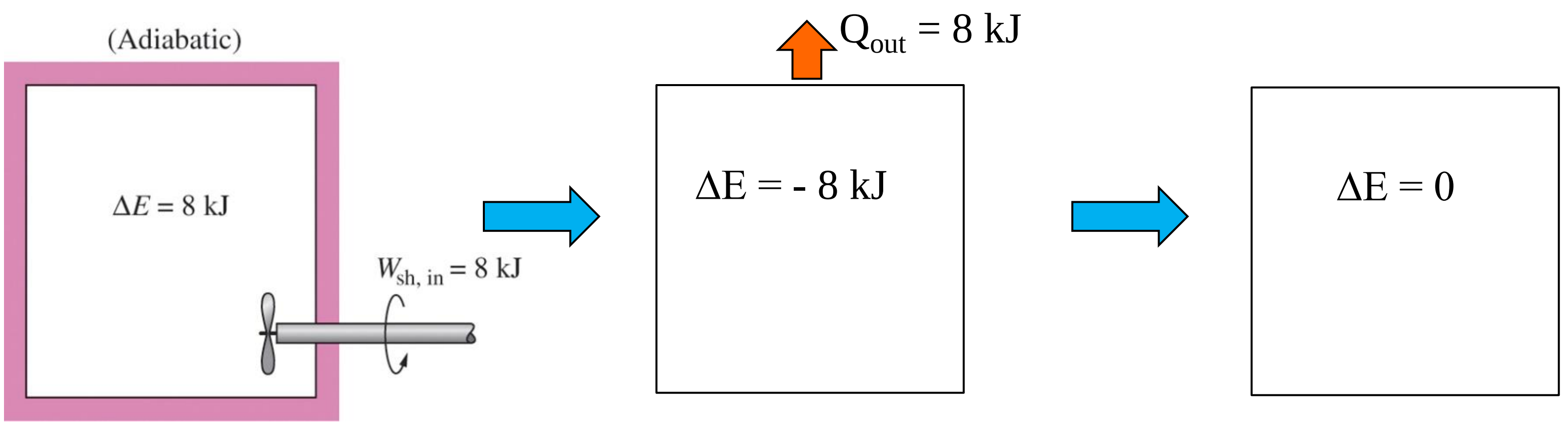
Factors which cause a process to be "irreversible"

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

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

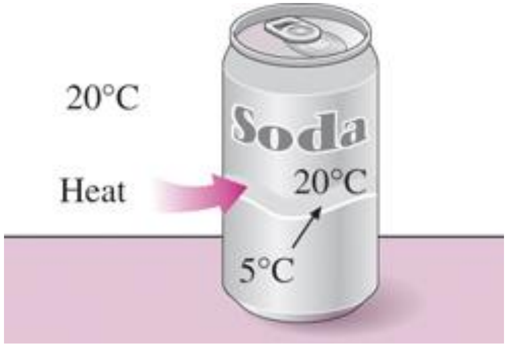
Factors which cause a process to be "irreversible"

1. **FRICTION:** "dissipation of energy that otherwise could do work into a heating effect"



- While the system can be easily returned to its original state, the surroundings will not since "W" was replaced by "Q"

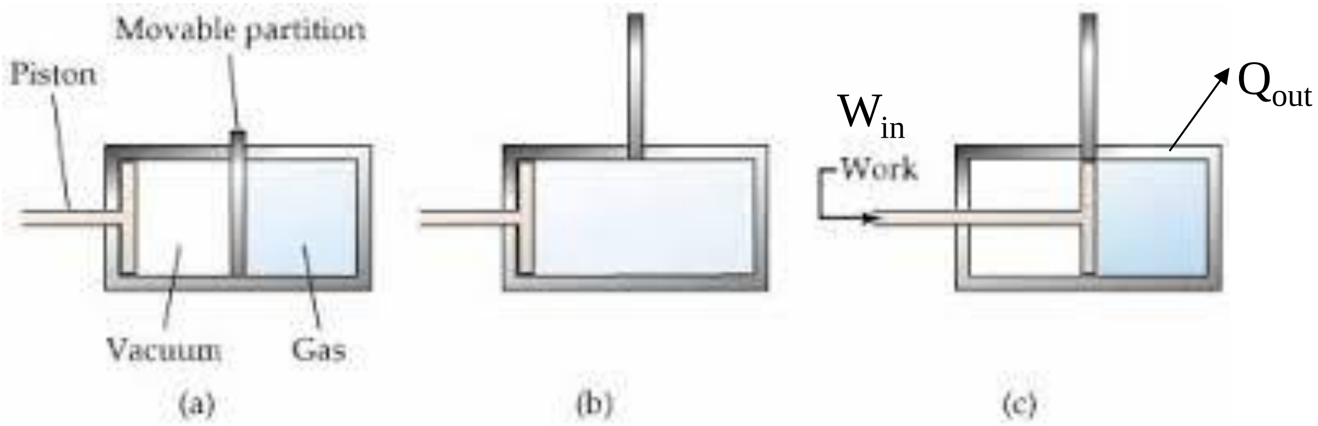
Heat Transfer Through a Finite Temperature Difference



Cooling a soda after it gets warm requires work

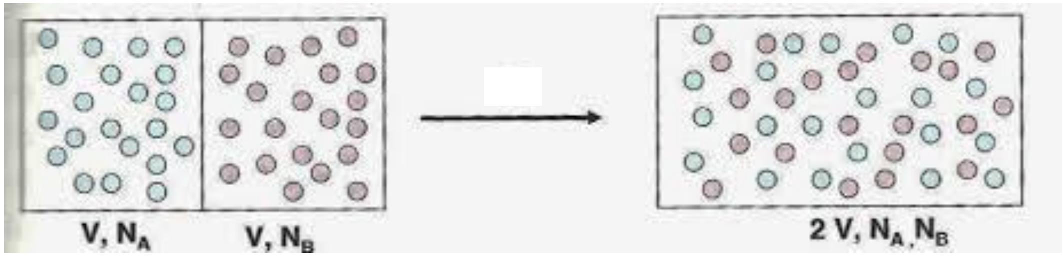
- Since heat, by itself, cannot flow from a low temperature to a higher temperature, all heat transfer processes through a finite temperature difference must be irreversible.
- Reversibility is approached as ΔT approaches zero. Such process requires either an infinite area or an infinite amount of time.

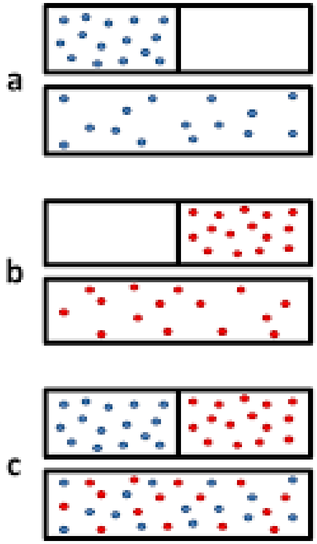
Unrestrained Expansion



- The gas can be returned to its original state by compressing it (work input "W_{in}") while transferring an equal amount of energy (Heat "Q_{out}") to the surroundings.
- For "reversible" expansion, there must be only an infinitesimal difference between the gas and the restraining force so that the boundary would move at an infinitesimal rate.

Mixing of Two Different Substances





- Mixing of two different substances is irreversible since a certain amount of work will be required to separate them.
- Mixing of two gases can be seen as two unrestrained expansions

"Internally", "Externally" & "Totally" Reversible Processes

- **Internally Reversible:**
  - No irreversibilities occur **within** the boundaries of the system during the process
  - No friction & no unrestrained expansion
  - system proceeds through a series of equilibrium states
  - Path forward and reverse coincide for an internally reversible process

"Internally", "Externally" & "Totally" Reversible Processes

- **Externally Reversible:**
  - No irreversibilities occur **outside** the system boundaries of the system during the process
  - No heat transfer through a finite ΔT
  - Heat transfer between a reservoir and a system during an externally reversible process means the system and reservoir are the same temperature ($\Delta T \approx 0$)

“Internally”, “Externally” & “Totally” Reversible Processes

- **Totally Reversible: (or “reversible”)**
  - No irreversibilities occur within either the system or its surroundings
  - No heat transfer through a finite ΔT
  - No friction or other dissipating effects
  - No non-equilibrium changes

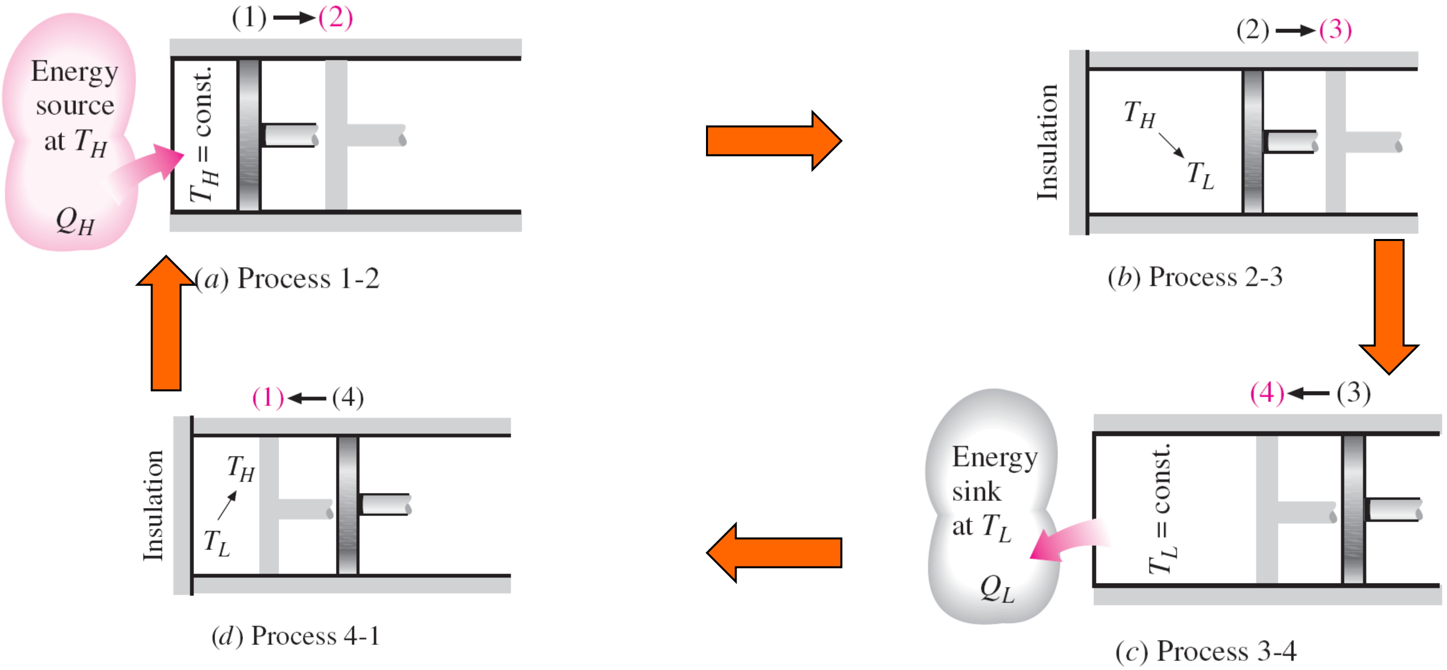
Real Processes

- **In reality, NO ideal, reversible processes exist.**
  - Real processes proceed either in one direction (hot to cold) or proceed at a finite rate and thus encounter some energy dissipation due to friction, turbulence, etc.
  - The concept of reversibility, however, is very useful since it establishes the limits of performance which can be achieved.

The Carnot Cycle

- To answer the question "what is the highest efficiency that a heat engine can achieve?," Carnot devised a power cycle with four reversible processes:
  - Reversible **isothermal** heat addition at T_H
  - Reversible **adiabatic** expansion in which the working fluid temperature decreases from T_H to T_L
  - Reversible **isothermal** heat rejection at T_L
  - Reversible **adiabatic** compression in which the working fluid temperature is returned to T_H

The Carnot Cycle



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)

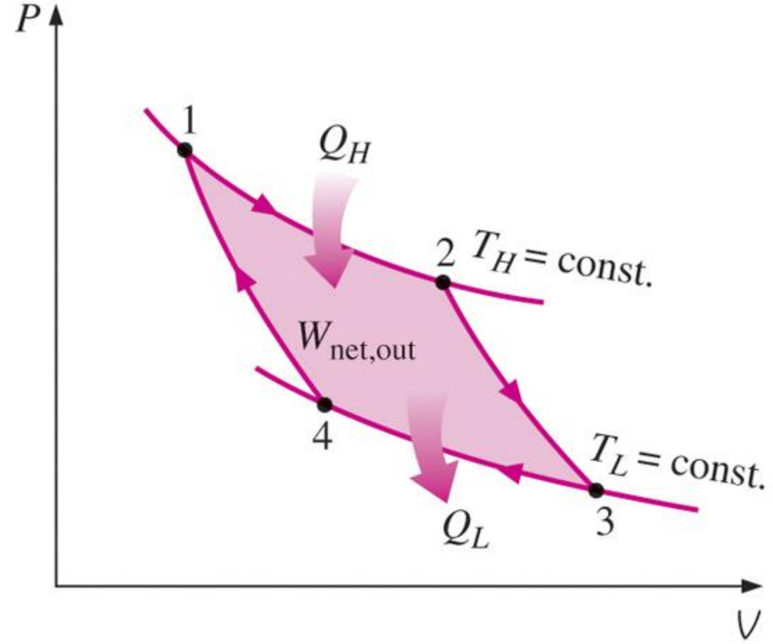
Process 4-1: Reversible Adiabatic Compression (temperature rises from T_L to T_H)

The Carnot Cycle

- Since every process is reversible, **the entire cycle is reversible**. If cycle is reversed, the heat engine becomes a refrigerator
  - Regardless of what the working fluid may be, the Carnot cycle has the same four basic processes

P-V Representation of Carnot Cycle (Heat Engine)

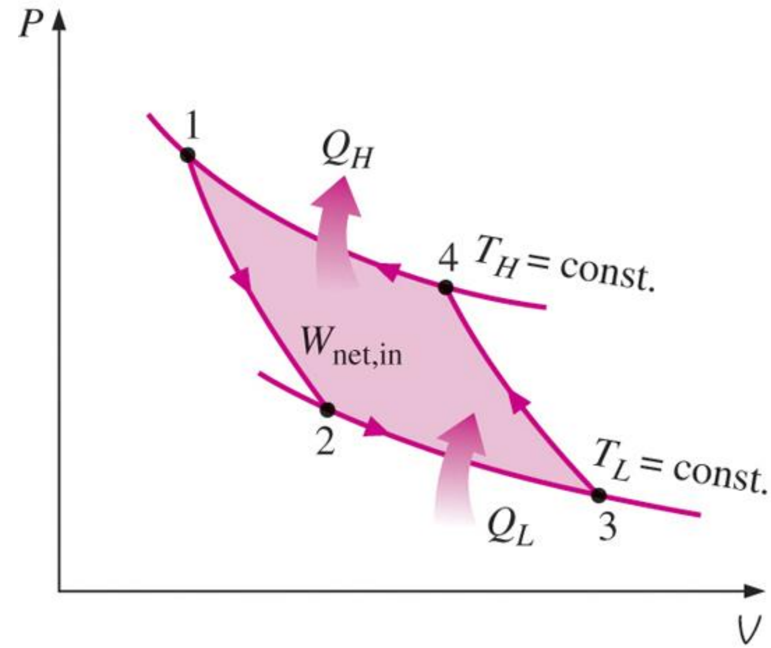
- The Carnot cycle satisfies all the conditions of a heat engine
- The net result is the conversion of part of Q_H to net work output ($W_{net} = Q_H - Q_L$).



- Note: Heat engines operating in a cycle proceed clock-wise on the P-V diagram. A net positive amount of work is produced
- For reversible cycles, net work output equals the area enclosed by the cycle on the P-V diagram

P-V Representation of Carnot Cycle (Refrigerator)

- 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.



- Note: Refrigerators/Heat Pumps operating in a cycle proceed counter clockwise on the P-V diagram. A net amount of work is added to the working fluid.
- For reversible cycles, the net work input equals the area enclosed by the cycle on the P-V diagram

The Carnot Principles

- The efficiency of an irreversible engine is always lower than the efficiency of a reversible engine operating between the same two temperatures

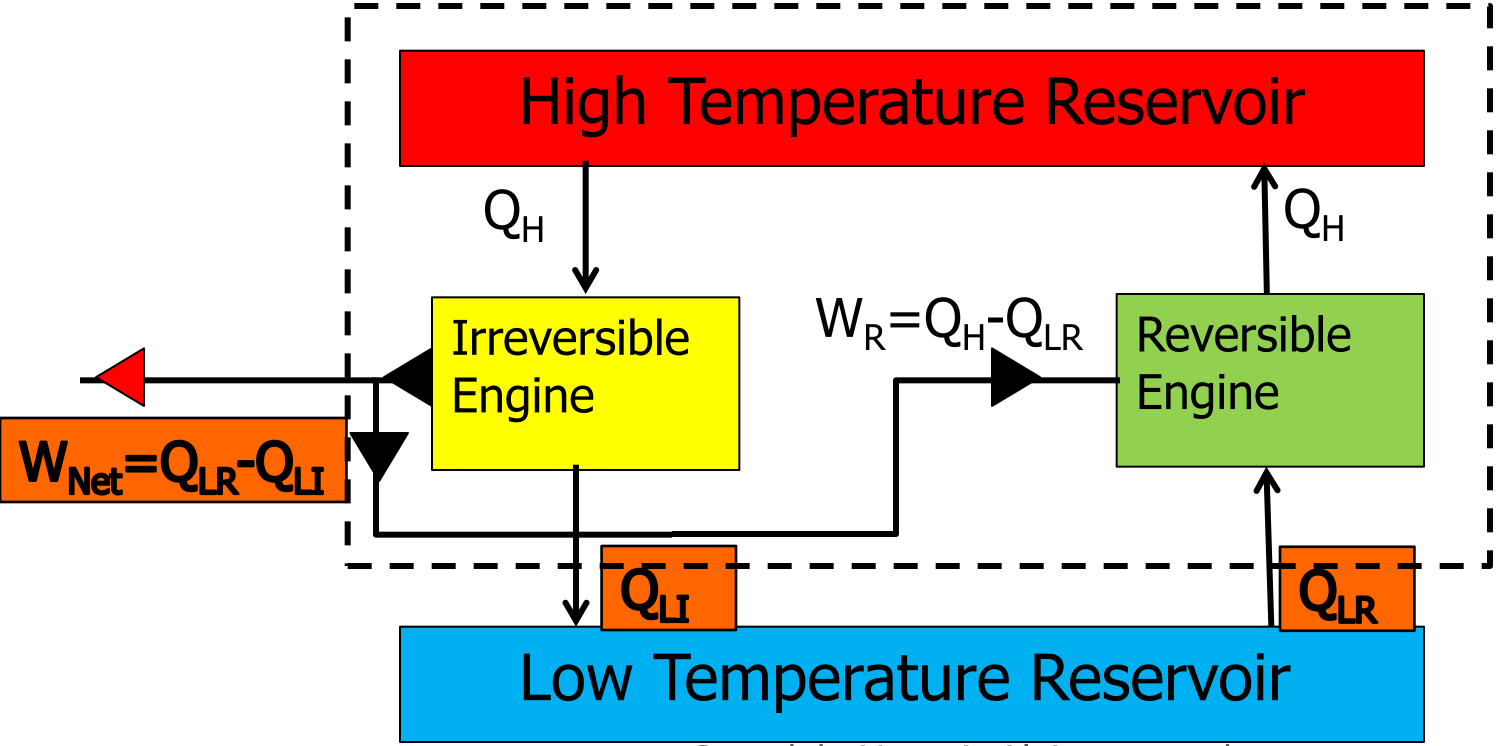
$$\eta_{th,irreversible} < \eta_{th,reversible} \text{ (for same } T_H \text{ \& } T_L\text{)}$$

- The efficiencies of all reversible engines operating between the same two temperatures are the same

$$\eta_{th,reversible} = f(T_H \text{ \& } T_L) \text{ only}$$

Proof of Carnot's Principles

$\eta_{th,irreversible} < \eta_{th,reversible}$ (for same T_H & T_L)

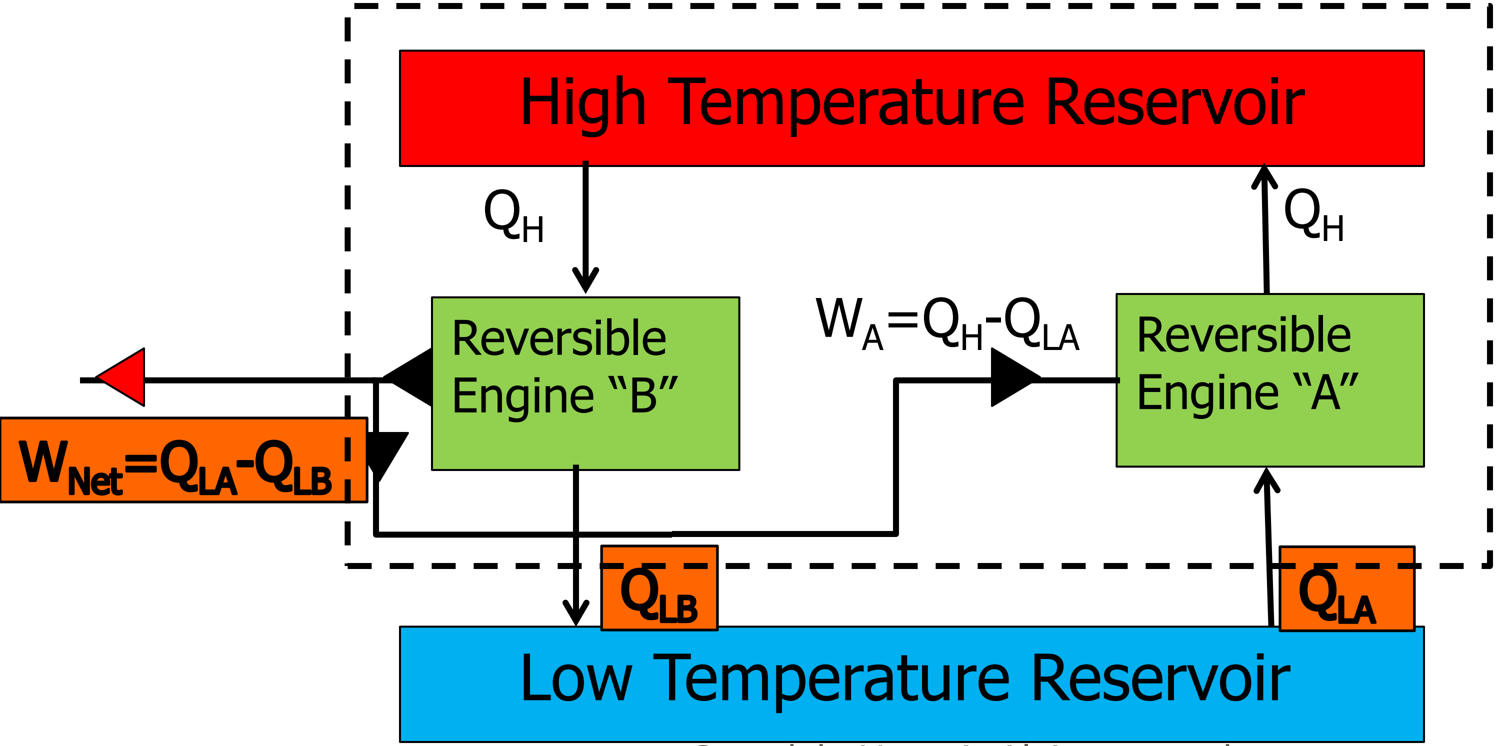


Proof -- Canot's Principles

- A similar proof can be used for the second principle -- **All reversible engines operating between the same two temperatures must have the same efficiency**
- $\eta_{th,reversible} = f(T_H \& T_L)$ only

Proof of Carnot's Principles

$\eta_{th,reversible} = f\,(T_H \;\&\; T_L)$ only



Thermodynamic Temperature Scale

- Lord Kelvin realized that since the Carnot efficiency is independent of the working fluid and depends only on the reservoir temperatures, it provides the basis for an absolute temperature scale

$$\eta_{th,reversible} = f(T_H \,\&\, T_L) = 1 - (Q_L / Q_H)$$

$$\therefore (Q_H / Q_L) = g(T_H \,\&\, T_L)$$

Thermodynamic Temperature Scale

- The form of the function $g(T_H \& T_L)$ can be developed using Carnot's second principle (text pp. 301-302)
  - $g(T_H \& T_L) = (Q_H / Q_L)_{rev} = [\Phi (T_H) / \Phi (T_L)]$
- Lord Kelvin **arbitrarily** selected the function Φ to be linearly proportional to the absolute temperature
  - $(Q_H / Q_L)_{rev} = (T_H / T_L)$

Thermodynamic Temperature Scale

- Therefore,
  - $\eta_{th,reversible} = [1 - (Q_L / Q_H)_{rev}] = [1 - (T_L / T_H)]$
  - T_L & T_H are absolute temperatures (K)
  - T(K) = T(°C) + 273.15

Second Law Implications

- $\eta_{th} < \eta_{th,reversible} \Rightarrow$ Irreversible Heat Engine
- $\eta_{th} = \eta_{th,reversible} \Rightarrow$ Reversible Heat Engine
- $\eta_{th} > \eta_{th,reversible} \Rightarrow$ Impossible Heat Engine

Carnot Refrigerator/Heat Pump

- $COP_R = 1 / [(Q_H / Q_L) - 1]$
- $COP_{HP} = 1 / [1 - (Q_L / Q_H)]$

$$\therefore \; COP_{R,\,rev} = 1 / [(T_H / T_L) - 1] = T_L / (T_H - T_L)$$

&

$$COP_{HP,\,rev} = 1 / [1 - (T_L / T_H)] = T_H / (T_H - T_L)$$

Second Law Implications

- $COP_R < COP_{R,reversible} \Rightarrow$ Irreversible Refrigerator
- $COP_R = COP_{R,reversible} \Rightarrow$ Reversible Refrigerator
- $COP_R > COP_{R,reversible} \Rightarrow$ Impossible Refrigerator

Second Law Implications

- $COP_{HP} < COP_{HP,reversible} \Rightarrow$ Irreversible Heat Pump
- $COP_{HP} = COP_{HP,reversible} \Rightarrow$ Reversible Heat Pump
- $COP_{HP} > COP_{HP,reversible} \Rightarrow$ Impossible Heat Pump

CHAPTER 6 -- The Second Law of Thermodynamics

OUTCOME:

- ✓ Identify Valid (possible) Processes as those that satisfy both the first and second laws of Thermodynamics
- ✓ Understand concepts of thermal energy reservoirs; reversible and irreversible processes; heat engines; refrigerators; and heat pumps.
- ✓ State the Kelvin-Plank and Clausius statements of the Second Law and demonstrate their equivalence
- ✓ Apply the Second Law of Thermodynamics to Cycles and cyclic devices
- ✓ Describe the Carnot Cycle; Carnot's principles; and idealized Carnot heat engines, refrigerators and heat pumps
- ✓ Obtain expressions for the thermal efficiencies and coefficients of performance for reversible heat engines, heat pumps & refrigerators