

**NANYANG
TECHNOLOGICAL
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SINGAPORE

MA3010 – 2nd Law of Thermodynamics

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Reference: Thermodynamics Chapter 6

Introduction

- Fulfilling the 1st law of thermodynamics does not guarantee that a process that take place
 - E.g. 1: Supplying light and heat to a filament lightbulb does not generate electric energy
 - E.g. 2: Hot coffee does not get hotter in a cooler room



<https://picsart.com/i/gif-light-important-part-of-life-light-gif-bulb-cool-195138003001202>



<https://giphy.com/gifs/hot-coffee-giudanskycom-2jd7CRuYayGpW>

- Processes occur in a certain direction and not in reverse
- A process must satisfy both 1st and 2nd laws of thermodynamics to proceed

Introduction – 2nd Law of Thermodynamics

1. It identifies the direction of processes
2. It determines the theoretical limits for the performance of engineering systems, e.g. heat engines, refrigerators
 - Defines “perfection” for thermodynamic processes
 - Used as a benchmark for real engineering systems
3. It asserts that energy has *quality* as well as quantity – determines degree of degradation of energy during a process
 - Energy at a high temperature has better quality than the same energy at a low temperature
4. Predicts degree of completion for chemical reactions
 - A process is completed when entropy stops increasing

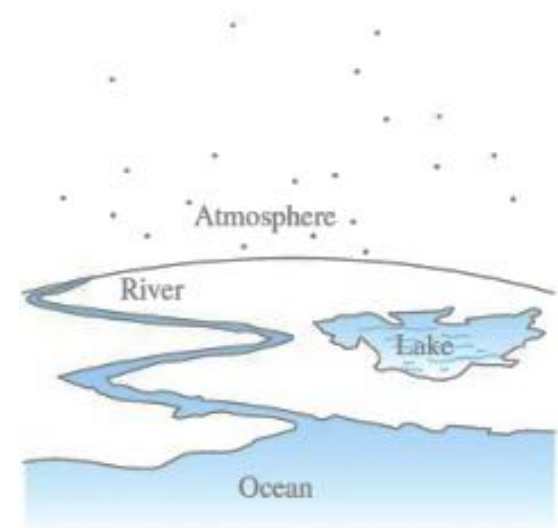
Thermal Energy Reservoirs

- Hypothetical body with a relatively large *thermal energy capacity* (*mass x specific heat*) that can absorb/supply finite amounts of heat **without undergoing any change in temperature**
- In practice, large bodies of water (oceans, lakes, rivers) and the atmospheric air can be modelled as thermal energy reservoirs

$$Q = m \times c \times \Delta T$$

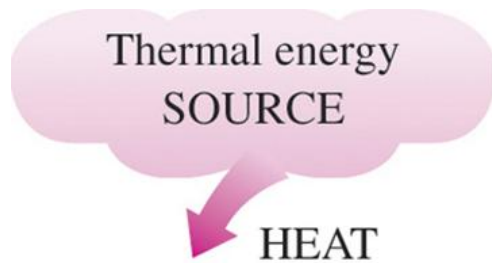
$$\Delta T = \frac{Q}{m \cdot c}$$

Thermal energy capacity



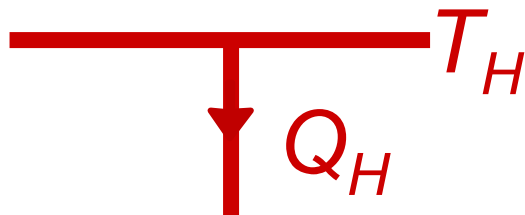
Thermal Energy Reservoirs – Heat Source & Heat Sink

- Source: supplies heat energy
- Sink: absorbs heat energy



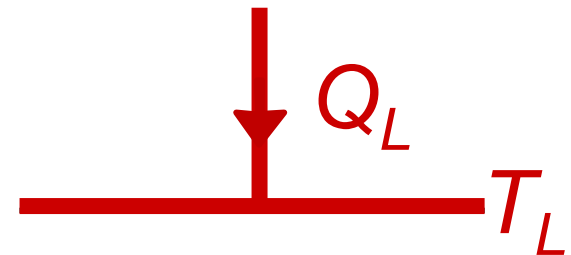
e.g. Sun, furnace, etc

Can be simplified to:



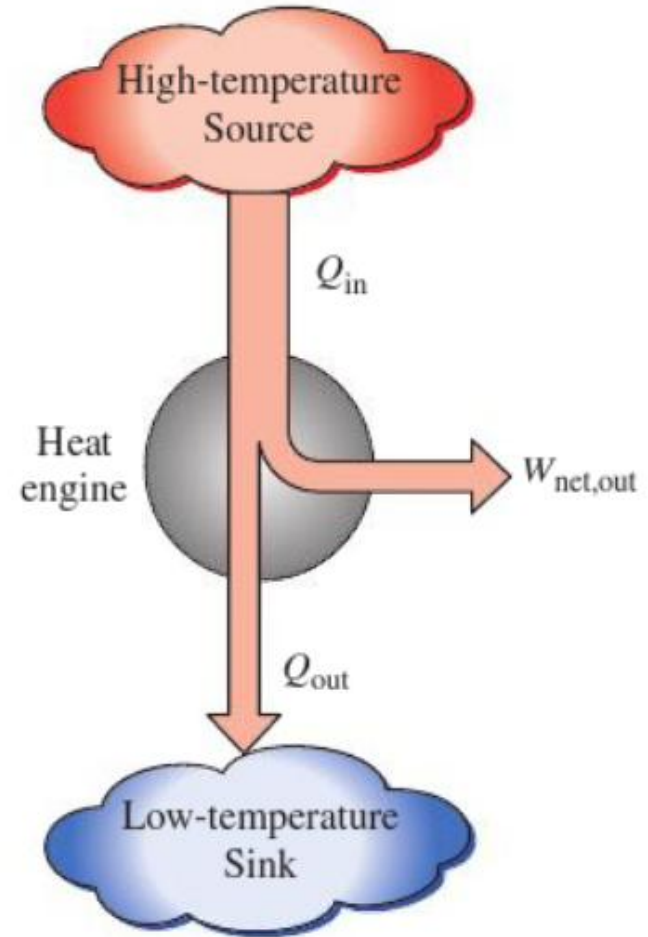
e.g. river, atmosphere, etc

Can be simplified to:



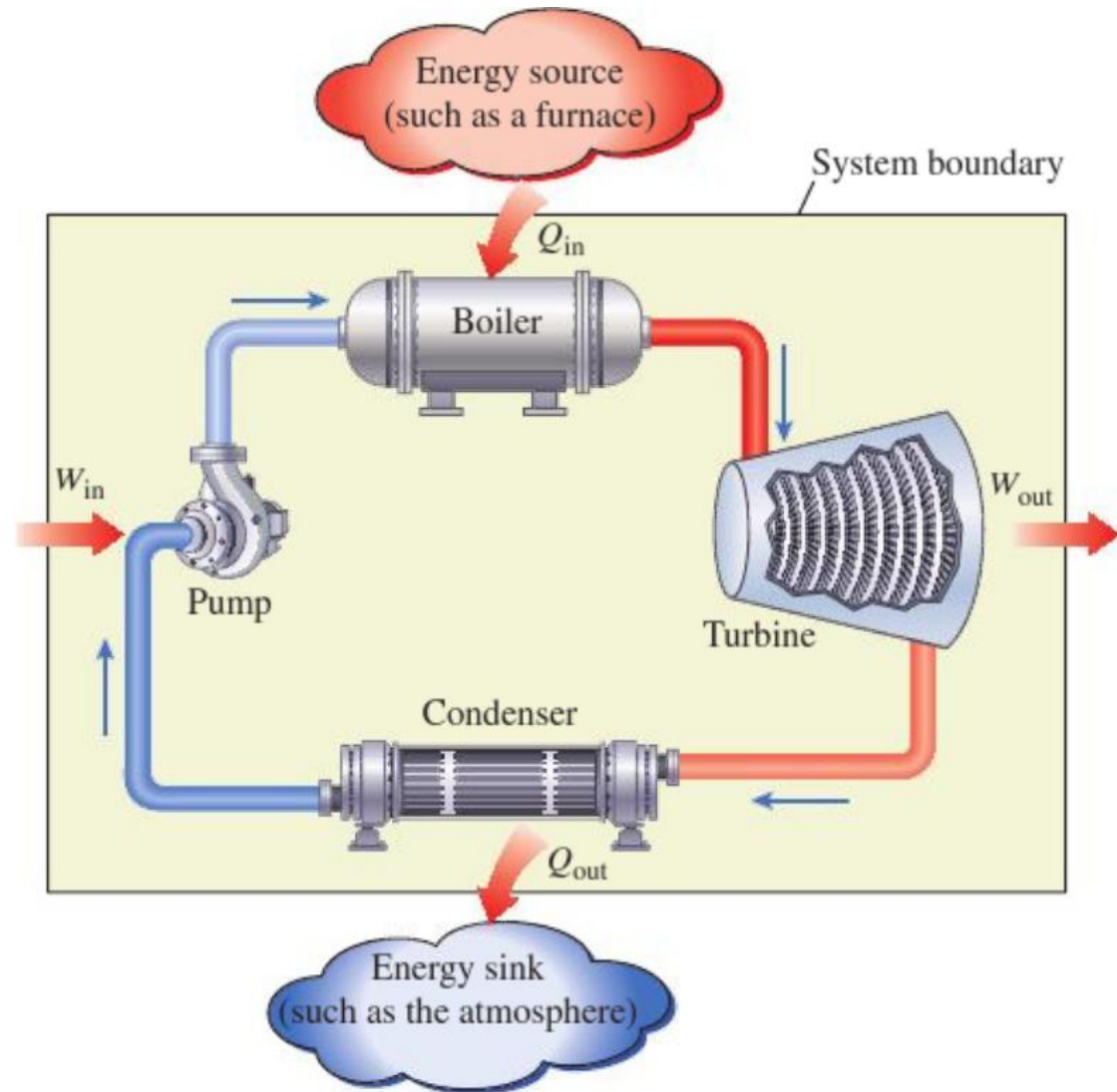
Heat Engines

- Work is *easily* converted into other forms of energy such as heat but the reverse is more difficult
- Heat engines convert heat to work
 - Receive heat from a high-temperature source
 - Convert part of the heat received to work
 - Reject the remaining waste heat to a low-temperature sink
 - Operate on a **cycle**
- Typically uses a fluid to transfer heat, known as the *working fluid*



Heat Engines – Steam Power Plant

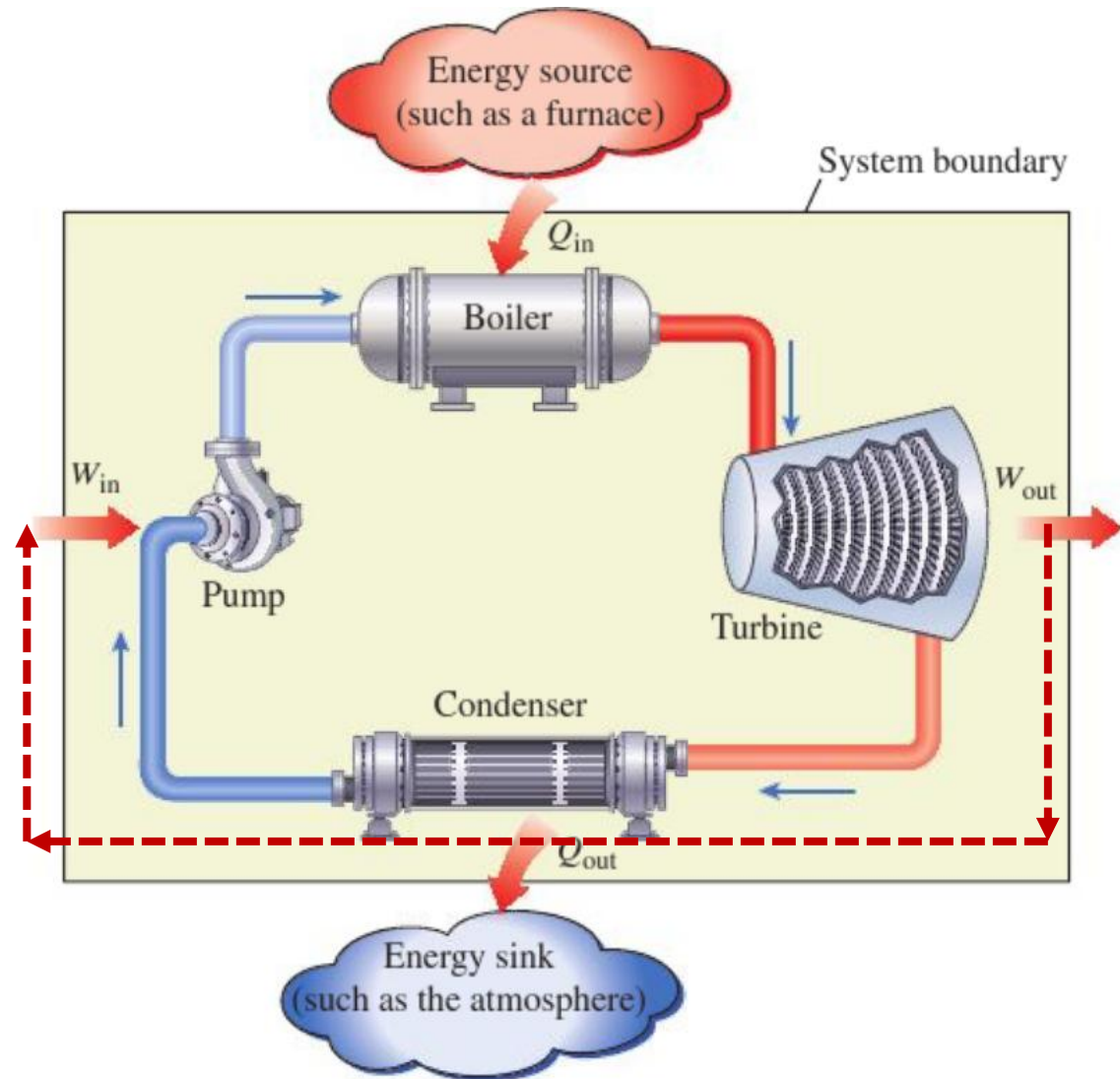
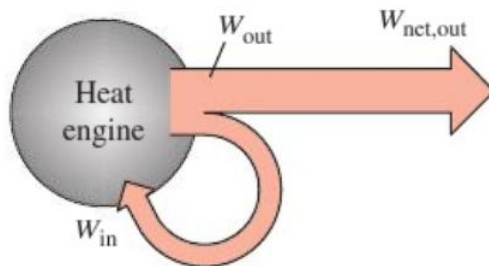
- Water/steam as the working fluid
- Q_{in} = heat supplied to steam in boiler
- W_{out} = work extracted from steam in turbine
- Q_{out} = heat rejected by steam in condenser
- W_{in} = work required to pump water into boiler



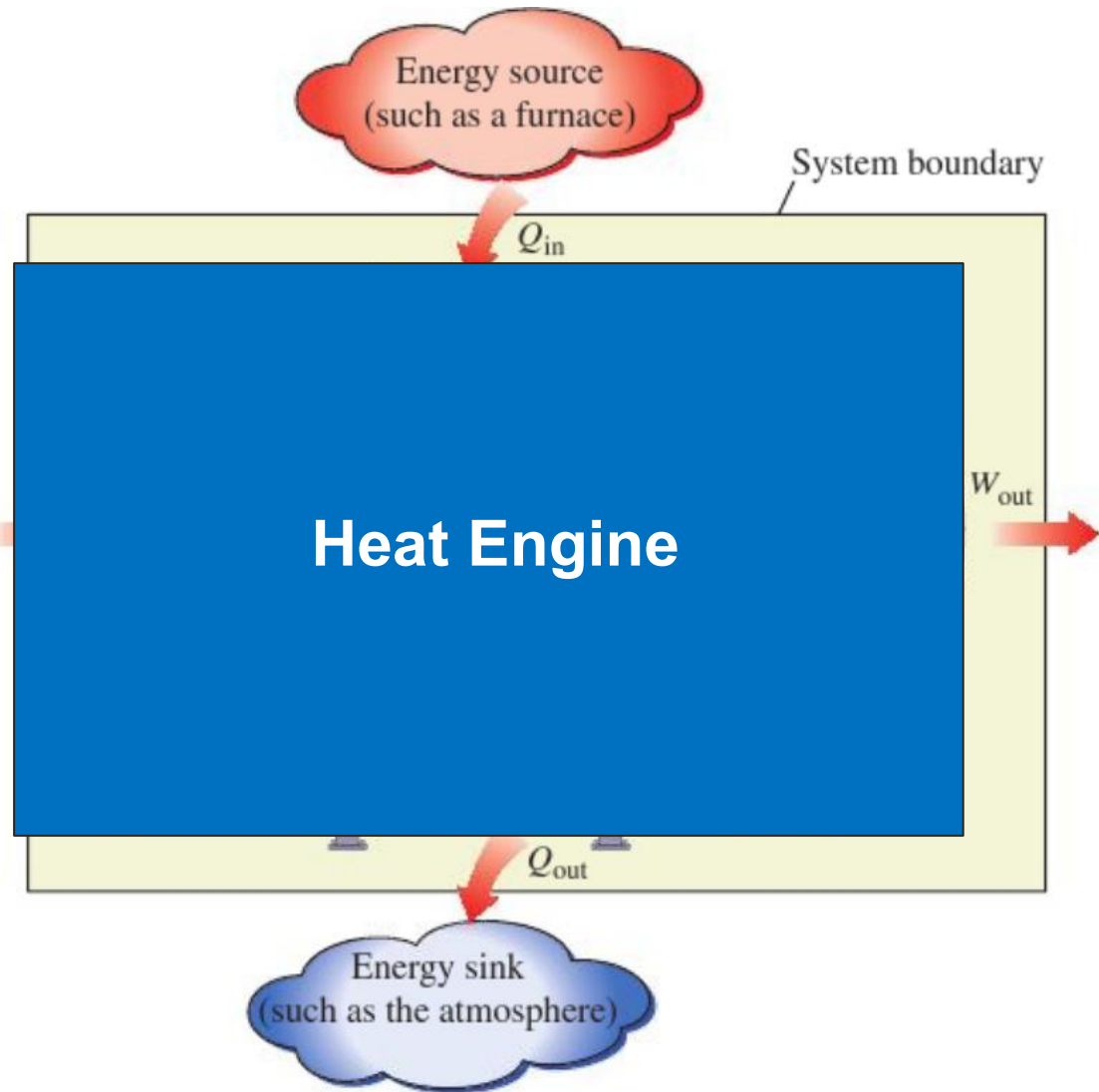
Heat Engines

- Part of work output is used to drive the pump
- Net output from heat engine:

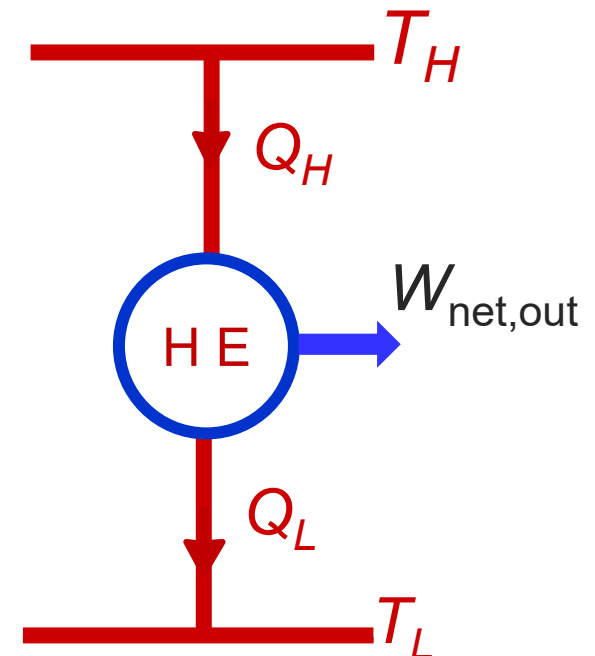
$$W_{net,out} = W_{out} - W_{in}$$



Heat Engines



Simplified:



Heat Engines – Energy Balance

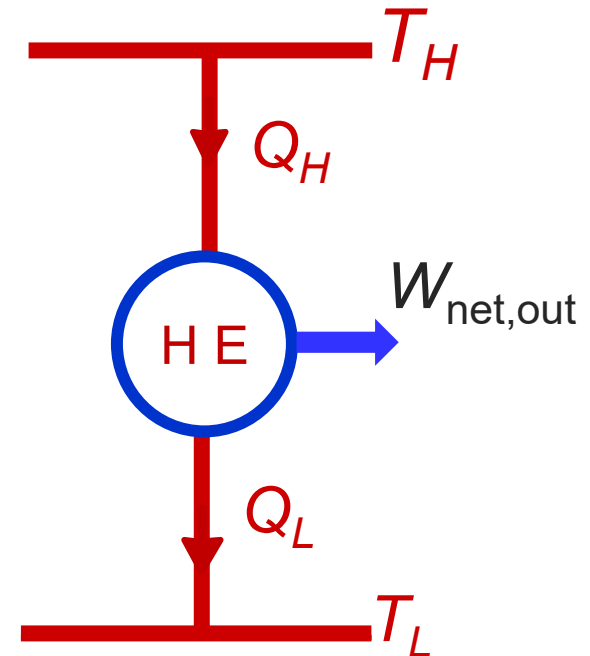
From 1st Law: $Q - W = \Delta U$

Sign convention: arrow going into system = +ve

For a cycle: $Q - W = 0$

$$Q_H + (-Q_L) - W_{net,out} = 0$$

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



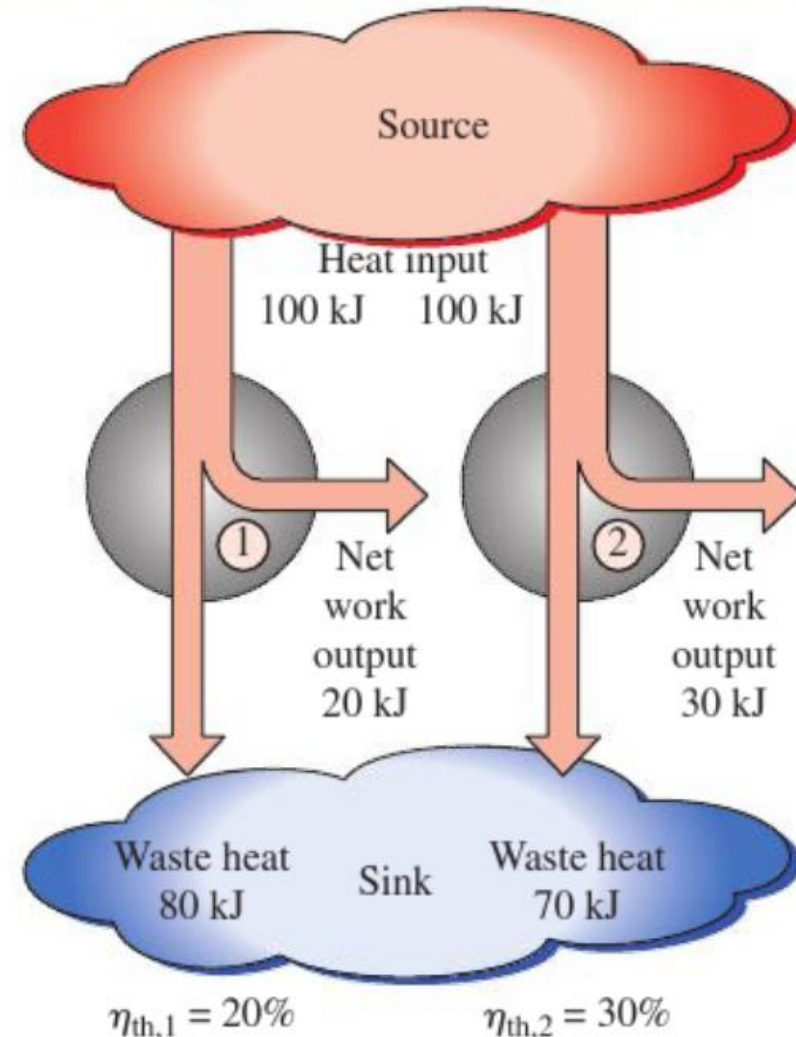
Heat Engines – Thermal Efficiency

- A measure of how well a heat engine converts heat input into useful work

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

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

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

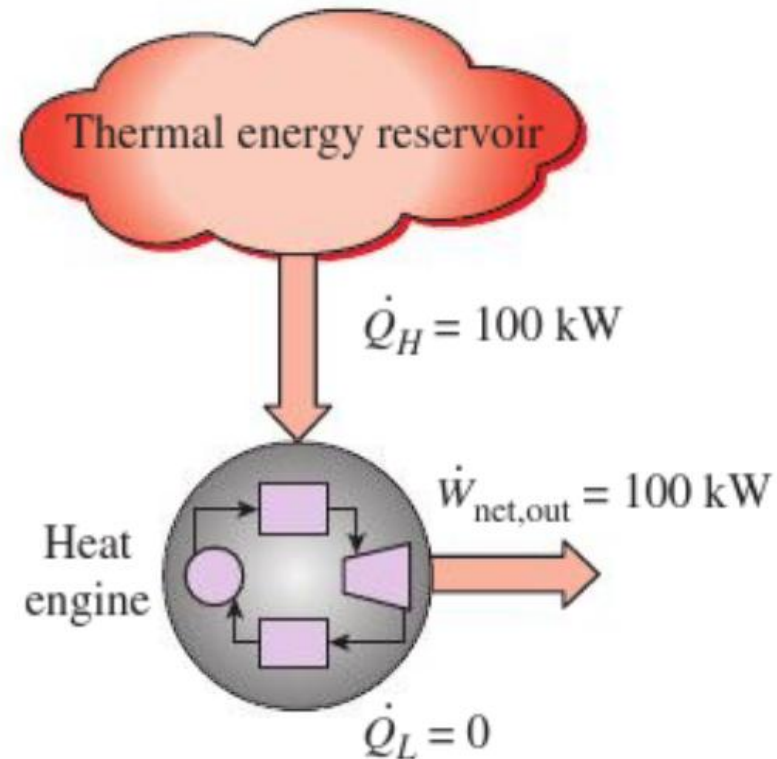


Is it possible to have 100% efficiency?

2nd Law of Thermodynamics – Kelvin-Planck Statement

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

- If $Q_L = 0$, heat engine will have 100% efficiency
- However, there is always waste heat produced
- The cycle cannot be completed without rejecting heat to a low-temperature sink



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.

Even *theoretically perfect* heat engines do not have an efficiency of 100%!

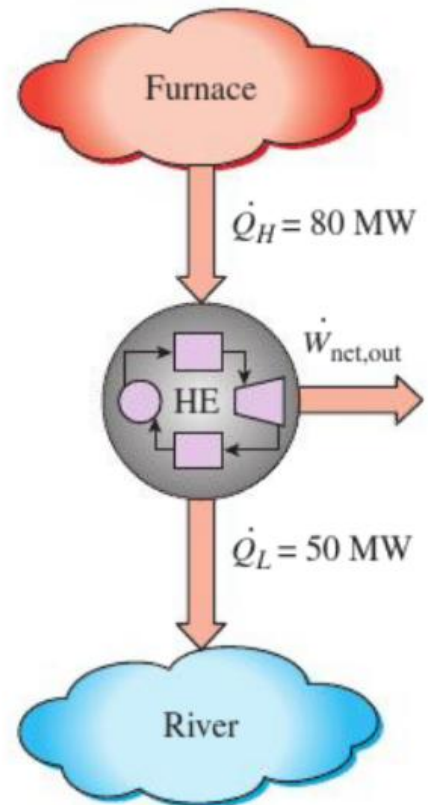
Example 1 – Net Power Production of a Heat Engine

Heat is transferred to a heat engine from a furnace at a rate of 80 MW. If the rate of waste heat rejection to a nearby river is 50 MW, determine the net power output and the thermal efficiency for this heat engine.

Assumptions: Negligible heat losses through pipes & other components

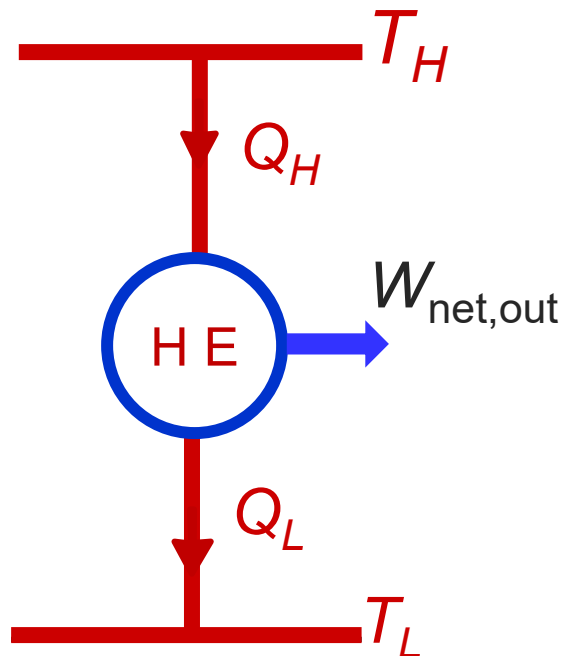
$$\begin{aligned}\dot{W}_{net,out} &= \dot{Q}_H - \dot{Q}_L \\ &= 80 - 50 = 30 \text{ MW}\end{aligned}$$

$$\begin{aligned}\eta_{th} &= \frac{\dot{W}_{net,out}}{\dot{Q}_H} \\ &= \frac{30 \text{ MW}}{80 \text{ MW}} = 0.375\end{aligned}$$

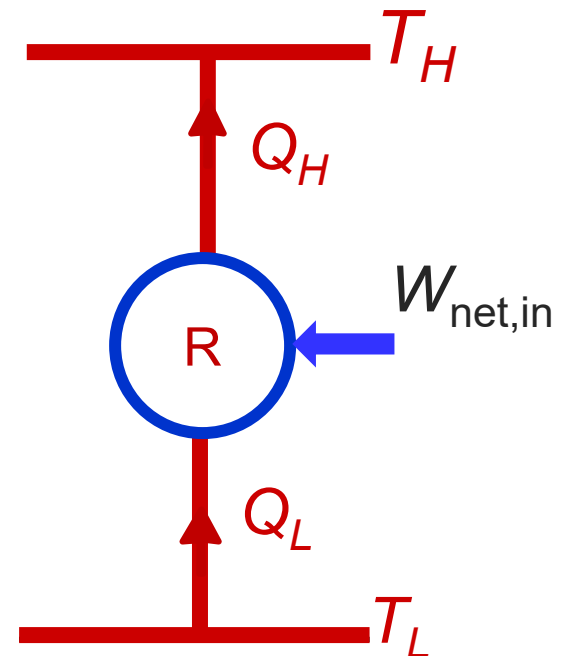


Reverse Heat Engines

Heat Engine:



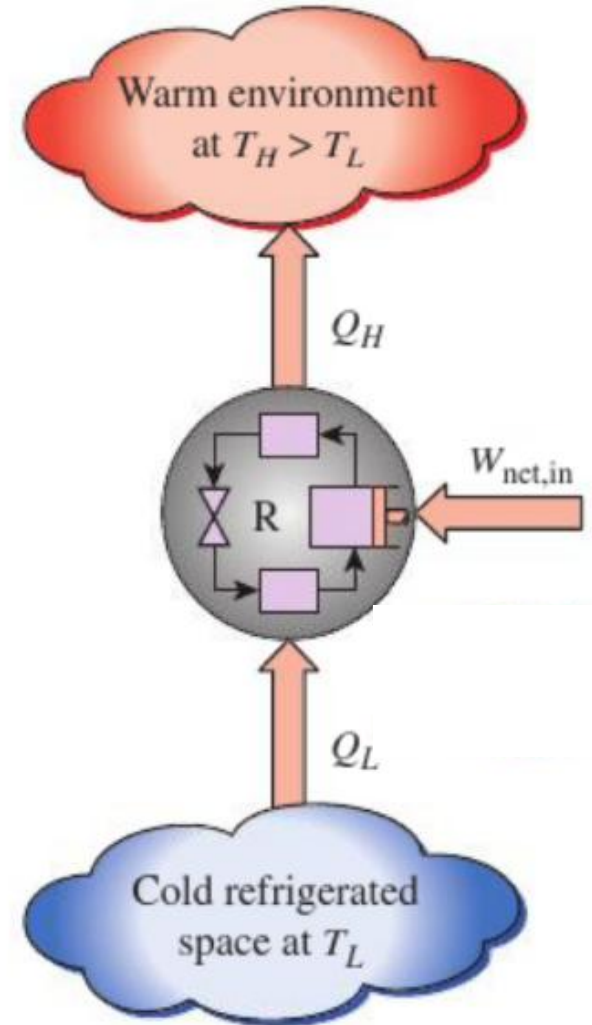
Reverse Heat Engine:



Refrigerator/Heat Pump

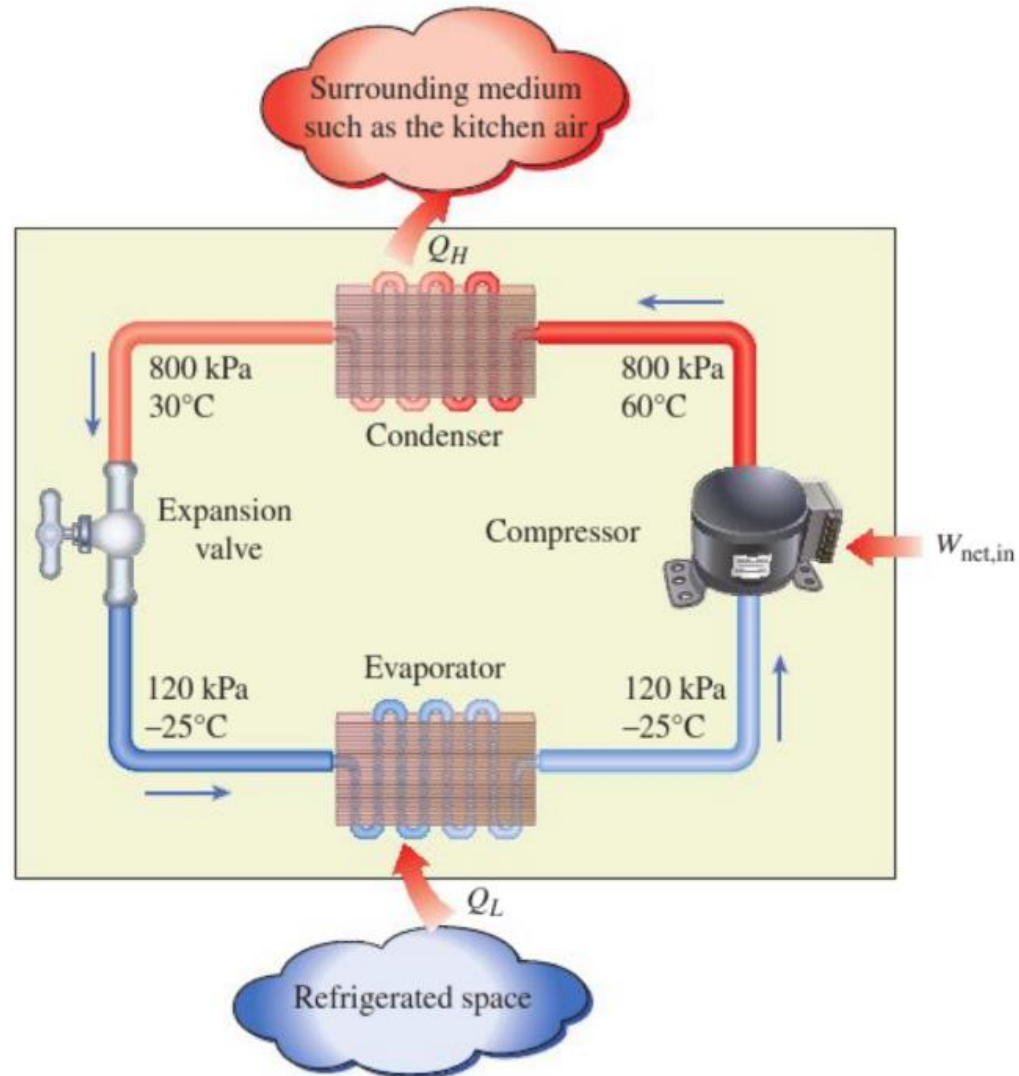
Refrigerators and Heat Pumps

- Heat transfer from high temperatures to low temperatures by nature
- The opposite can only be achieved using refrigerators and heat pumps
- Refrigerators and heat pumps are simply “reverse heat engines”
- Operate in a cycle
- Working fluid is called a refrigerant

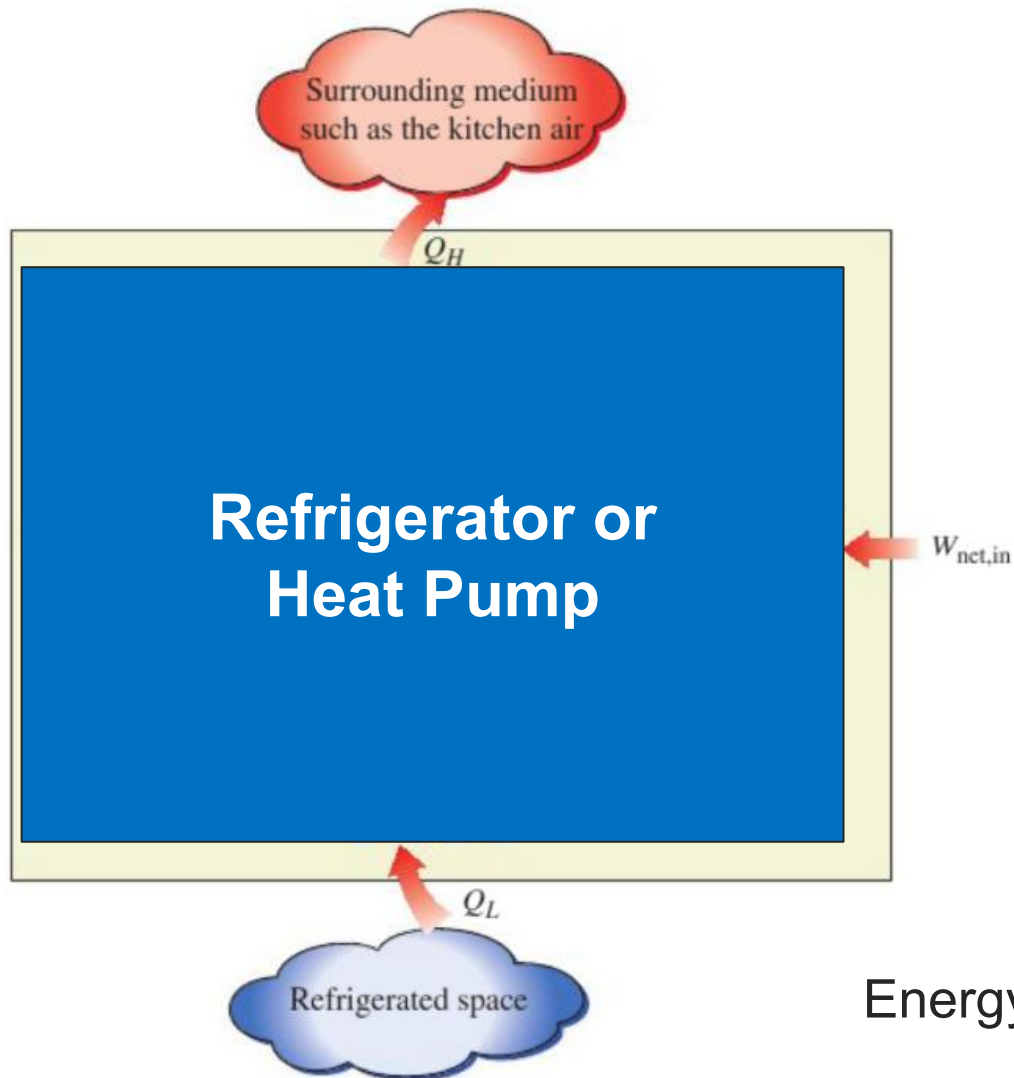


Refrigerators and Heat Pumps

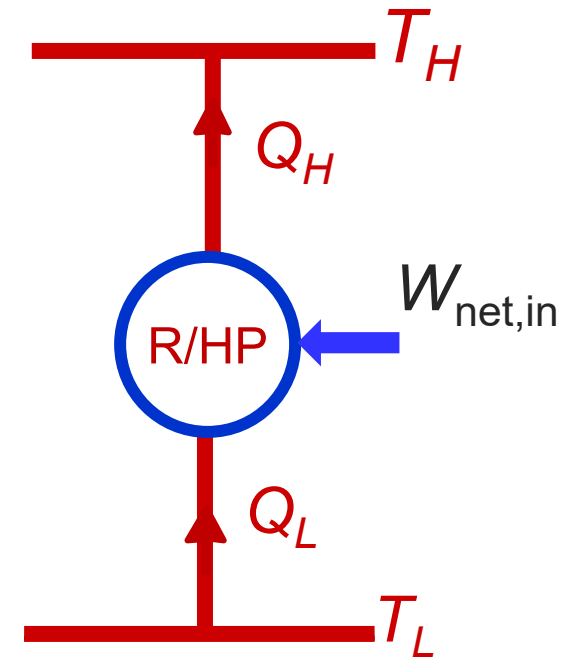
- Vapour-compression refrigeration system is the most commonly used cycle
- W_{in} = work input to compressor to compress refrigerant from low to high pressure
- Q_H = heat rejected by refrigerant in condenser
- Q_L = heat absorbed by refrigerant in evaporator



Refrigerators and Heat Pumps



Simplified:



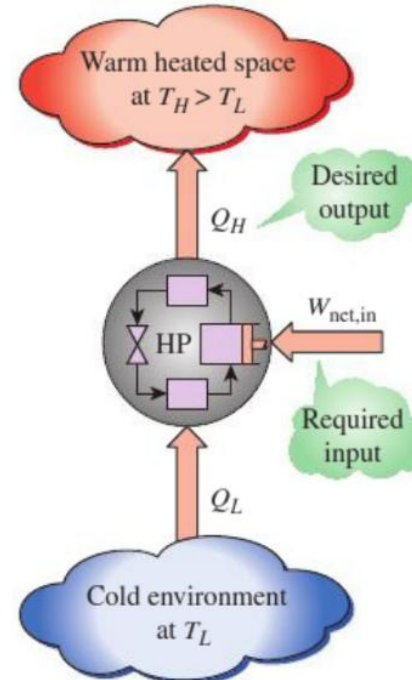
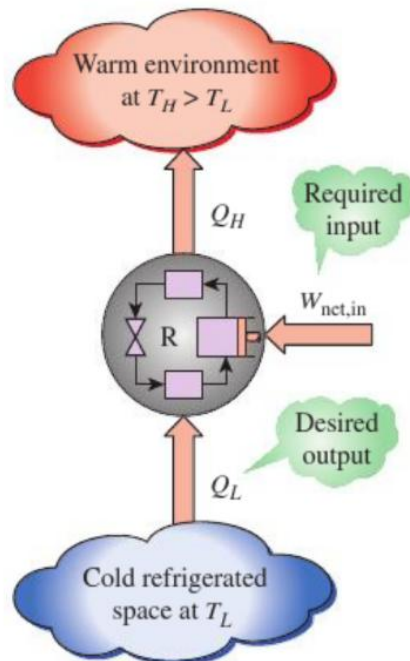
Energy balance: $W_{net,in} = Q_H - Q_L$

Coefficient of Performance

- Efficiency of refrigerators and heat pumps is expressed in terms of **coefficient of performance**

$$\text{Coefficient of Performance} = \frac{\text{Desired output}}{\text{Required input}}$$

- Formula depends on the function of the machine:



Coefficient of Performance – Refrigerator

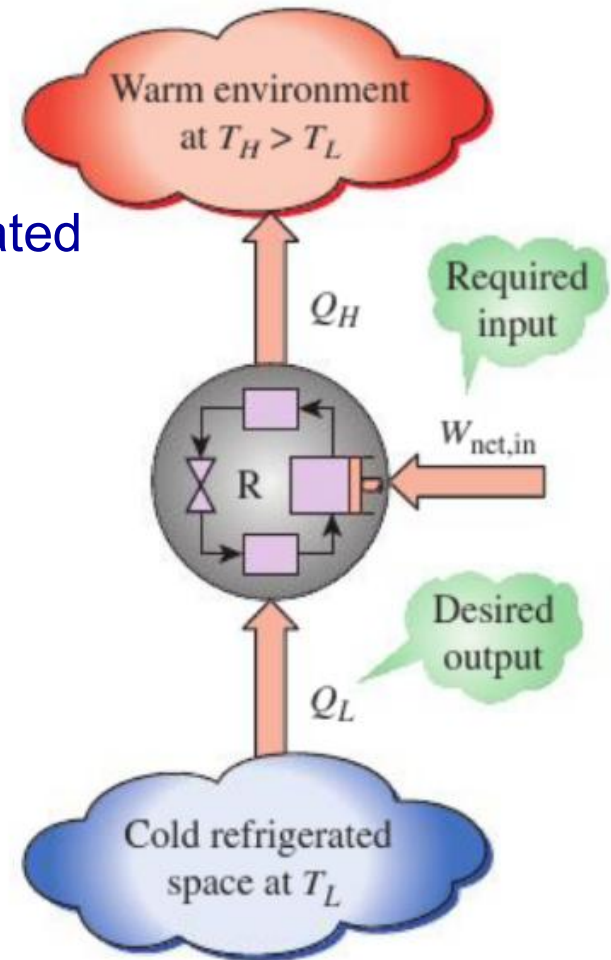
$$\text{Coefficient of Performance} = \frac{\text{Desired output}}{\text{Required input}}$$

Function of a refrigerator is to cool the refrigerated space:

$$\text{COP}_R = \frac{Q_L}{W_{\text{net,in}}}$$

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

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



Coefficient of Performance – Heat Pump

$$\text{Coefficient of Performance} = \frac{\text{Desired output}}{\text{Required input}}$$

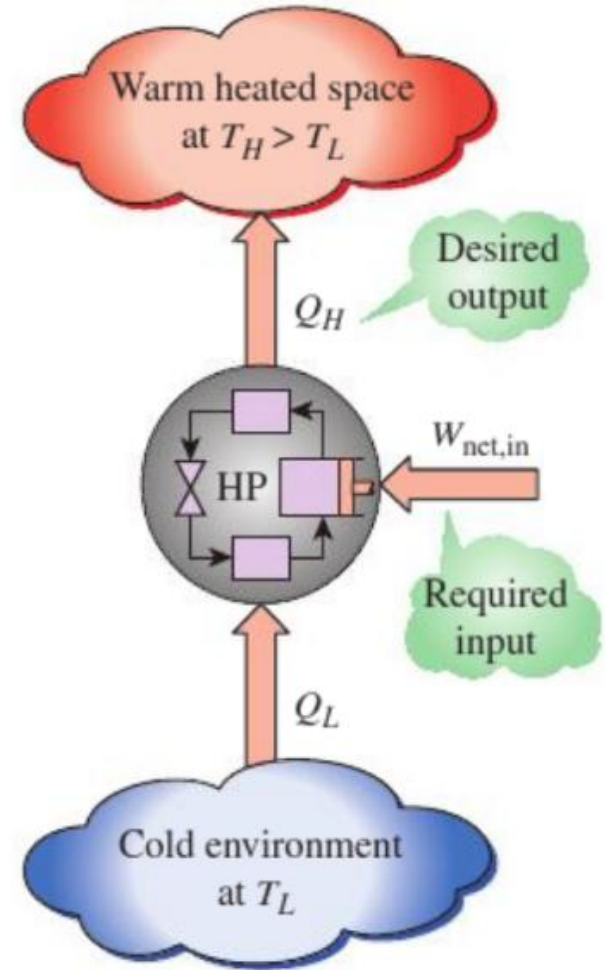
Function of a heat pump is to warm the heated space:

$$\text{COP}_{\text{HP}} = \frac{Q_H}{W_{\text{net,in}}}$$

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

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

$$\text{For the same } Q_H \text{ \& } Q_L, \text{ COP}_{\text{HP}} = \text{COP}_{\text{R}} + 1$$

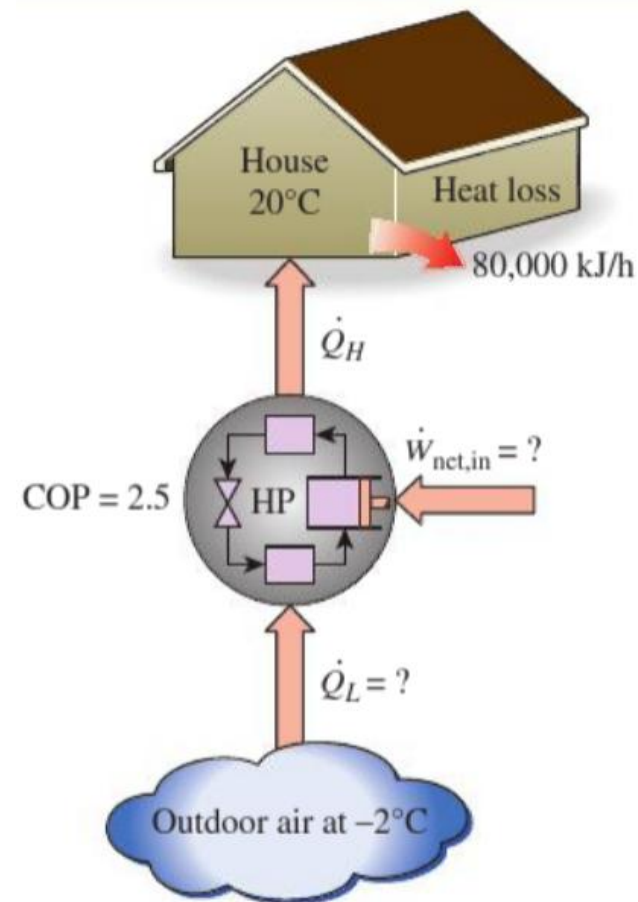


Example 2 – Heating a House with a Heat Pump

A heat pump is used to meet the heating requirements of a house and maintain it at 20°C. On a day when the outdoor air temperature drops to −2°C, the house is estimated to lose heat at a rate of 80,000 kJ/h. If the heat pump under these conditions has a COP of 2.5, determine the power consumed by the heat pump and the rate at which heat is absorbed from the cold outdoor air.

Assumptions:

Steady-state operating conditions



Example 2 – Heating a House with a Heat Pump

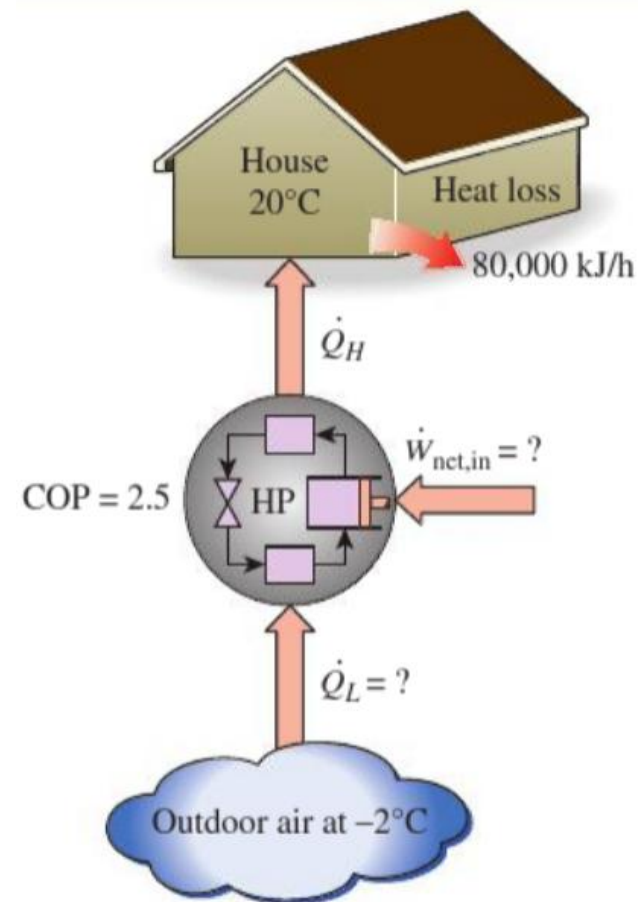
Heat pump delivers the same rate of heat as the heat loss of the house to maintain the indoor temperature:

$$\dot{Q}_H = 80,000 \text{ kJ/h}$$

$$\text{COP}_{\text{HP}} = \frac{Q_H}{W_{\text{net,in}}}$$

$$\begin{aligned}\dot{W}_{\text{net,in}} &= \frac{\dot{Q}_H}{\text{COP}_{\text{HP}}} \\ &= \frac{80,000 \text{ kJ/h}}{2.5} = 32,000 \text{ kJ/h}\end{aligned}$$

$$\begin{aligned}\dot{Q}_L &= \dot{Q}_H - \dot{W}_{\text{net,in}} \\ &= 80,000 - 32,000 = 48,000 \text{ kJ/h}\end{aligned}$$

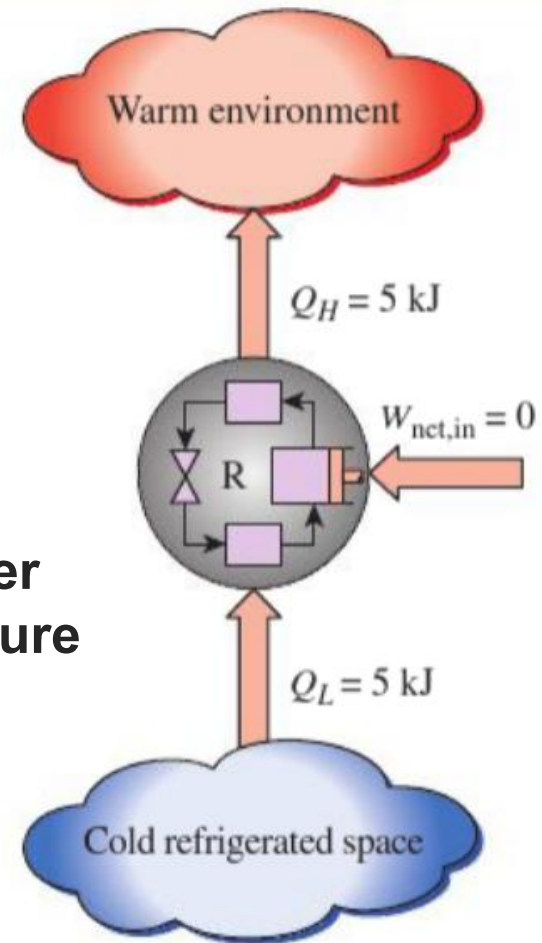


2nd Law of Thermodynamics – Clausius Statement

- Heat is never transferred from a cold medium to a warmer one in nature
- Impossible to have a working refrigerator/heat pump that requires no power input

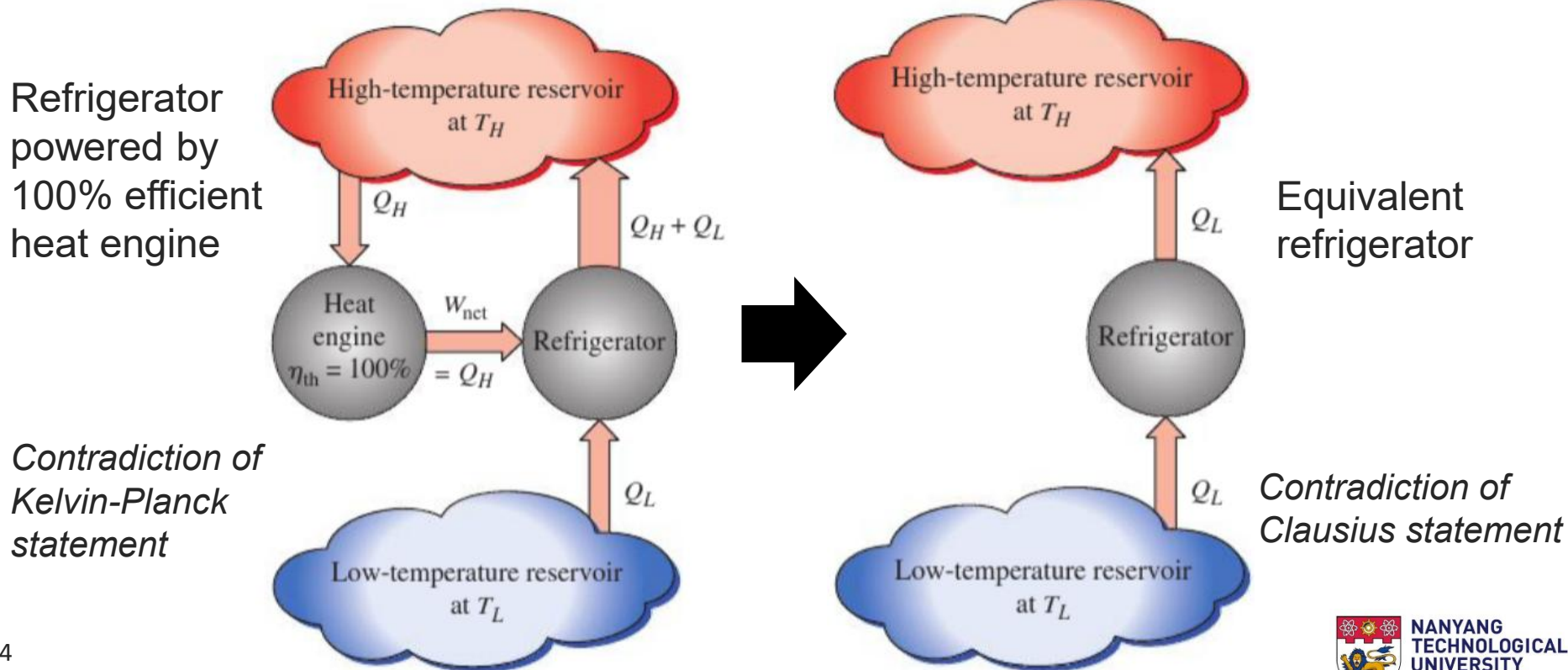
Clausius Statement:

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.



Equivalence of the Two Statements

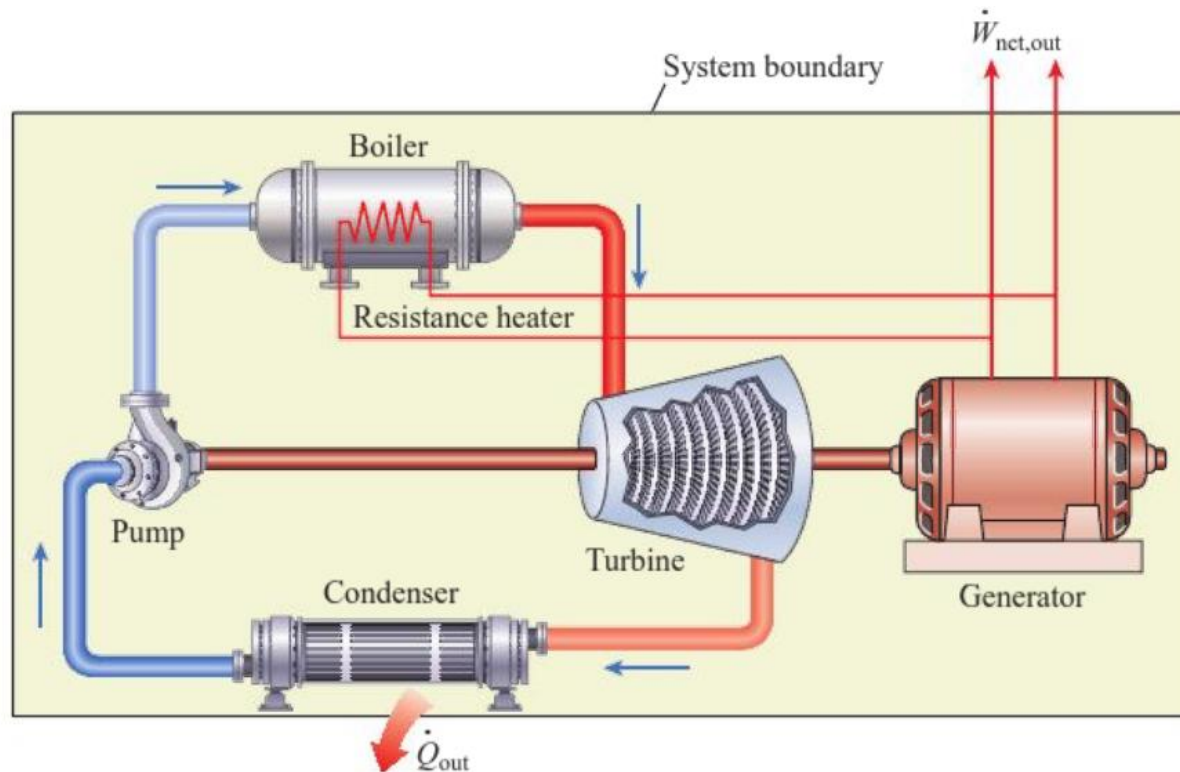
- Kelvin-Planck statement and the Clausius statement are equivalent
- Any device that contradicts either statement, would contradict the other statement as well



Perpetual Motion Machines (PMM)

- A device that contradicts either the 1st law or 2nd law of thermodynamics
 - Contradiction of the 1st law: perpetual motion machine of the first kind (PMM1)

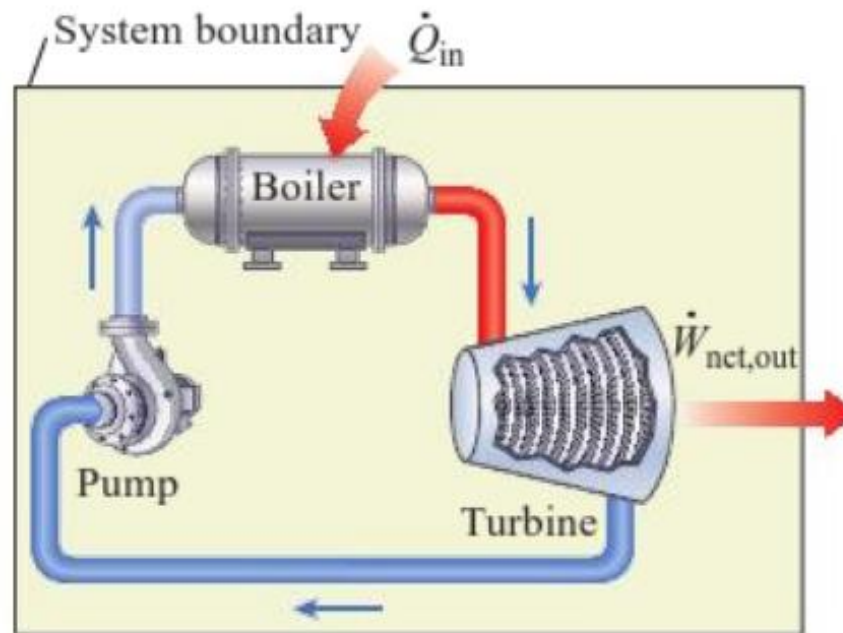
PMM1:



Perpetual Motion Machines (PMM)

- A device that violates either the 1st law or 2nd law of thermodynamics
 - Contradiction of the 2nd law: perpetual motion machine of the second kind (PMM2)

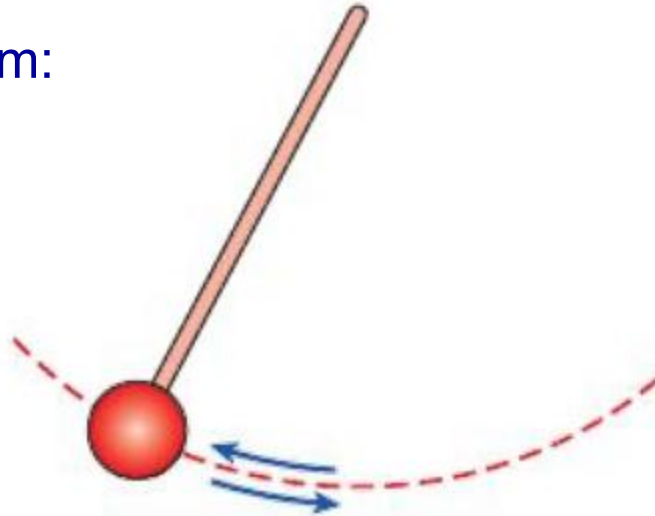
PMM2:



Reversible & Irreversible Processes

Recall: 2nd law can determine the *theoretical limits* for performance of engineering systems/processes

Consider a pendulum:



Process in which there is continuous conversion between potential and kinetic energy of the mass

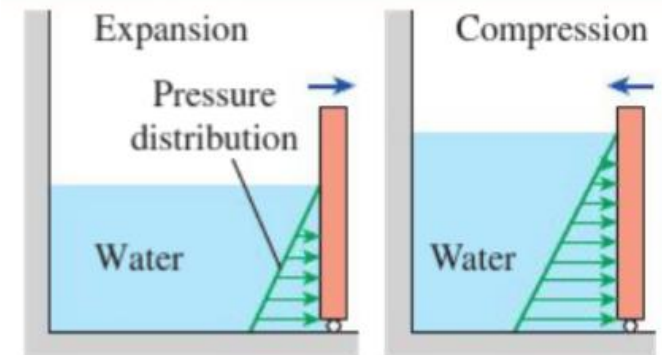
What is its theoretical limit?

Reversible & Irreversible Processes

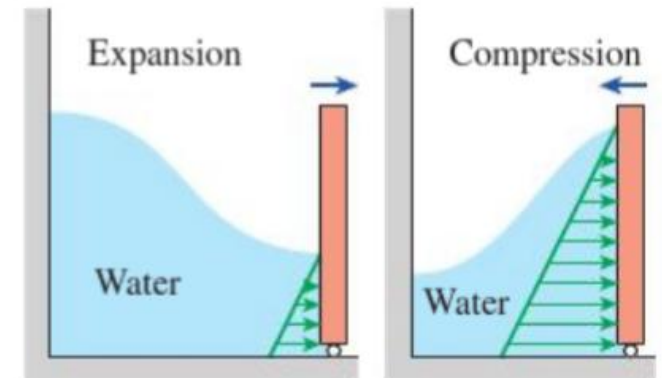
- An ideal pendulum would be a *frictionless* pendulum
 - ‘Perfect’ conversion between kinetic and potential energy
- A **reversible process** is defined as one which can be reversed without leaving any trace on the surroundings
 - The state of the *system & surroundings* can be reverted to initial states at the end of the reverse process
 - Theoretical/ideal process
- An **irreversible process** is the opposite of a reversible process
 - Characteristic of ***all*** processes in nature
- Reversible processes deliver the most and consume the least work
 - Serve as the theoretical limit for its corresponding irreversible process
 - Easy to analyse

Reversible & Irreversible Processes

- Reversible processes are *idealizations* of actual processes
- Actual devices/systems can be approximated as reversible processes at best
- Actual processes are compared against their corresponding idealized/reversible processes to determine its efficiency



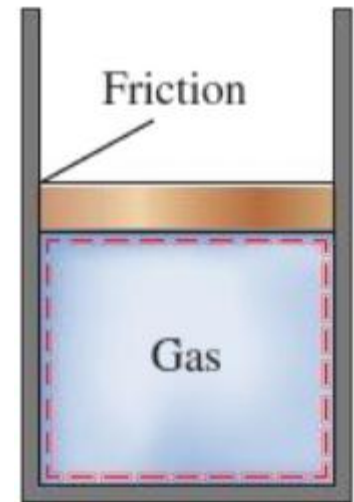
(a) Slow (reversible) process



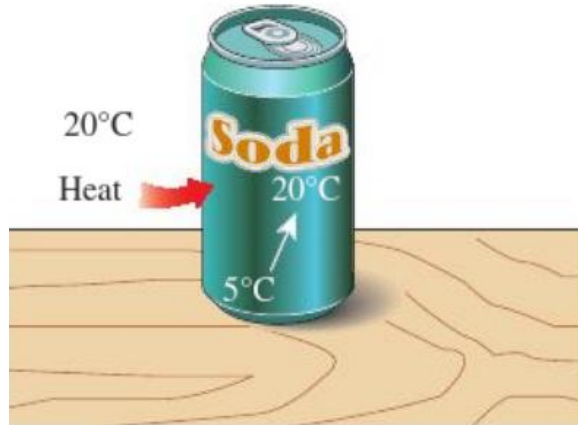
(b) Fast (irreversible) process

Irreversibilities

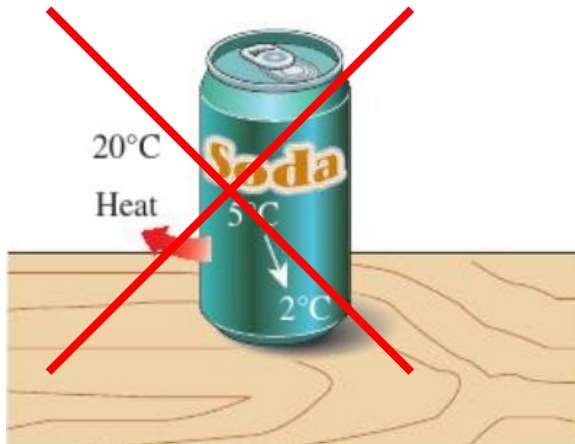
- Factors that cause a process to be irreversible
 - Friction
 - Heat transfer across finite temperature difference
 - Mixing of two fluids
 - Unrestrained expansion
 - Electrical resistance
 - Inelastic deformation of solids
 - Chemical reaction
- Presence of any one factor would cause the process to be irreversible



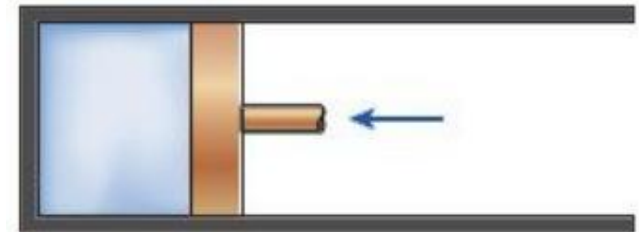
Irreversibilities



Heat transfer across
finite temp. difference



Impossible reverse process



(a) Fast compression



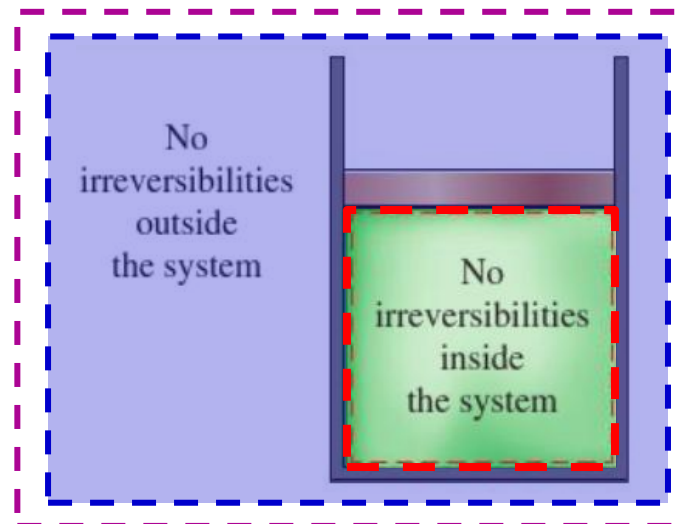
(b) Fast expansion



(c) Unrestrained expansion

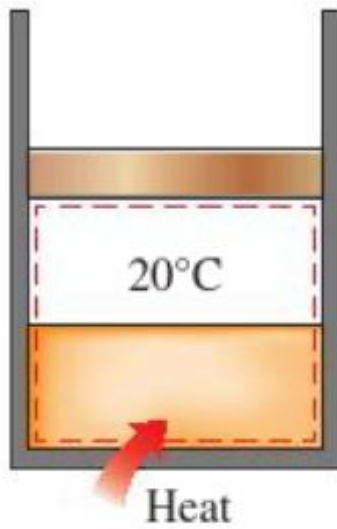
Internally & Externally Reversible Processes

- **Internally reversible:** if no irreversibilities occur within the system boundaries (red box)
- **Externally reversible:** if no irreversibilities occur outside the system boundaries (blue box)
- **Totally reversible:** internally + externally reversible; i.e. no irreversibilities within the system or surroundings (magenta box)



Internally & Externally Reversible Processes

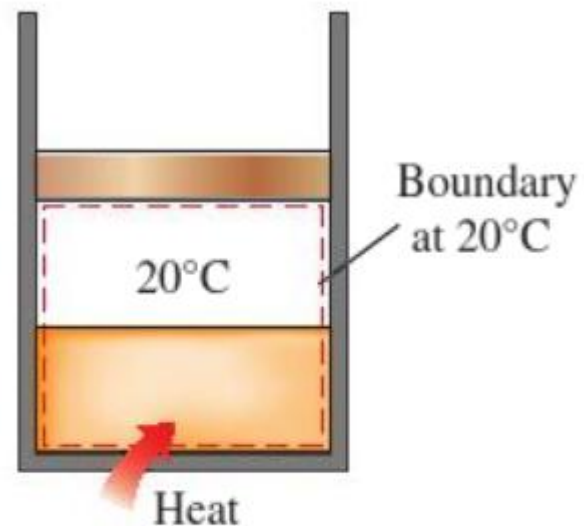
- Example of internally reversible process: boiling of a fluid (constant temperature & pressure process)



Thermal energy
reservoir at 20.000...1°C

(a) Totally reversible

$$\begin{aligned}\Delta T &= 20.00 \dots 1 - 20 \\ &= 0.000 \dots 1^\circ\text{C} \\ &\approx 0^\circ\text{C}\end{aligned}$$



Thermal energy
reservoir at 30°C

(b) Internally reversible

$$\Delta T = 10^\circ\text{C}$$

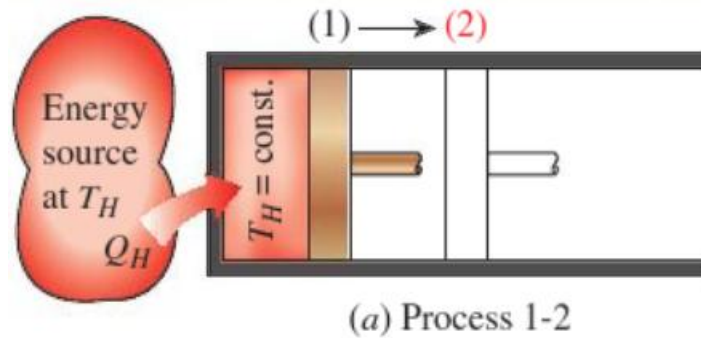
Carnot Cycle

- Proposed by French engineer Sadi Carnot in 1824
- Theoretical cycle
- Consists of 4 reversible processes:
 - 2 isothermal processes
 - 2 adiabatic processes
- Applicable to closed systems or steady flow systems
- Sets the theoretical limits for heat engines, refrigerators and heat pumps

Carnot Cycle

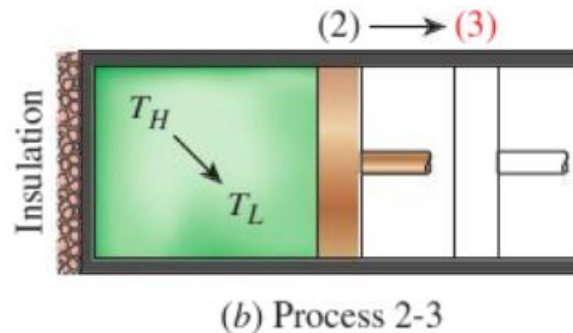
a) Reversible Isothermal Expansion (1 – 2, $T_H = \text{const.}$)

- Gas expands at constant temp. while absorbing heat from energy source



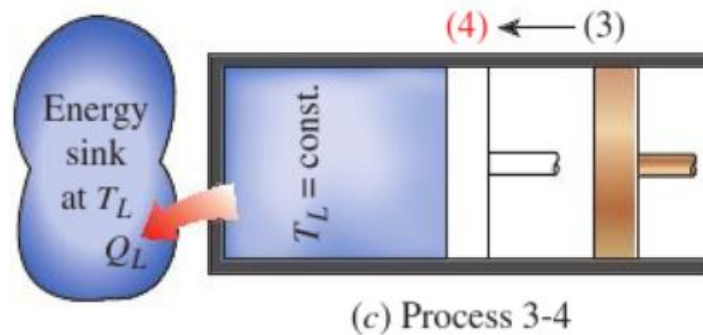
b) Reversible Adiabatic Expansion (2 – 3, T_H drops to T_L)

- Gas does work on surroundings and expands while its temp. drops

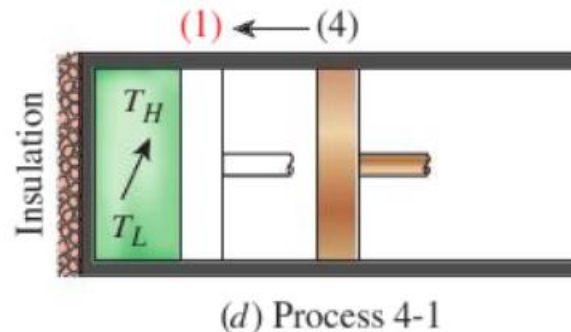


Carnot Cycle

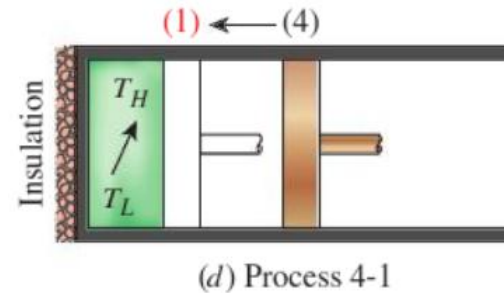
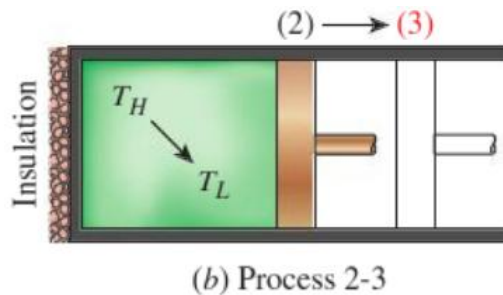
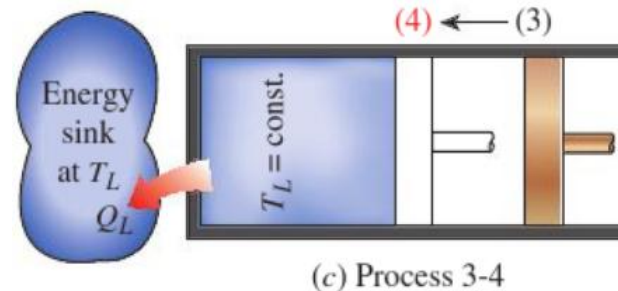
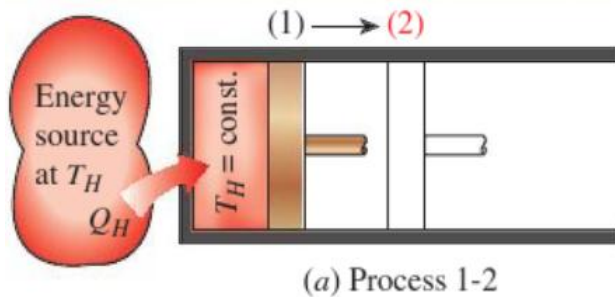
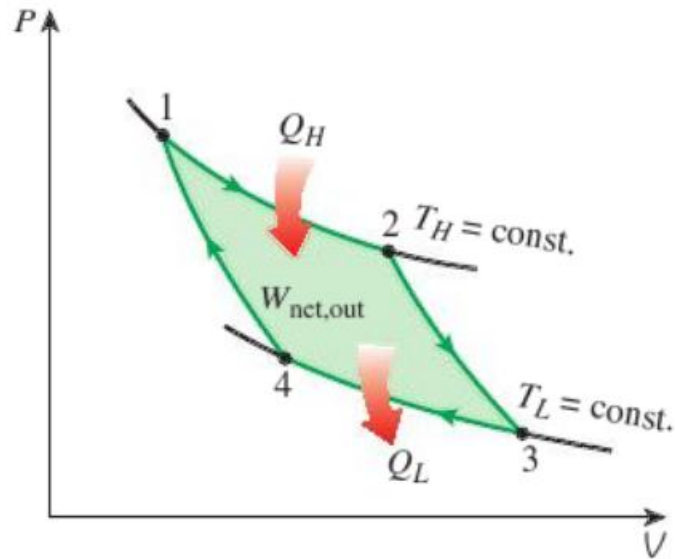
- c) Reversible Isothermal Compression (3 – 4, $T_L = \text{const.}$)
- Gas compression at constant temp. while losing heat to energy sink



- d) Reversible Adiabatic Compression (4 – 1, T_L rises to T_H)
- Work done on gas to compress it and its temp. rises

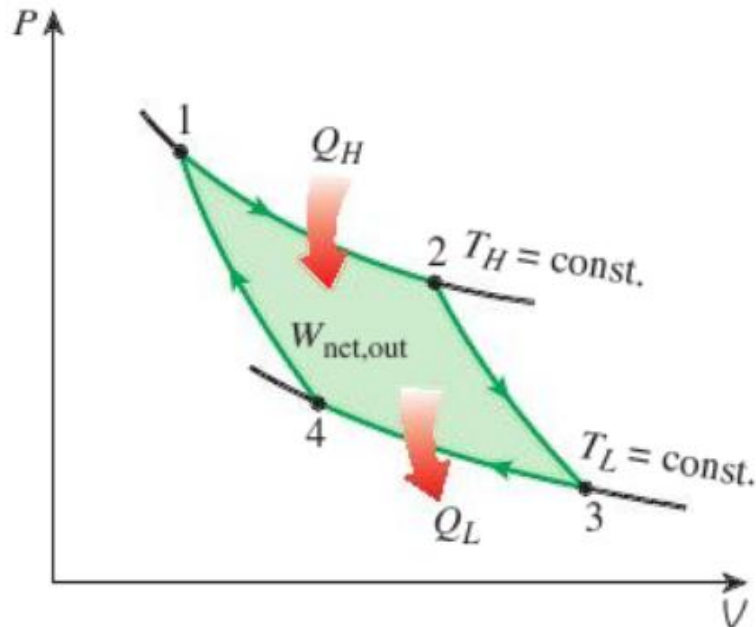


Carnot Cycle – PV Diagram

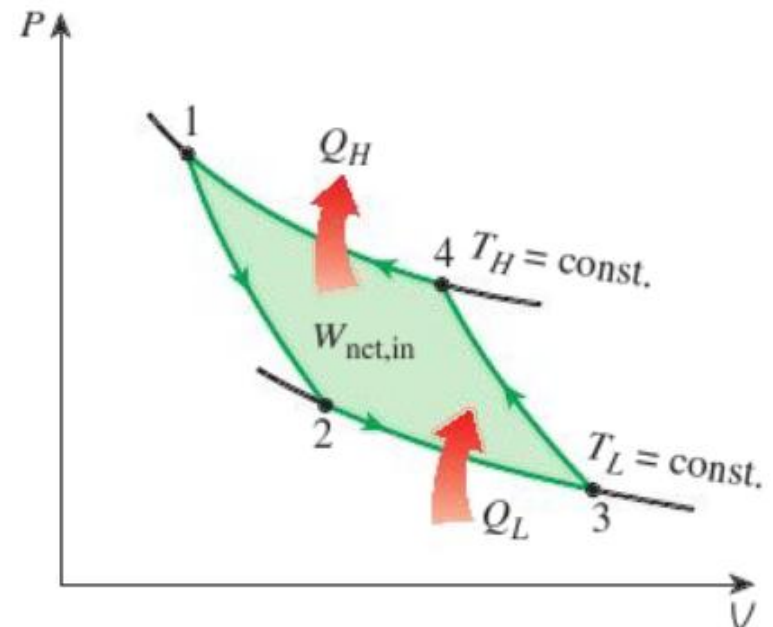


Reversed Carnot Cycle

- The Carnot cycle is a totally reversible cycle
- A reversed Carnot cycle becomes the Carnot refrigeration cycle



Carnot heat-engine cycle



Reversed Carnot heat-engine cycle
Carnot refrigeration cycle

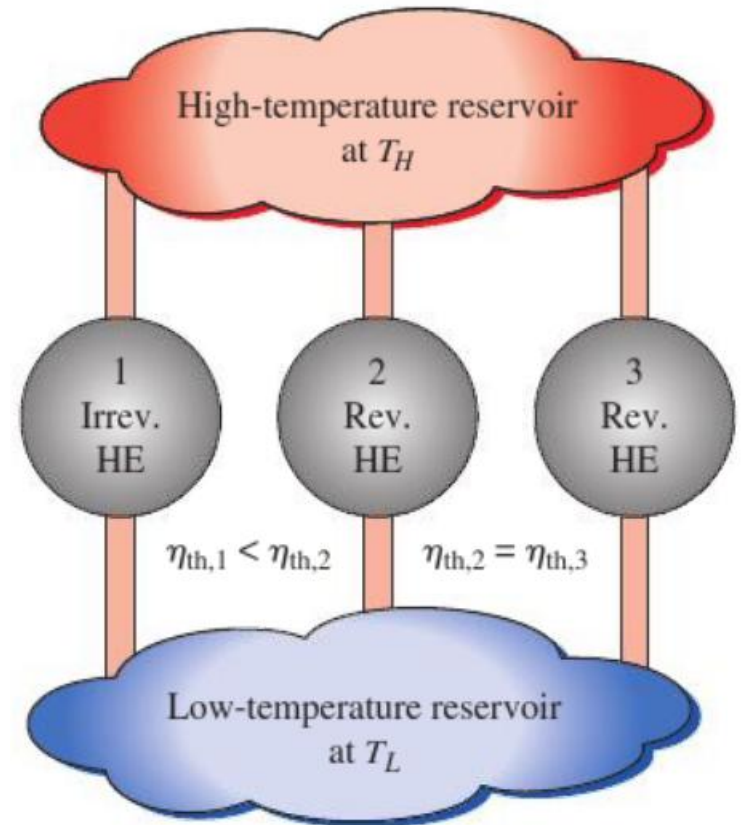
Carnot Principles

1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.

$$\eta_{th,1,irrev} < \eta_{th,2,rev}$$

2. The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.

$$\eta_{th,2,rev} = \eta_{th,3,rev}$$



Proof of Carnot Principles – Part 1

- Assume a violation of the principles such that:

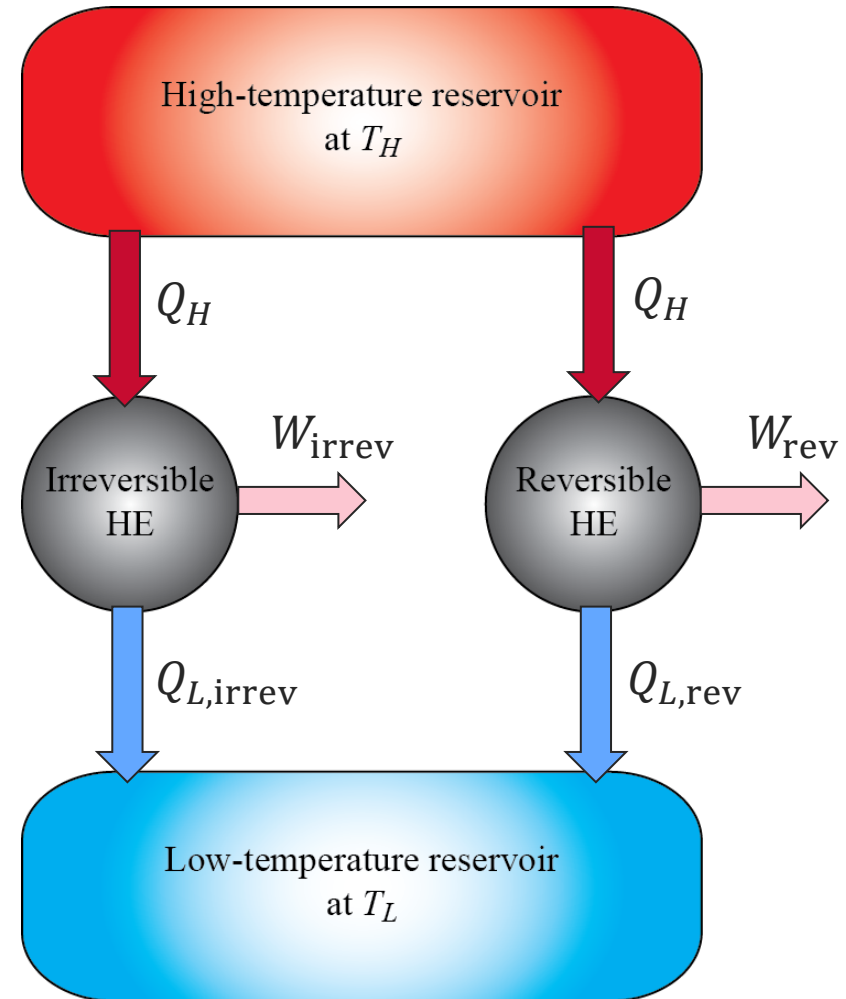
$$\eta_{th,irrev} > \eta_{th,rev}$$

- The output work from an irreversible HE would be higher than a reversible HE in this case:

$$W_{irrev} > W_{rev}$$

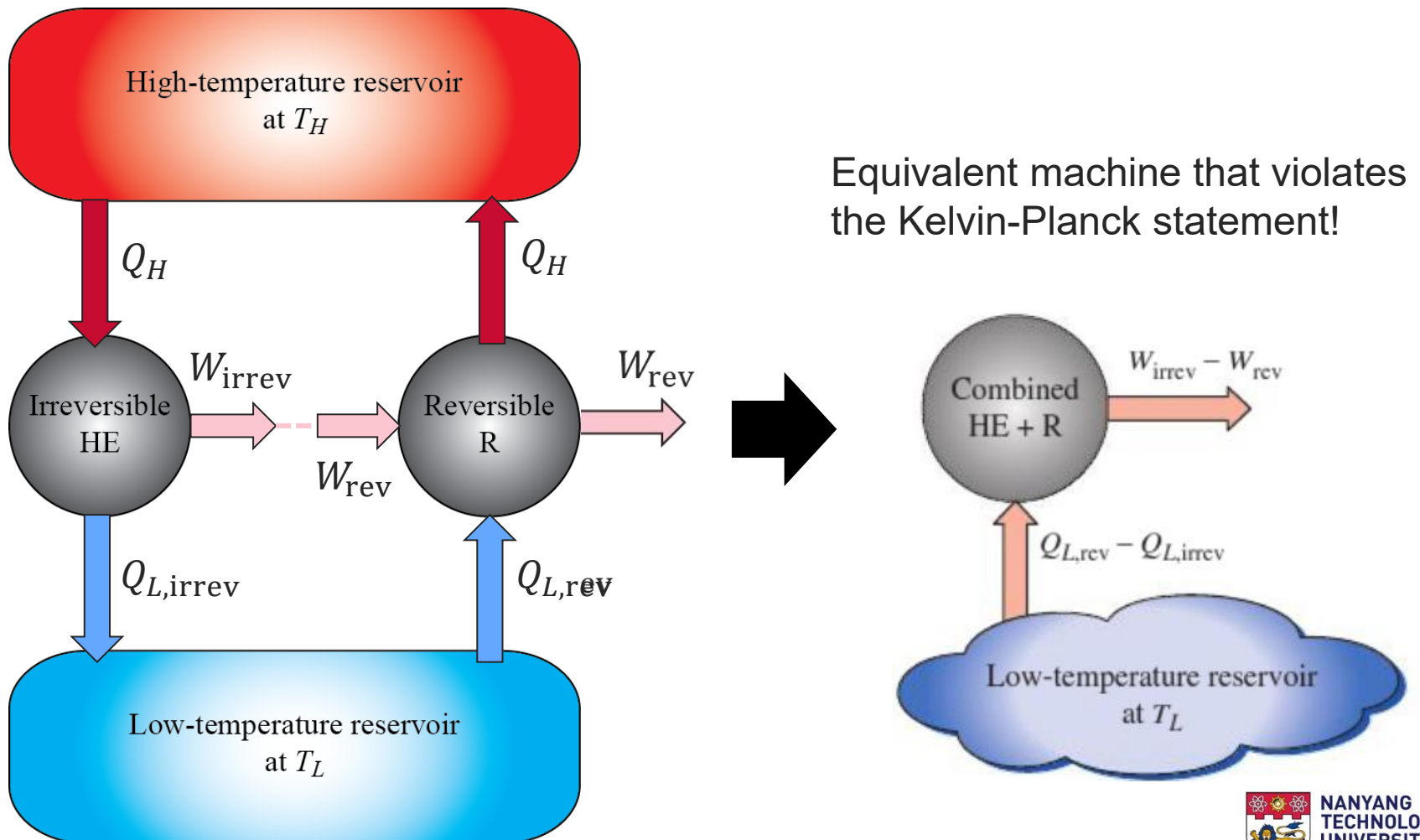
- The heat rejected for an irreversible HE would consequently lower than a reversible HE:

$$Q_{L,irrev} < Q_{L,rev}$$



Proof of Carnot Principles – Part 1

- Reverse the reversible HE, power the reversible R with the HE:



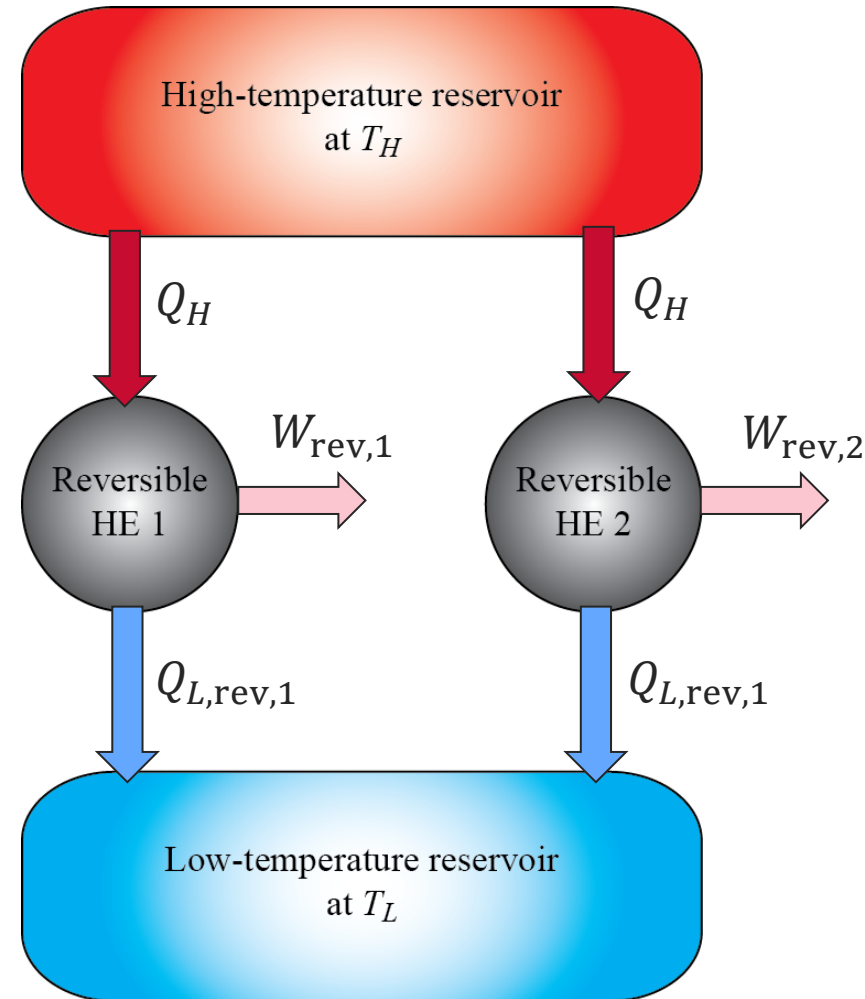
Proof of Carnot Principles – Part 2

- Assume a violation of the principles such that:
 $\eta_{th,rev,1} > \eta_{th,rev,2}$
- The output work from reversible HE 1 would be higher than reversible HE 2:
 $W_{rev,1} > W_{rev,2}$
- The heat rejected for reversible HE 1 would then be lower than reversible HE 2:
 $Q_{L,rev,1} < Q_{L,rev,2}$

$$W_{rev,1} > W_{rev,2}$$

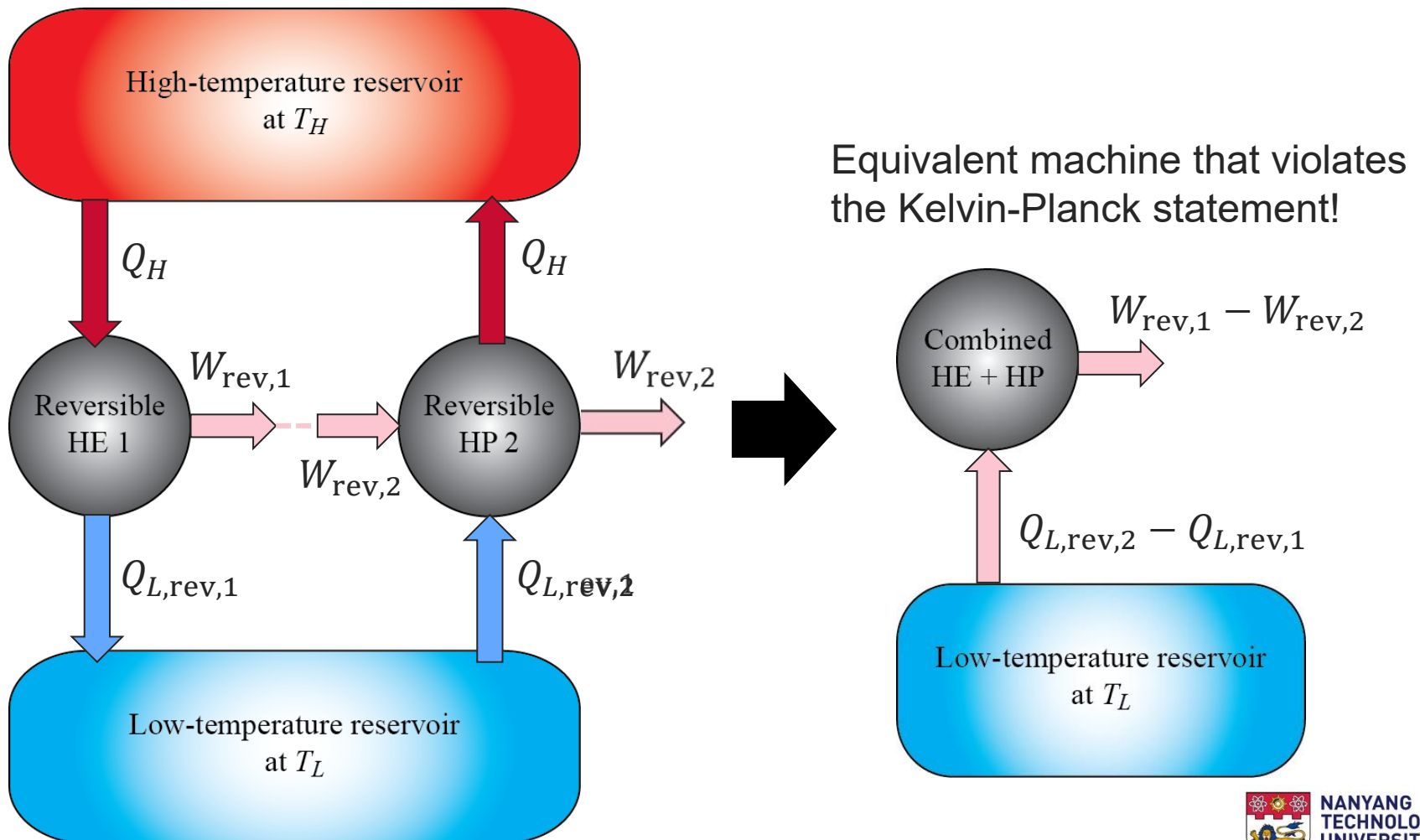
- The heat rejected for reversible HE 1 would then be lower than reversible HE 2:
 $Q_{L,rev,1} < Q_{L,rev,2}$

$$Q_{L,rev,1} < Q_{L,rev,2}$$



Proof of Carnot Principles – Part 2

- Reverse HE 2, power it with HE 1:



Thermodynamic Temperature Scale

- A temperature scale that is independent of the properties of substances that are used to measure temperature is called a **thermodynamic temperature scale**
- Offers great convenience for thermodynamic calculations
- Recall the Carnot principle: all reversible heat engines operating between the same two reservoirs have the same efficiency.
- Thermal reservoirs are characterized only by their temperatures
- Thermal efficiencies of reversible heat engines can be expressed as a function of reservoir temperatures

Thermodynamic Temperature Scale – Derivation

- Thermal efficiencies of rev. HE is a function of temperature only:

$$\eta_{th,rev} = g(T_H, T_L) = 1 - \frac{Q_L}{Q_H}$$

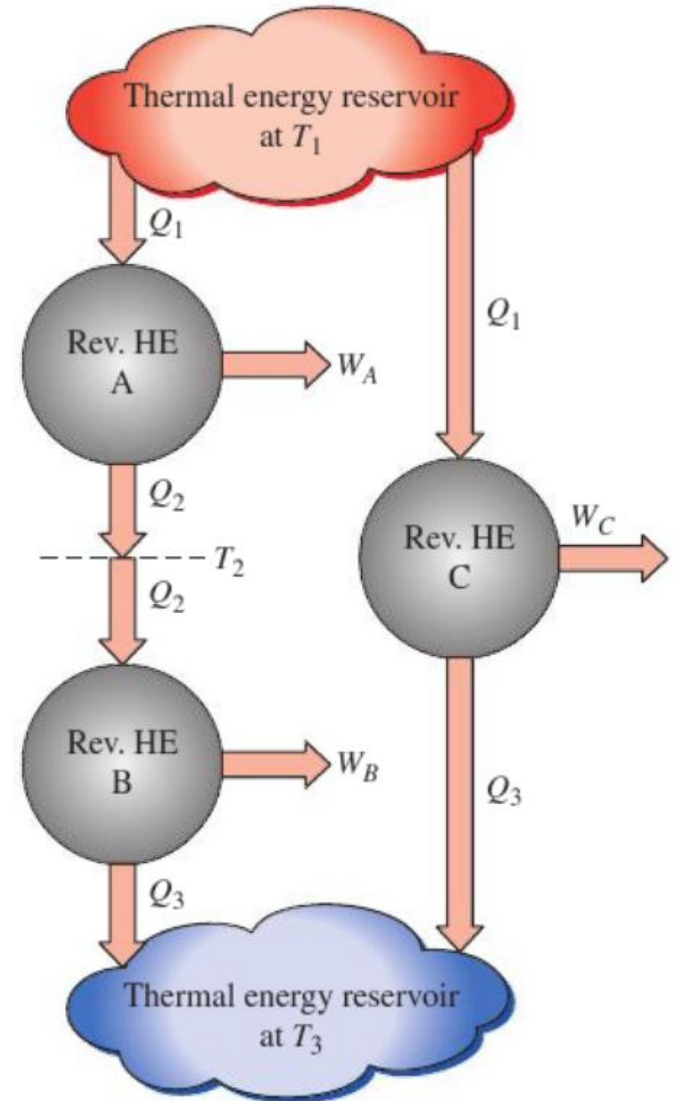
$$\rightarrow \frac{Q_L}{Q_H} \text{ or } \frac{Q_H}{Q_L} = f(T_H, T_L)$$

- For the three heat engines:

$$\frac{Q_1}{Q_2} = f(T_1, T_2)$$

$$\frac{Q_2}{Q_3} = f(T_2, T_3)$$

$$\frac{Q_1}{Q_3} = f(T_1, T_3)$$



Thermodynamic Temperature Scale – Derivation

- Let's consider:

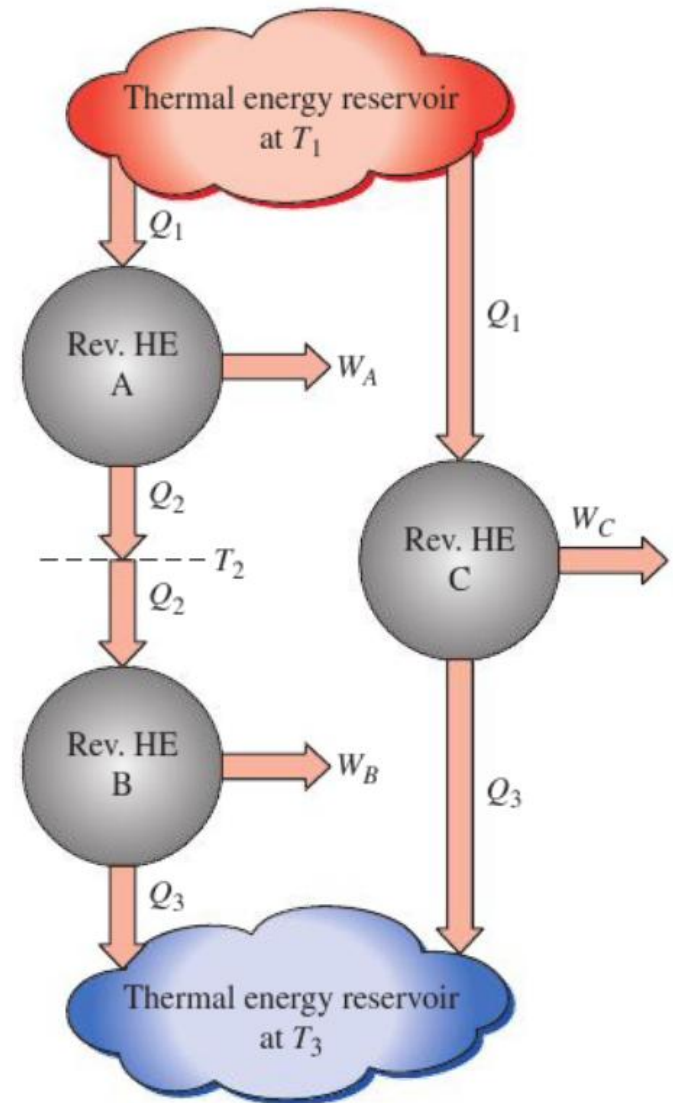
$$\therefore \frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \cdot \frac{Q_2}{Q_3}$$

$$\therefore f(T_1, T_3) = f(T_1, T_2) \cdot f(T_2, T_3)$$

- Product of functions on RHS must cause the T_2 term to disappear
- Only possible if function f is of the form:

$$f(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)} \quad f(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$$

$$\rightarrow f(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_3)} = \frac{Q_1}{Q_3}$$



Thermodynamic Temperature Scale – Derivation

- Therefore, for a reversible HE:

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

- Lord Kelvin thus propose and define:

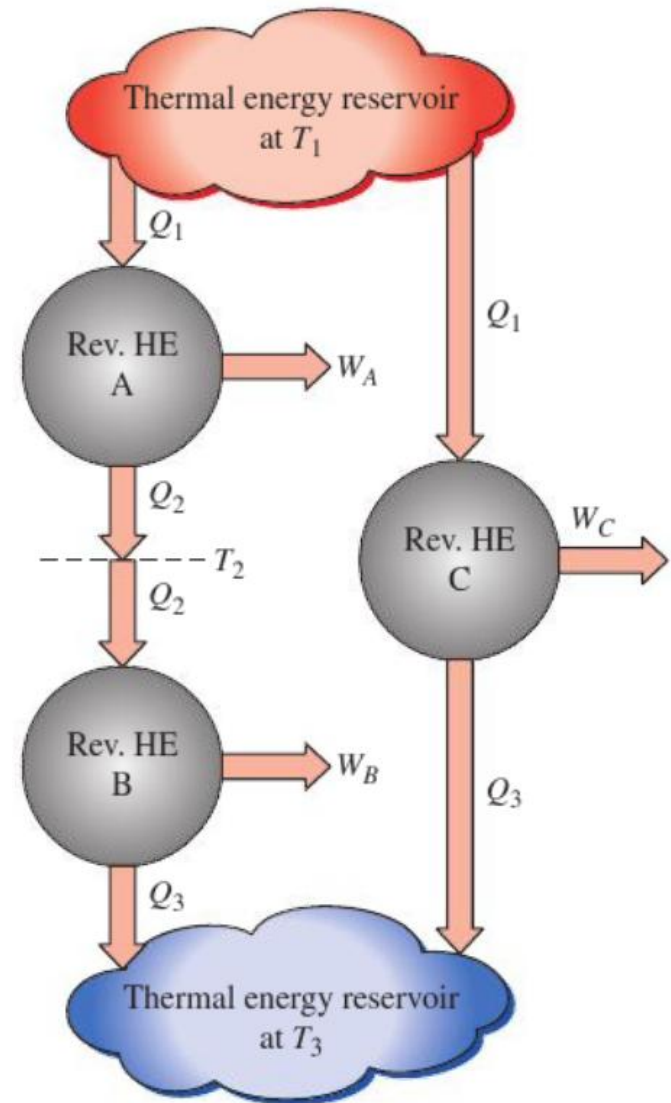
$$\phi(T) = T$$

- The thermodynamic temperature scale is therefore defined as:

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

Note: $Q_H \neq T_H$

$Q_L \neq T_L$



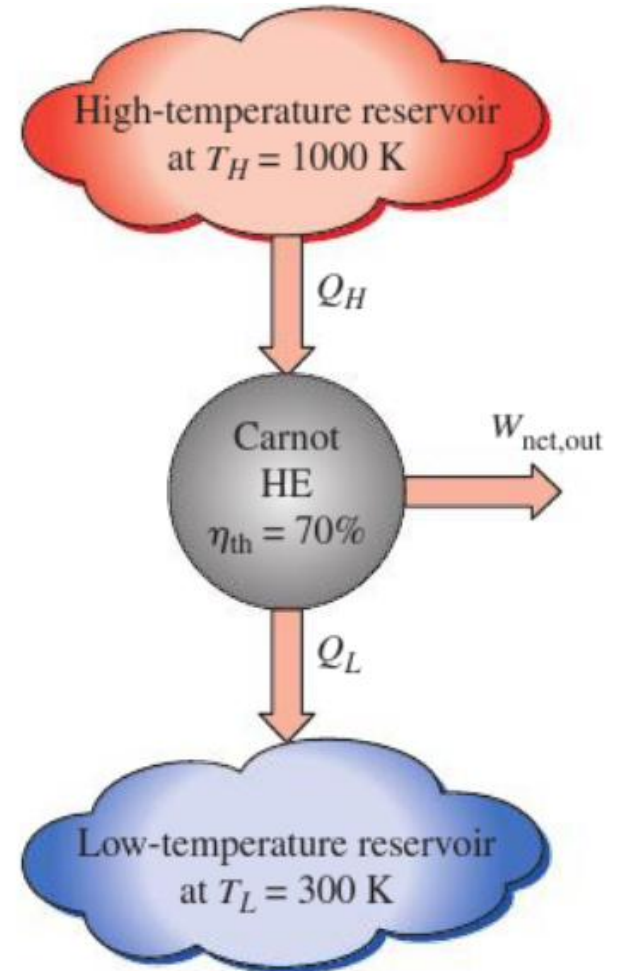
Thermodynamic Temperature Scale

- This temperature scale is called the **Kelvin scale**
- Temperatures on this scale are called **absolute temperatures**

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15$$

- Magnitudes of temperature units on the Kelvin and Celsius scales are the same:

$$1 \text{ K} \equiv 1^{\circ}\text{C}$$



Carnot Heat Engines

- Hypothetical heat engine operating on the Carnot cycle
- Most efficient (ideal) heat engine

- Recall that the thermal efficiency of **any** heat engine is:

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

- From the thermodynamic temperature scale,

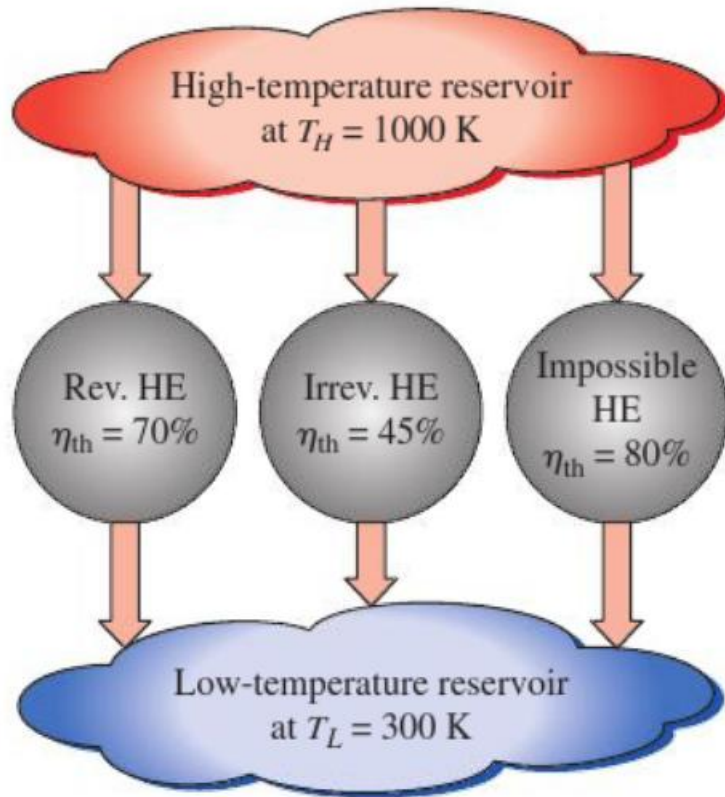
$$\left(\frac{Q_H}{Q_L}\right)_{\text{rev}} = \frac{T_H}{T_L} \quad \text{or} \quad \left(\frac{Q_L}{Q_H}\right)_{\text{rev}} = \frac{T_L}{T_H}$$

- Thermal efficiency of a **Carnot heat engine**:

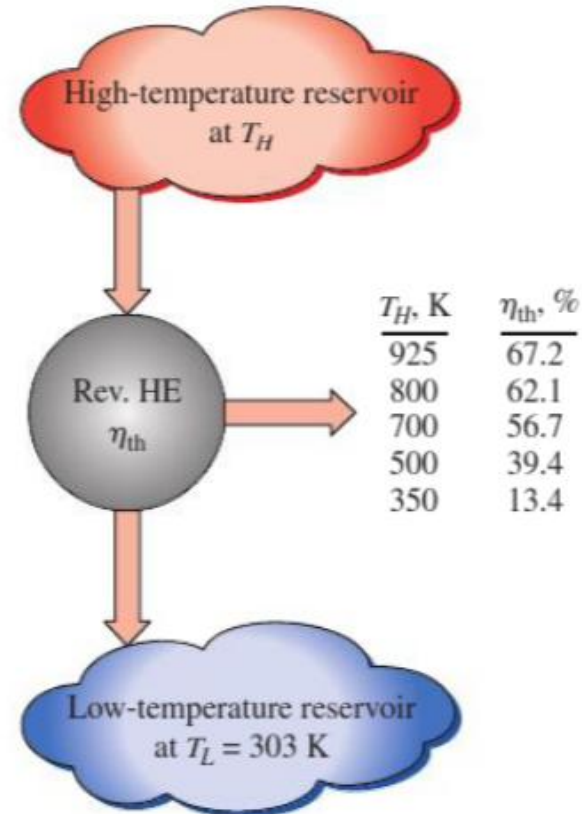
$$\eta_{th,\text{rev}} = 1 - \frac{T_L}{T_H} \quad (\text{Carnot efficiency})$$

Absolute temperatures only!

Carnot Heat Engines



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



- Efficiency increases with source temperature
- Energy has higher **quality** at higher temperatures.

Carnot Refrigerators & Heat Pumps

- A device that operates on the reversed Carnot cycle
- Recall that the coefficient of performance for any refrigerator or heat pump are:

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

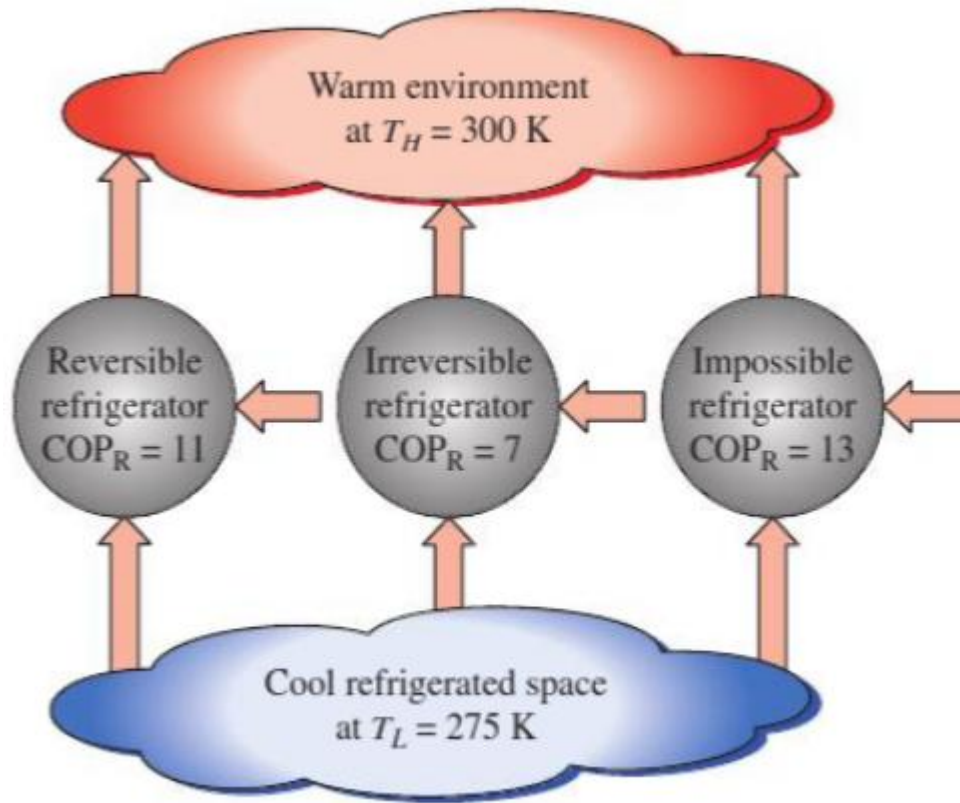
- Coefficient of performance for a Carnot refrigerator:

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

- Coefficient of performance for a Carnot heat pump:

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

Carnot Refrigerators & Heat Pumps



$$\text{COP}_R \begin{cases} < \text{COP}_{R,\text{rev}} & \text{irreversible refrigerator} \\ = \text{COP}_{R,\text{rev}} & \text{reversible refrigerator} \\ > \text{COP}_{R,\text{rev}} & \text{impossible refrigerator} \end{cases}$$

*Same principles
apply to heat pumps*

Example 3: Analysis of a Carnot Heat Engine

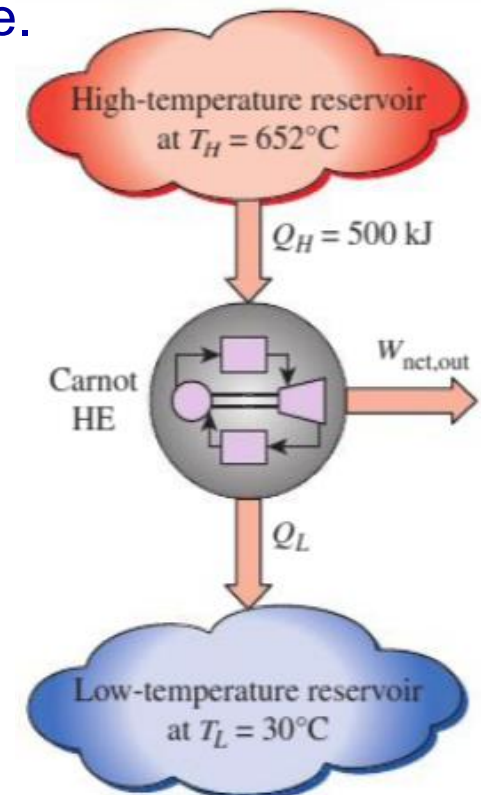
A Carnot heat engine receives 500 kJ of heat per cycle from a high-temperature source at 652°C and rejects heat to a low-temperature sink at 30°C. Determine the thermal efficiency of this Carnot engine and the amount of heat rejected to the sink per cycle.

$$\eta_{th,rev} = 1 - \left(\frac{Q_L}{Q_H} \right)_{rev} = 1 - \frac{T_L}{T_H}$$
$$= 1 - \frac{(30 + 273)\text{K}}{(652 + 273)\text{K}} = 0.672$$

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

$$Q_{L,rev} = \frac{T_L}{T_H} \cdot Q_{H,rev}$$

$$= \frac{(30 + 273)\text{K}}{(652 + 273)\text{K}} (500\text{kJ}) = 164 \text{ kJ}$$



Summary

- Processes can only proceed in one direction and satisfy both the 1st and 2nd Laws of Thermodynamics
- Thermal energy reservoirs can absorb/supply finite amounts of heat without any change in temperature
- Two classes of cyclic devices that operate between T_H and T_L thermal energy reservoirs:
 - Heat engines that produce work output
 - Refrigerators absorb heat from T_L reservoirs and heat pumps supply heat to T_H reservoirs, both require work input
- Thermal efficiency of a heat engine: $\eta_{\text{th}} = 1 - \frac{Q_L}{Q_H}$
- Coefficients of performance (refrigerators & heat pumps):

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

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

Summary

- Reversible processes are ideal processes that can be reversed and are the most efficient
- Actual processes are irreversible due to the presence of irreversibilities
- The Carnot cycle is a reversible cycle that possess the best possible efficiency which is dependent only on T_H and T_L
- The thermodynamic temperature scale is derived from the Carnot principles
- For a reversible Carnot cycle: $\left(\frac{Q_L}{Q_H}\right)_{\text{rev}} = \frac{T_L}{T_H}$
- Carnot efficiency for heat engines: $\eta_{th,\text{rev}} = 1 - \frac{T_L}{T_H}$
- Coefficients of performance for reversed Carnot cycle:

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