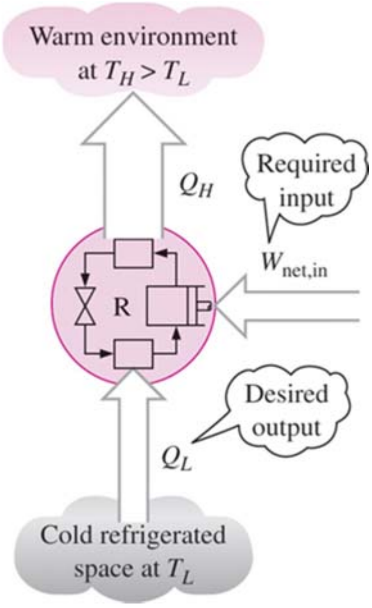
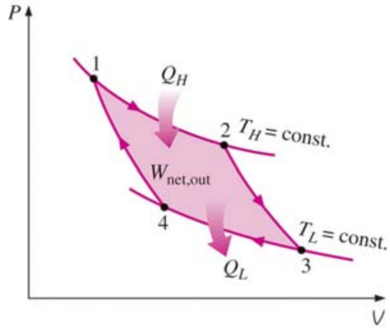
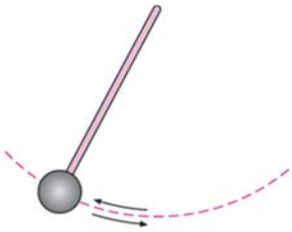
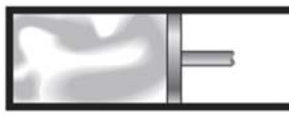
# Thermodynamics I



(a) Frictionless pendulum



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

## The 2nd Low of Thermodynamics

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# Content





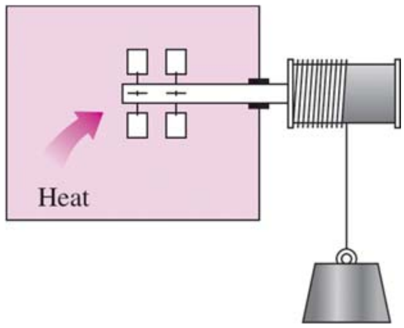
# Introduction to the 2nd Law of Thermodynamics

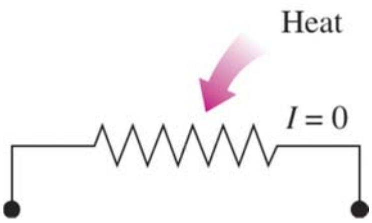
- A process must satisfy the first law to occur.
- However, satisfying the first law alone does not ensure that the process will actually take place.
- The first law, however, places no restrictions on the direction of flow of heat and work.

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


Impossibility of transferring heat directly from a low-temperature body to a high-temperature body.

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



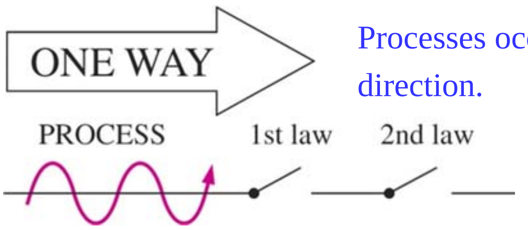




Transferring heat to a wire will not generate electricity.

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



# Introduction to the 2nd Law of Thermodynamics



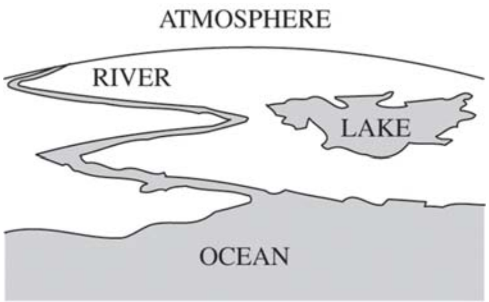

Processes occur in a certain direction, and not in the reverse direction.

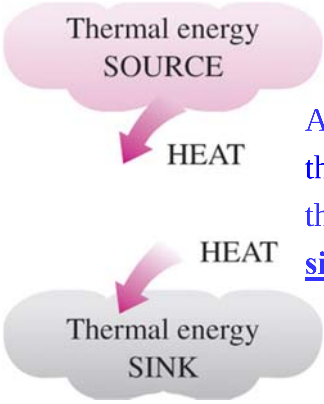
A process must satisfy both the first and second laws of thermodynamics to proceed, otherwise it cannot occur

## MAJOR USES OF THE SECOND LAW

1. The second law may be used to identify the direction of processes.
2. The second law also asserts that energy has *quality* as well as quantity. The first law is concerned with the quantity of energy and the transformations of energy from one form to another with no regard to its quality. The second law provides the necessary means to determine the quality as well as the degree of degradation of energy during a process.
3. The second law of thermodynamics is also used in determining the *theoretical limits* for the performance of commonly used engineering systems, such as heat engines and refrigerators, as well as predicting the *degree of completion* of chemical reactions.

# Thermal Energy Reservoirs




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

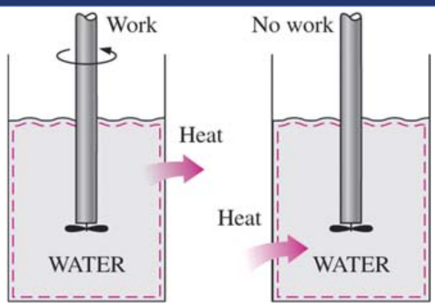
Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.

- A hypothetical body with a relatively large *thermal energy capacity* (mass x specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature is called a **thermal energy reservoir**, or just a reservoir.
- In practice, large bodies of water such as oceans, lakes, and rivers as well as the atmospheric air can be modeled accurately as thermal energy reservoirs because of their large thermal energy storage capabilities or thermal masses.
- Another familiar example of a thermal energy reservoir is the *industrial furnace*

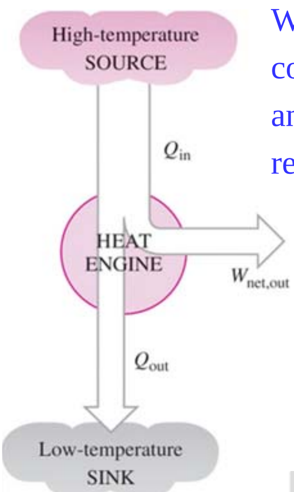




# Heat Engines




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

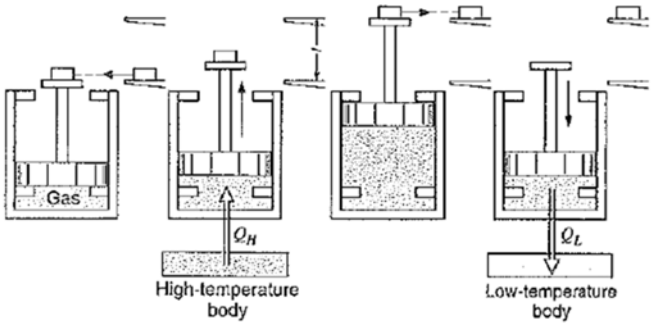


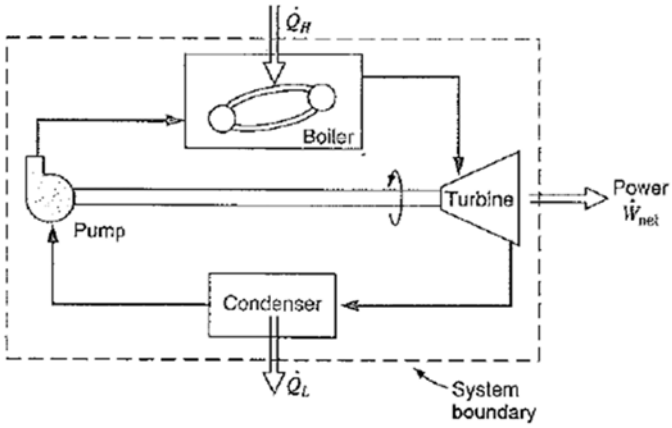

Part of the heat received by a heat engine is converted to work, while the rest is rejected to a sink.

- Converting heat to work requires the use of some special devices (Heat Engine)
- They receive heat from a high-temperature source (solar energy, oil furnace, nuclear reactor, etc.).
- They convert part of this heat to work (usually in the form of a rotating shaft.)
- They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).
- 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**.

# Heat Engines

- Heat engines vary greatly in size and shape,
- large steam engines, gas turbines, or jet engines, to gasoline engines for cars and diesel engines for trucks or cars,
- Smaller engines for lawn mowers or hand-held devices such as chain saws or trimmers.
- Devices as internal combustion such as gas turbines and car engines (the working fluid, i.e. the combustion gases does not undergo a complete cycle) operate in a mechanical cycle.

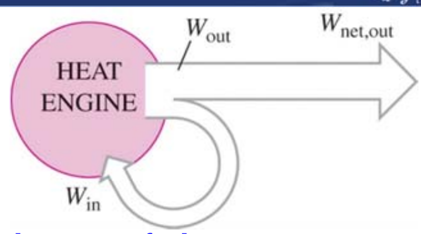


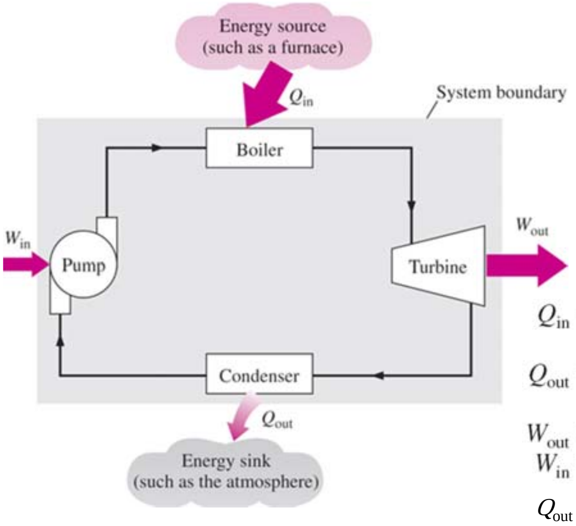






# A Steam Power Plant

- Is an external-combustion engine. That is, combustion takes place outside the engine, and the thermal energy released during this process is transferred to the steam as heat




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

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

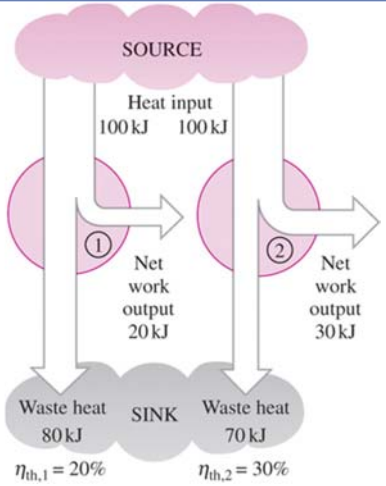
$$W_{net,out} = Q_{in} - Q_{out} \qquad \text{(kJ)}$$

$Q_{in}$ = amount of heat supplied to steam in boiler from a high-temperature source (furnace)
$Q_{out}$ = amount of heat rejected from steam in condenser to a low-temperature sink (the atmosphere, a river, etc.)
$W_{out}$ = amount of work delivered by steam as it expands in turbine
$W_{in}$ = amount of work required to compress water to boiler pressure

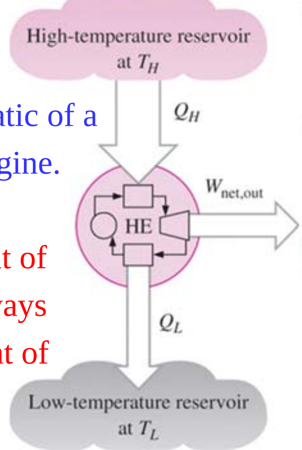
$Q_{out}$ represents the magnitude of the energy wasted in order to complete the cycle

- Cyclic devices (heat engines, refrigerators, and heat pumps) operate between a high-temperature medium (or reservoir) at temperature $T_H$ and a low-temperature medium (or reservoir) at temperature $T_L$. $T_o$

# Thermal Efficiency




Schematic of a heat engine.




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

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

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

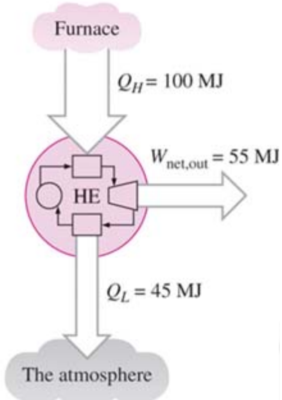
The net work output of a heat engine is always less than the amount of heat input

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

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

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

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




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



# Thermal Efficiency

- Thermal efficiency is a measure of how efficiently a heat engine converts the heat that it receives to work or
- It is the fraction of the heat input that is converted to net work output is a measure of the performance of a heat engine
- $Q_{out}$ represents the magnitude of the energy wasted in order to complete the cycle
- $Q_{out}$ is never zero; thus, the net work output of a heat engine is always less than the amount of heat input. That is, only part of the heat transferred to the heat engine is converted to work
- Typical values for the thermal efficiency of real engines are about
- 35-60% for large power plants,
- 30--35% for gasoline engines, and
- 35-40% for diesel engines.
- Smaller utility-type engines may have only about 20% efficiency

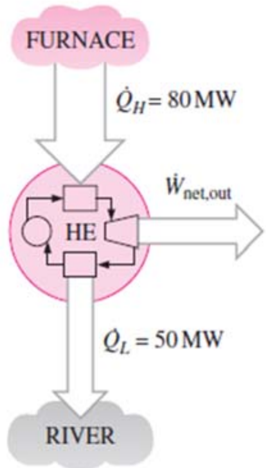
# Example

An automobile engine produces 136 hp on the output shaft with a thermal efficiency of 30%. The fuel it burns gives 35 000 kJ/kg as energy release. Find the total rate of energy rejected to the ambient and the rate of fuel consumption in kg/s.

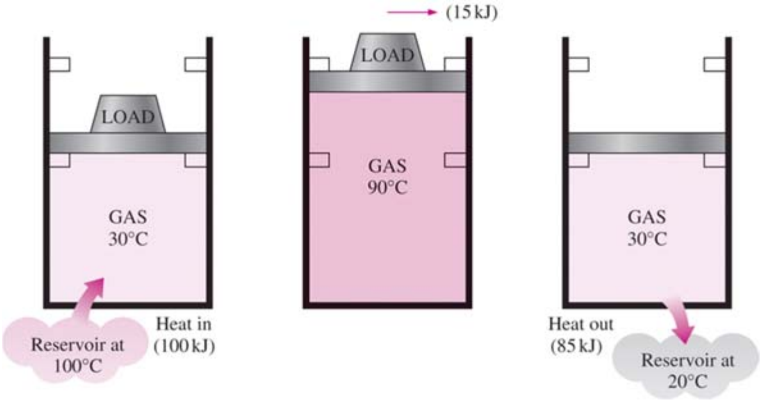


# Example

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.



## Can we save $Q_{out}$?




A heat-engine cycle cannot be completed without rejecting some heat to a low-temperature sink.

Every heat engine must *waste* some energy by transferring it to a low-temperature reservoir in order to complete the cycle, even under idealized conditions.

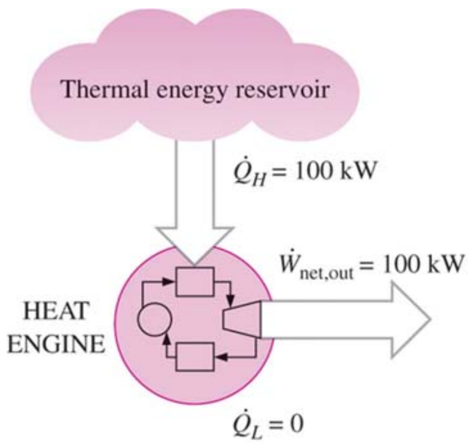
- In a steam power plant, the condenser is the device where large quantities of waste heat is rejected to rivers, lakes, or the atmosphere.
- Can we not just take the condenser out of the plant and save all that waste energy?
- The answer is, unfortunately, a firm ***no*** for the simple reason that without a heat rejection process in a condenser, the cycle cannot be completed.



## The 2nd Law of Thermodynamics: Kelvin–Planck Statement

It is impossible for any device that operates on a cycle to receive a given amount of heat from a single high temperature reservoir and produce an equal amount of work.

- Some heat must be transferred from the working fluid at a lower temperature to a low-temperature body.
- Thus, work can be done by the transfer of heat only if there are two temperature levels, and heat is transferred from the high-temperature body to the heat engine and also from the heat engine to the low-temperature body.




**Impossible**

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

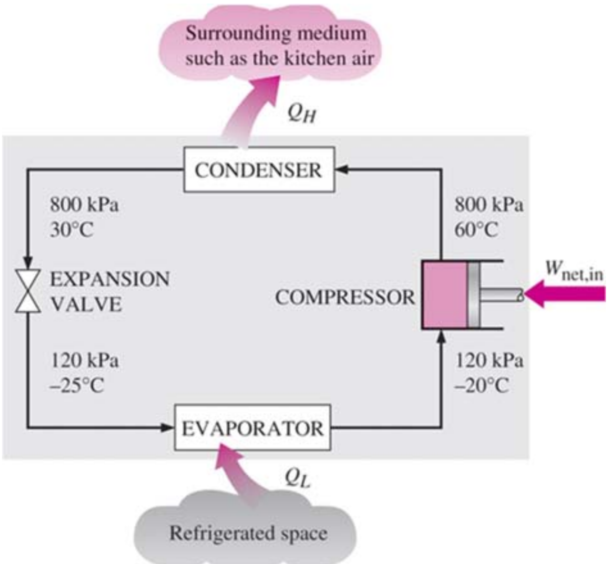
## The 2nd Law of Thermodynamics: Kelvin–Planck Statement

- No heat engine can have a thermal efficiency of 100 percent, or as for a power plant to operate, the working fluid must exchange heat with the environment as well as the furnace.
- The impossibility of having a 100% efficient heat engine is not due to friction or other dissipative effects. It is a limitation that applies to both the idealized and the actual heat engines.
- It is impossible to build a heat engine that has a thermal efficiency of 100%.




## Refrigerators and Heat Pumps

- The second cycle that we can not complete is transferring heat directly from a low-temperature body to a high-temperature body.



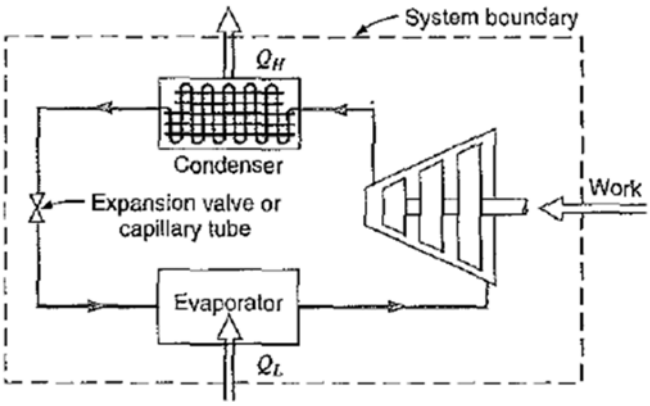

Basic (4) components of a refrigeration system and typical operating conditions.

- The transfer of heat from a low-temperature medium to a high-temperature one requires special devices called **refrigerators**.
- Refrigerators, like heat engines, are cyclic devices.
- The working fluid used in the refrigeration cycle is called a **refrigerant**.
- The most frequently used refrigeration cycle is the *vapor-compression refrigeration cycle*.

In a household refrigerator, the freezer compartment where heat is absorbed by the refrigerant serves as the evaporator, and the coils usually behind the refrigerator where heat is dissipated to the kitchen air serve as the condenser.

# Refrigerators and Heat Pumps

- With the heat pump we can have a system that operates in a cycle and has heat transferred to it from a low-temperature body and heat transferred from it to a high-temperature body, though work is required to do this.
- **In a refrigerators**
  - i. Heat is transferred to the refrigerant in the evaporator, where its pressure and temperature are low.
  - ii. Work is done on the refrigerant in the compressor, and
  - iii. Heat is transferred from refrigerant in the condenser, where its pressure and temperature are high.
  - iv. The pressure drops as the refrigerant flows through the throttle valve or capillary tube.

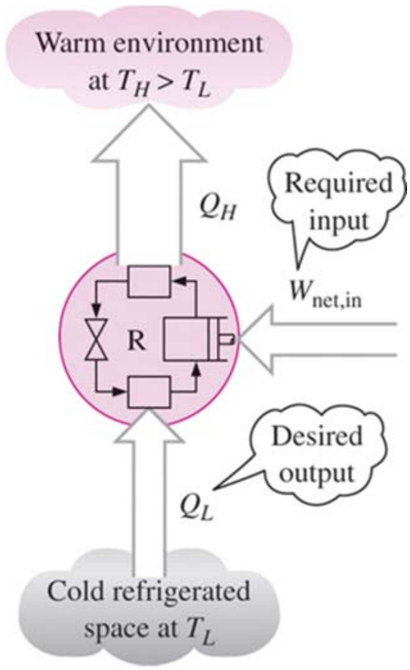



The objective of a refrigerator is to remove heat ($Q_L$) from the refrigerated space

A work input of $W_{net,in.}$ is required



# Coefficient of Performance




The objective of a refrigerator is to remove $Q_L$ from the cooled space.

- 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.

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

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

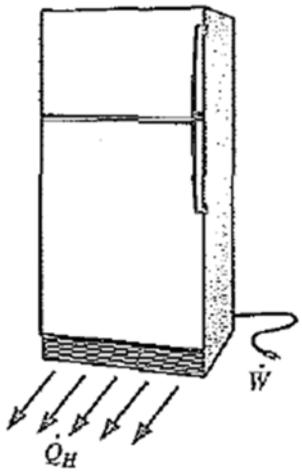
$$COP_R = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1}$$

Can the value of $COP_R$ be greater than unity?

**Yes,** the amount of heat removed from the refrigerated space can be greater than the amount of work input.

# Example

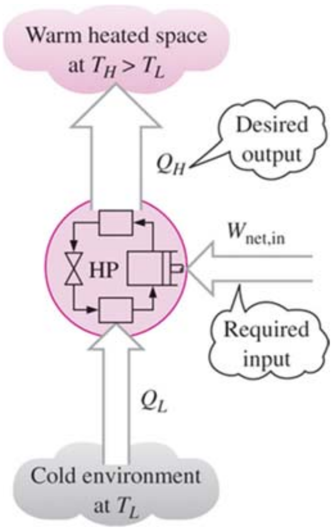
A refrigerator in a kitchen receives an electrical input power of 150 W to drive the system, and it rejects 400 W to the kitchen air. Find the rate of energy taken out of the cold space and the coefficient of performance of the refrigerator.






# Heat Pumps

- Another device that transfers heat from a low-temperature medium to a high-temperature one




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

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

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

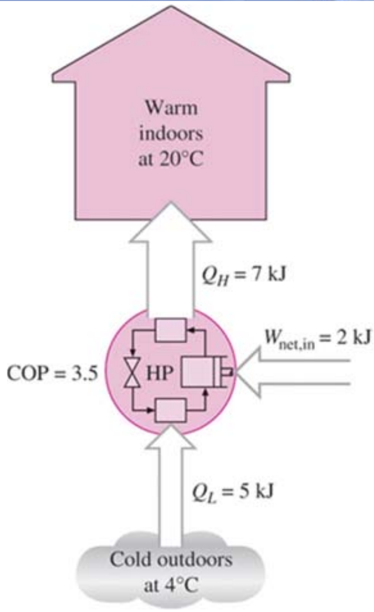
$$COP_{HP} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$

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

for fixed values of $Q_L$ and $Q_H$

# Refrigerators and Heat Pumps

- Refrigerators and heat pumps operate on the same cycle but differ in their objectives.
  - The objective of a refrigerator is to maintain the refrigerated space at a low temperature by removing heat from it.
  - Discharging this heat to a higher-temperature medium is merely a necessary part of the operation, not the purpose.
  - The objective of a heat pump, however, is to maintain a heated space at a high temperature.
  - This is accomplished by absorbing heat from a low-temperature source, such as well water or cold outside air in winter, and
  - Supplying this heat to the high-temperature medium such as a house




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

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

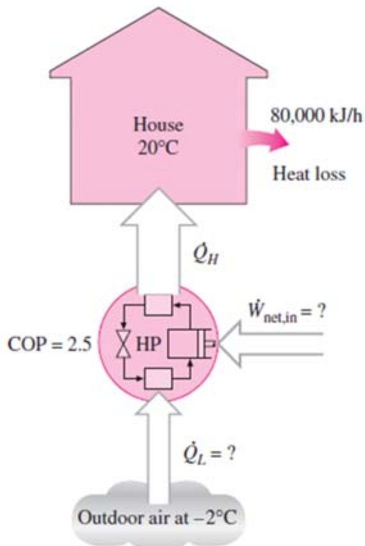
when the outside air temperature is too low.

Operate as a resistance heater, supplying as much energy to the house as it consumes



# Example

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 (*a*) the power consumed by the heat pump and (*b*) the rate at which heat is absorbed from the cold outdoor air.



# Example Cont.

- An ordinary refrigerator that is placed in the window of a house with its door open to the cold outside air in winter will function as a heat pump since
- It will try to cool the outside by absorbing heat from it and
- Rejecting this heat into the house through the coils behind it

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# When installed backward, an air conditioner functions as a heat pump.

- Most heat pumps in operation today have a seasonally averaged COP of 2 to 3.
- Most existing heat pumps use the cold outside air as the heat source in winter (*air-source* HP).
- In cold climates their efficiency drops considerably when temperatures are below the freezing point.
- In such cases, *geothermal* (*ground-source*) HP that use the ground as the heat source can be used.
- Such heat pumps are more expensive to install, but they are also more efficient.
- Geothermal heat pumps require the burial of pipes in the ground 1 to 2 m deep.
- Such heat pumps are more expensive to install, but they are also more efficient (up to 45 percent more efficient than air-source heat pumps).
- The COP of ground-source heat pumps is about 4.0.

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## When installed backward, an air conditioner functions as a heat pump.

- **Air conditioners** are basically refrigerators whose refrigerated space is a room or a building instead of the food compartment.
- The COP of a refrigerator decreases with decreasing refrigeration temperature.
- Therefore, it is not economical to refrigerate to a lower temperature than needed.
- Air-conditioning systems that are equipped with proper controls and a reversing valve operate as air conditioners in summer and as heat pumps in winter.
- **Energy efficiency rating (EER):** The amount of heat removed from the cooled space in Btu's for 1 Wh (watt-hour) of electricity consumed.

$$\text{EER} = 3.412\ \text{COP}_R$$


When installed backward, an air conditioner functions as a heat pump



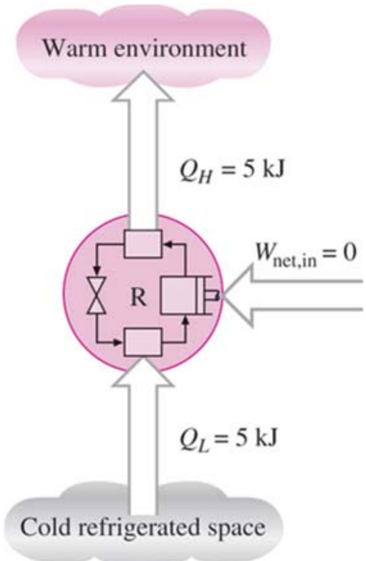
## The Second Law of Thermodynamics: Clasius Statement

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

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

  **i.e. it is impossible to construct a refrigerator that operates without an input of work**

- This way, the net effect on the surroundings involves the consumption of some energy in the form of work, in addition to the transfer of heat from a colder body to a warmer one.
- To date, no experiment has been conducted that contradicts the second law, and this should be taken as sufficient proof of its validity.




**Impossible**

A refrigerator that violates the **Clausius statement** of the second law.

## Observations Regarding the statements of the 2nd Law

- Both are negative statements.
- It is impossible to "prove" these negative statements. However,
- The basis of the second law of thermodynamics (like every other law of nature) rests on experimental evidence
- The two statements are equivalent if the truth of each statement implies the truth of the other, or if the violation of each statement implies the violation of the other.

**i.e. the violation of the Clausius statement implies a violation of the Kelvin-Planck statement and vies verse**

- 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.
- The second law of thermodynamics has been stated as the impossibility of constructing a **perpetual-motion machine of the second kind.**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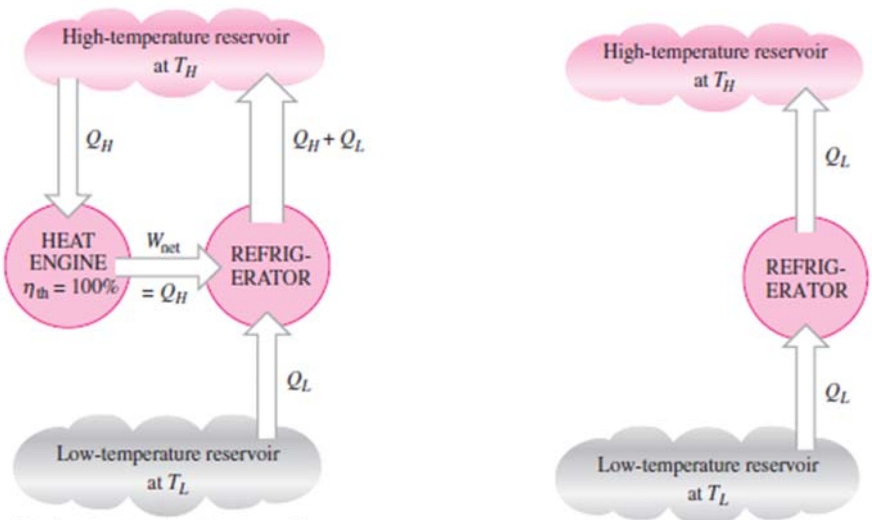
## Equivalence of the Two Statements



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

(b) The equivalent refrigerator

- The heat engine is assumed to have, in violation of the Kelvin–Planck statement, a thermal efficiency of 100 percent,
- And therefore it converts all the heat $Q_H$ it receives to work $W$.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# Equivalence of the Two Statements

- This work is now supplied to a refrigerator that removes heat in the amount of $Q_L$ from the low-temperature reservoir and
- Rejects heat in the amount of $Q_L + Q_H$ to the high-temperature reservoir.
- During this process, the high temperature reservoir receives a net amount of heat $Q_L$
- The combination of these two devices can be viewed as a refrigerator,
- That transfers heat in an amount of $Q_L$ from a cooler body to a warmer one without requiring any input from outside.
- This is clearly a violation of the Clausius statement



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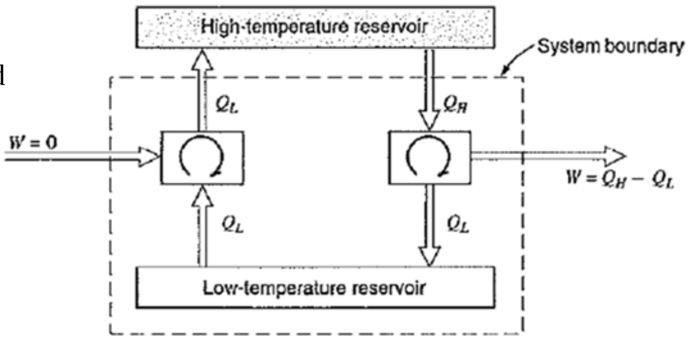
# Equivalence of the Two Statements

- The device at the left is a refrigerator that requires no work and thus violates the Clausius statement.
- Let an amount of heat $Q_L$ be transferred from the low temperature reservoir to this refrigerator, and let the same amount of heat $Q_L$ be transferred to the high-temperature reservoir.
- Let an amount of heat $Q_H$ that is greater than $Q_L$ be transferred from the high-temperature reservoir to the heat engine, and
- let the engine reject the amount of heat $Q_L$ as it does an amount of work $W$, which equals $Q_H - Q_L$




- Because there is no net heat transfer to the low-temperature reservoir, the low-temperature reservoir, along with the heat engine and the refrigerator, can be considered together as a device that operates in a cycle and produces no effect other than work and the exchange of heat with a single reservoir.
- Thus, a violation of the Clausius statement implies a violation of the Kelvin-Planck statement.



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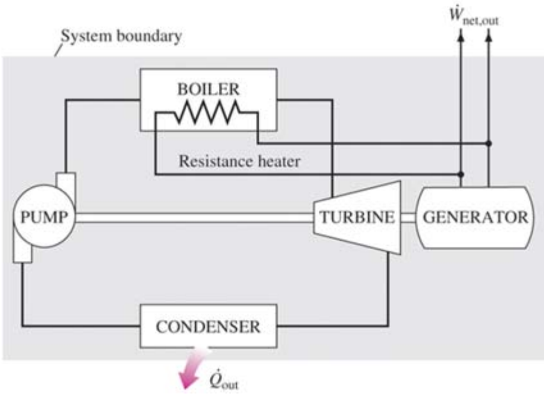
# Perpetual-Motion Machines



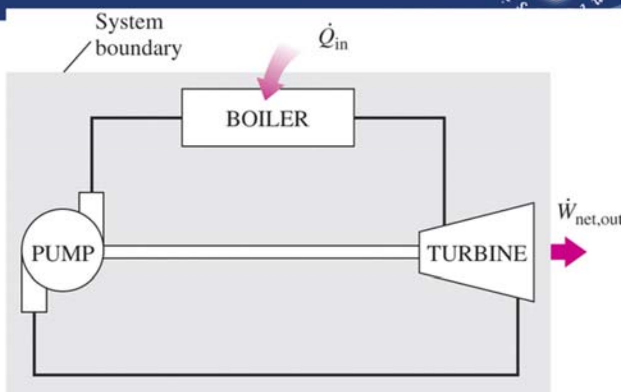

A perpetual-motion machine that violates the first law (PMM1).

- **Perpetual-motion machine:** Any device that violates the first or the second law.
- A device that violates the first law (by creating work from nothing or create mass or energy) is called a PMM1.




# Perpetual-Motion Machines


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

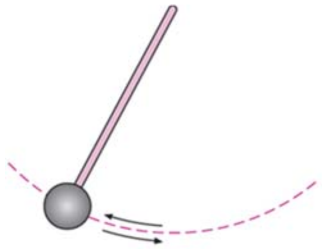



A perpetual-motion machine that violates the second law of thermodynamics (PMM2).

- A perpetual-motion machine of the third kind would have no friction, and thus would run indefinitely but produce no work.
- Despite numerous attempts, no perpetual-motion machine is known to have worked. ***If something sounds too good to be true, it probably is.***

# Reversible and Irreversible processes

- **Reversible process:** *A process that can be reversed without leaving any trace on the surroundings.*
- Both the system *and* the surroundings are returned to their initial states at the end of the reverse process
- This is possible only if the net heat *and* net work exchange between the system and the surroundings is zero for the combined (original and reverse) process
- Reversible processes, do not occur in nature, are merely *idealizations* of actual processes.



(*a*) Frictionless pendulum

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

- Reversible processes deliver the most and consume the least work.



# Reversible and Irreversible processes

- **Irreversible process:** A process that is not reversible, i.e. these processes cannot reverse themselves spontaneously and restore the system to its initial state
- 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.
- 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.

# Reversible and Irreversible processes

## Irreversibilities

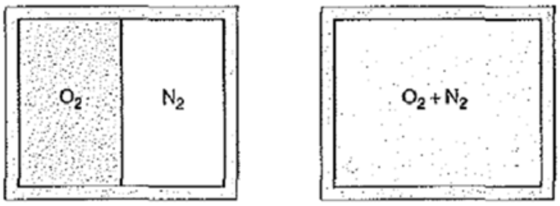

i. Friction renders a process irreversible.

ii. Irreversible compression and expansion processes.

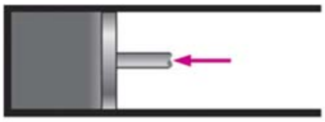
iii. (*a*) Heat transfer through a temperature difference is irreversible, and (*b*) the reverse process is impossible.


(*a*) An irreversible heat transfer process

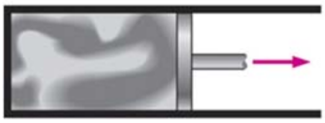

(*b*) An impossible heat transfer process



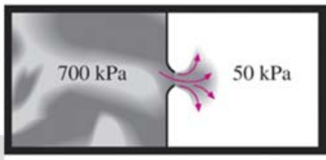

iv. Mixing of Two Different Substances



(*a*) Fast compression



(*b*) Fast expansion

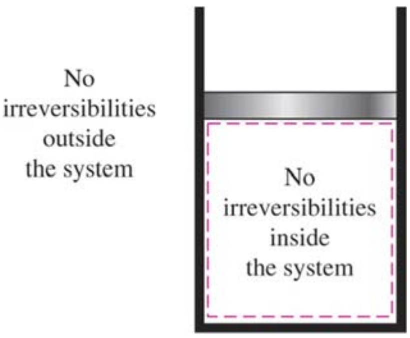



(*c*) Unrestrained expansion

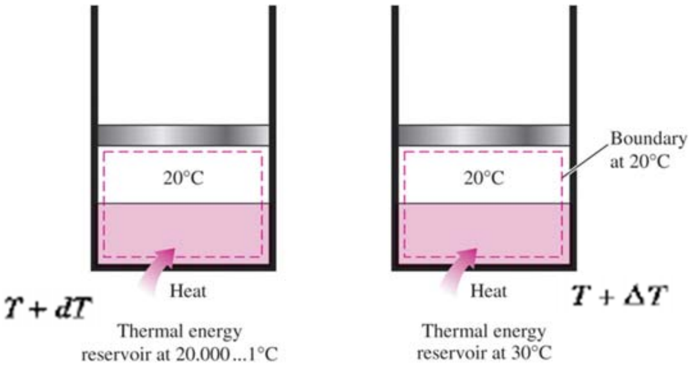


# Internally and Externally Reversible Processes

- **Internally reversible process:** If no irreversibilities occur within the boundaries of the system during the process.
- **Externally reversible:** If no irreversibilities occur outside the system boundaries.
- **Totally reversible process:** It involves no irreversibilities within the system or its surroundings.
- A totally reversible process involves no heat transfer through a finite temperature difference, no nonquasi-equilibrium changes, and no friction or other dissipative effects.




A reversible process involves no internal and external irreversibilities.



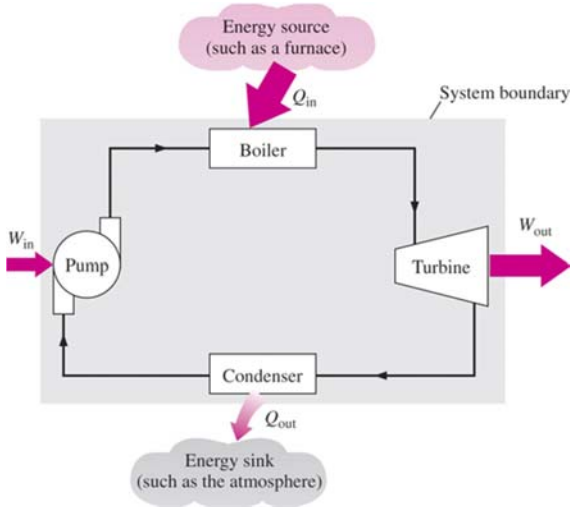

(*a*) Totally reversible (*b*) Internally reversible

Totally and internally reversible heat transfer processes.

# The Carnot Cycle

- The efficiency of a heat-engine cycle greatly depends on how the individual processes that make up the cycle are executed, reversible or irreversible

- Work is done by the working fluid during one part of the cycle and on the working fluid during another part.
- The difference between these two is the net work delivered by the heat engine.
- The net work, thus the cycle efficiency, can be maximized by using processes that require the least amount of work and deliver the most, that is, by **using reversible processes.**



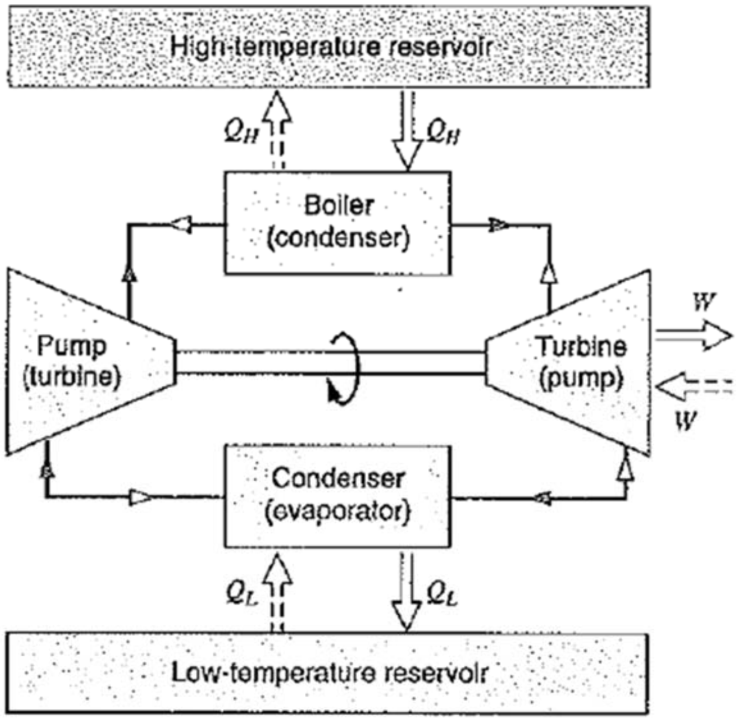

$$\eta_{th} = \frac{W_{net,out}}{Q_H}$$

- The best known reversible cycle is the **Carnot cycle**

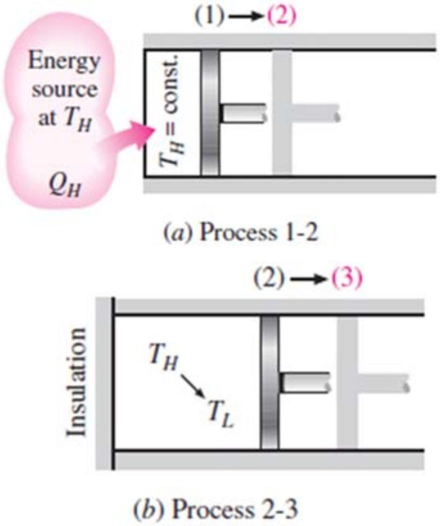


# The Carnot Cycle

- A heat engine, which operates between the given high temperature and low-temperature reservoirs, does so in a cycle in which every process is reversible.
- If every process is reversible, the cycle is also reversible; and if the cycle is reversed, the heat engine becomes a refrigerator **or heat pump cycle, with maximum coefficient of performance.**
- A heat engine operating in a completely reversible manner is called a ***Carnot engine***

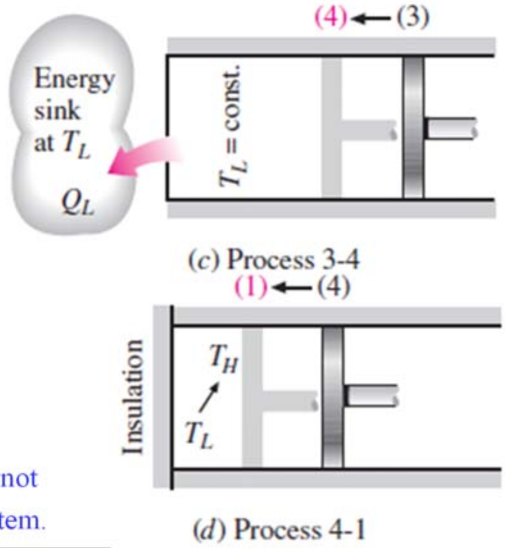


# The Carnot Cycle




Work is done on the surroundings, **T= $T_H$-dT, $Q_H$ transfer to keep T = $T_H$**

Work is done on the surroundings, **Q = 0.0**




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 $T_H$)



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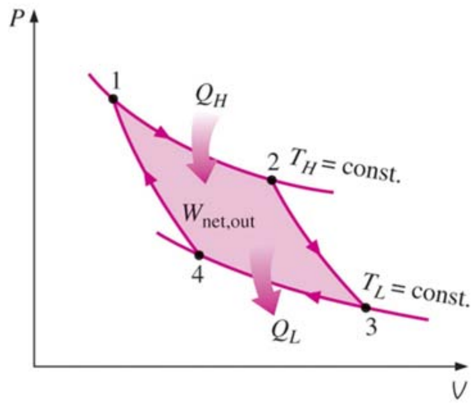
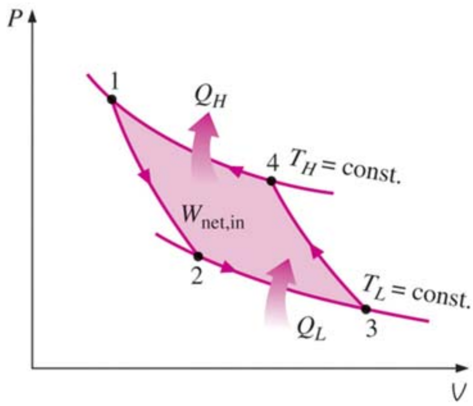
# The Carnot Cycle




*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**.



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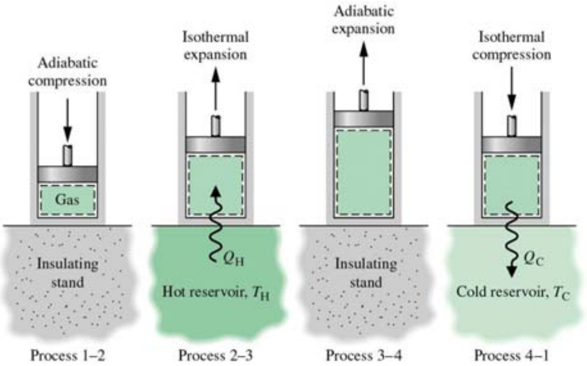
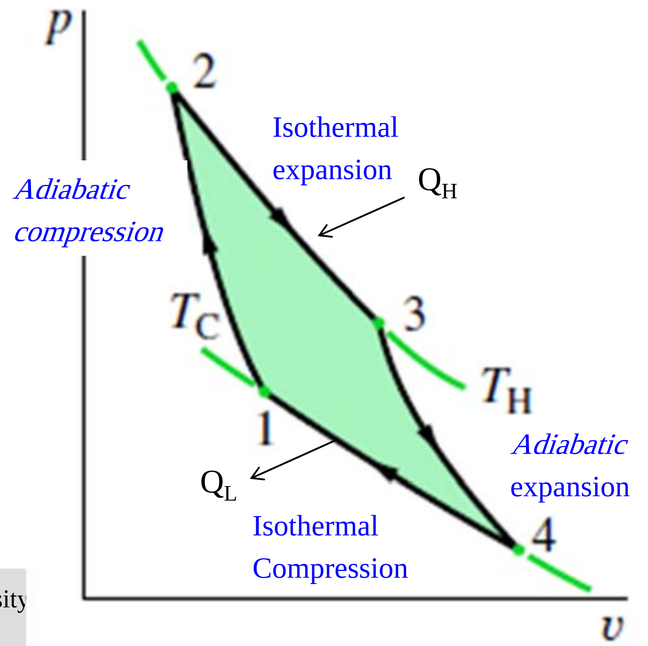
# The Carnot Cycle

Reversible power cycle: Two adiabatic processes alternated with two isothermal processes

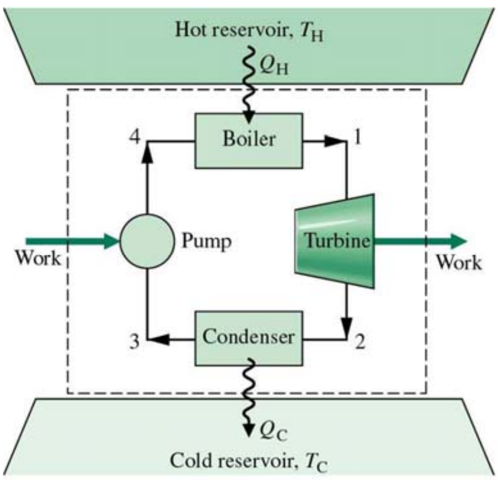


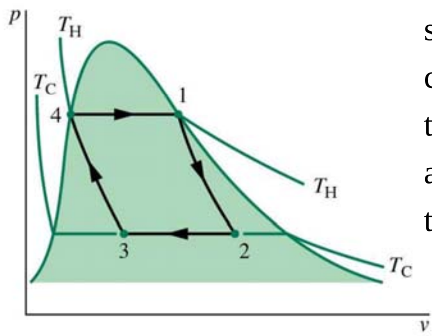

- The Carnot cycle is not limited to processes of a closed system taking place in a piston–cylinder assembly



# The Carnot Cycle




**1-2:** Adiabatic expansion through the turbine and work is developed, temperature decreases to $T_C$, and there is an accompanying decrease in pressure.



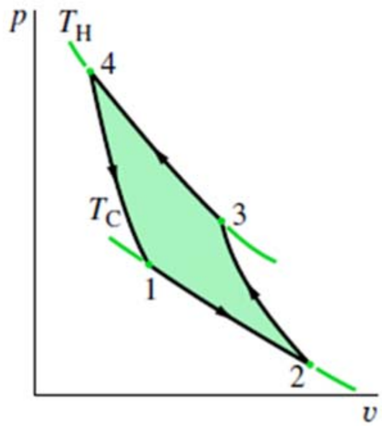

**2-3:** $Q_C$ transfer occurs, some of the vapor condenses at constant temperature $T_C$, pressure also remains constant, two phase liquid–vapor

**4-1:** A *change of phase* from liquid to vapor at constant temperature $T_H$ occurs, $Q_H$ transfer, pressure also remains constant during the phase change

**3-4:** Adiabatic compression to the state of boiler entrance, a work input is required to increase the pressure, the temperature increases from $T_C$ to $T_H$.

# The Carnot Refrigeration Cycle.

- If a Carnot power cycle is operated in the opposite direction,
  - The magnitudes of all energy transfers remain the same but the energy transfers are oppositely directed.
  - Such a cycle may be regarded as a reversible refrigeration or heat pump cycle




***Process 1–2:*** The gas expands *isothermally* at $T_C$ while *receiving* energy $Q_C$ from the cold reservoir by heat transfer.

***Process 2–3:*** The gas is compressed *adiabatically* until its temperature is $T_H$.

***Process 3–4:*** The gas is compressed *isothermally* at $T_H$ while it *discharges* energy $Q_H$ to the hot reservoir by heat transfer.

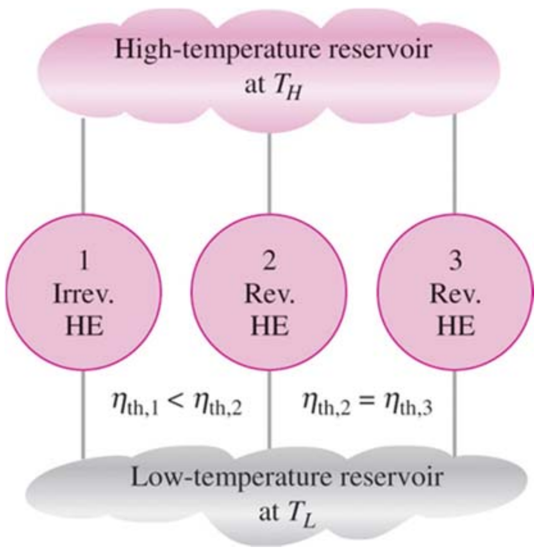
***Process 4–1:*** The gas expands *adiabatically* until its temperature decreases to $T_C$.





# The Carnot Principles

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.

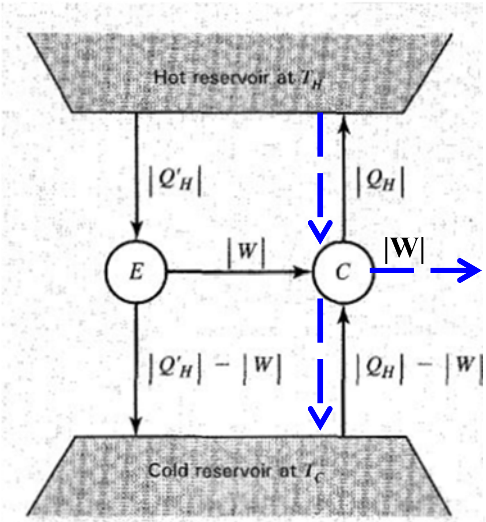
# The Carnot Principles

For two given heat reservoirs no engine can have a thermal efficiency higher than that of a Carnot engine (reversible engine).

- Statement 2 of the second law is the basis for *Carnot's theorem*

- Assume the existence of an engine E with a thermal efficiency *greater than* that of a Carnot engine.
- Carnot engine absorbs heat $|Q_H|$ from the hot reservoir, produces work |W|, and discards heat $|Q_H|$ - |W| to the cold reservoir.
- Engine E absorbs heat $|Q''_H|$ from the same hot reservoir, produces the same work |W|, and discards heat $|Q''_H|$ - |W| to the same cold reservoir.
- If engine E has the greater efficiency,

$$\frac{|W|}{|Q'_H|} > \frac{|W|}{|Q_H|} \qquad \text{and} \qquad |Q_H| > |Q'_H|$$



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# The Carnot Principles

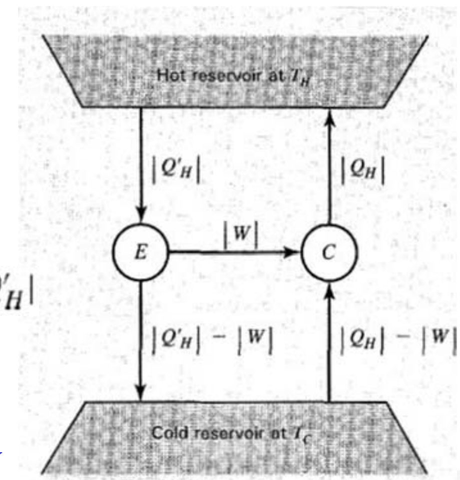
- Since a Carnot engine is reversible, it may be operated in reverse; the Carnot cycle is then traversed in the opposite direction, and it becomes a reversible refrigeration cycle for which the quantities $|Q_H|$, $|Q_L|$ and |W| are the same as for the engine cycle but are reversed in direction.
- Let engine E drive the Carnot engine backward as a Carnot refrigerator,
- For the engine-refrigerator combination, the net heat extracted from the cold reservoir is:

$$|Q_H| - |W| - (|Q'_H| - |W|) = |Q_H| - |Q'_H|$$

The net heat delivered to the hot reservoir is also $|Q_H| - |Q'_H|$

Transfer of heat from temperature $T_c$ to the higher temperature $T_H$

Violation of statement 2 (the Clausius statement) of the 2nd law



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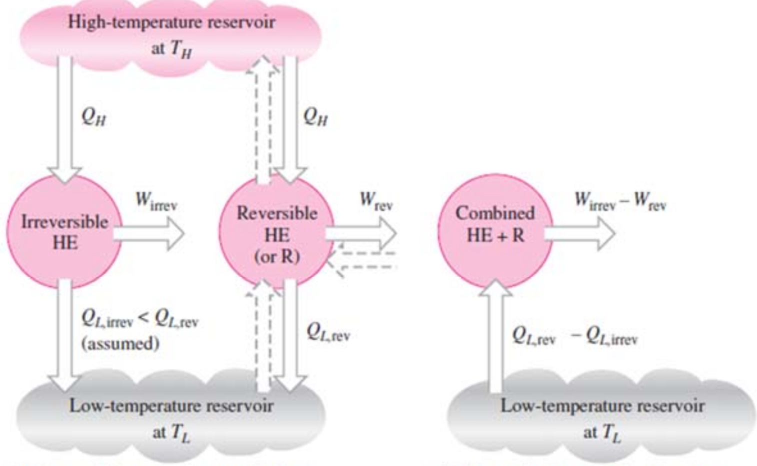
# The Carnot Principles

Proof of the first Carnot principle.

- One engine is reversible and the other is irreversible.
- Each engine is supplied with the same amount of heat $Q_H$.
- The amount of work produced by the reversible heat engine is $W_{rev}$, and the amount produced by the irreversible one is $W_{irrev}$.
- Assume that the irreversible heat engine is more efficient than the reversible one




(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

$$\eta_{th,irrev} > \eta_{th,rev}$$ delivers more work than the reversible one





# The Carnot Principles

- Let the reversible heat engine be reversed and operate as a refrigerator.
- This refrigerator will receive a work input of $W_{rev}$ and reject heat to the high-temperature reservoir.
- Since the refrigerator is rejecting heat in the amount of $Q_H$ to the high temperature reservoir and the irreversible heat engine is receiving the same amount of heat from this reservoir, the net heat exchange for this reservoir is zero.
- Considering the refrigerator and the irreversible engine together, we have an engine that produces a net work in the amount of $W_{irrev}$ - $W_{rev}$ while exchanging heat with a single reservoir—a **violation of the Kelvin–Planck statement of the second law**

$$\eta_{th,irrev} > \eta_{th,rev} \text{ is incorrect.}$$



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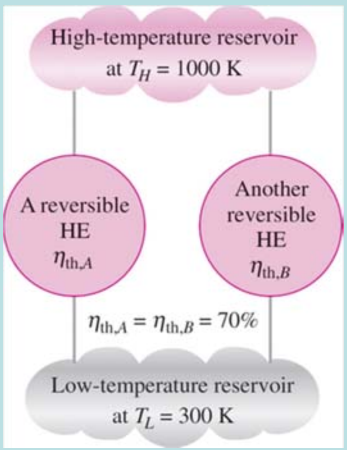
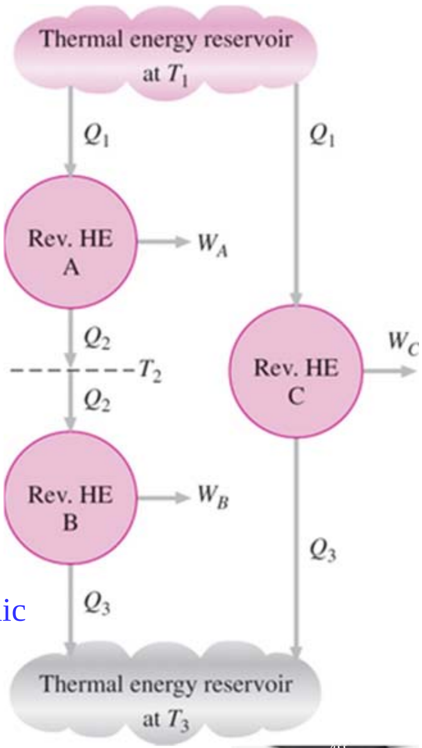
# The Thermodynamic Temperature Scale




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

- A temperature scale that is independent of the properties of the substances that are used to measure temperature is called a **thermodynamic temperature scale**.
- Such a temperature scale offers great conveniences in thermodynamic calculations.




The arrangement of heat engines used to develop the thermodynamic temperature scale.



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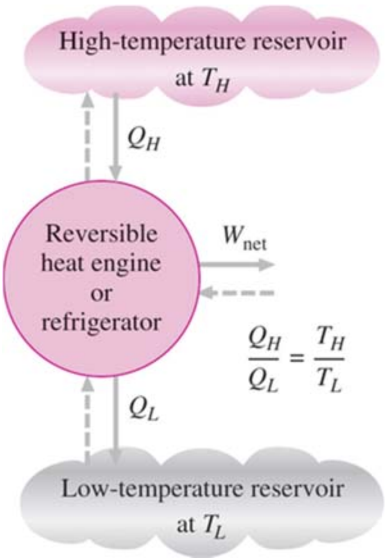
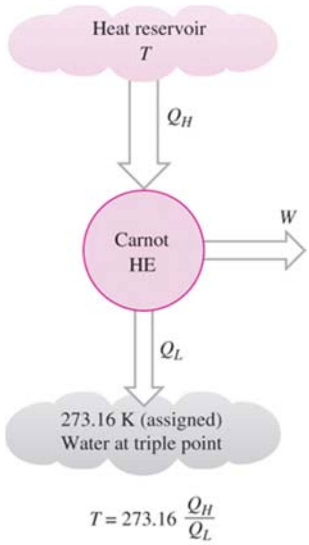
# The Thermodynamic Temperature Scale




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




- A conceptual experimental setup to determine thermodynamic temperatures on the Kelvin scale by measuring heat transfers $Q_H$ and $Q_L$.

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

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

$$T(°C) = T(K) - 273.15$$



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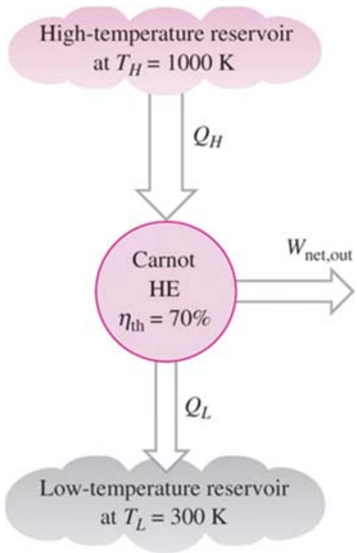
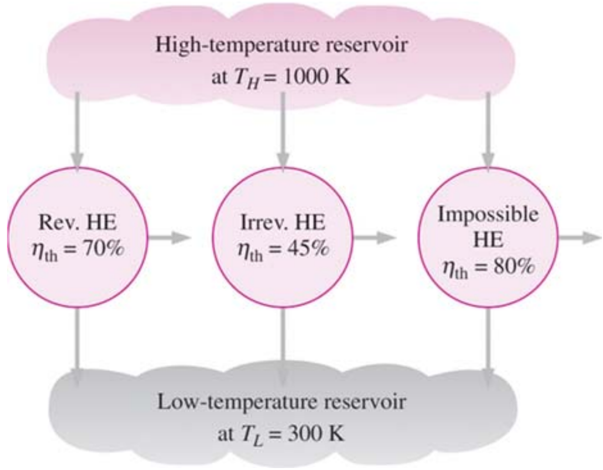
# The Carnot Heat Engine




The Carnot heat engine is the most efficient of all heat engines operating between the same high- and low-temperature reservoirs.




No heat engine can have a higher efficiency than a reversible heat engine operating between the same high- and low-temperature reservoirs.



# The Carnot Heat Engine

Any heat engine

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

Carnot heat engine

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

$T_L$ and $T_H$ are *absolute temperatures*.

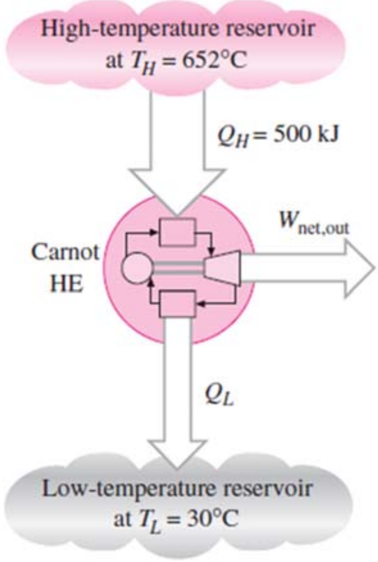
- The thermal efficiencies of actual and reversible heat engines operating between the same temperature limits compare as follows

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

- The thermal efficiency of actual heat engines can be maximized by supplying heat to the engine at the highest possible temperature (limited by material strength) and rejecting heat from the engine at the lowest possible temperature (limited by the temperature of the cooling medium such as rivers, lakes, or the atmosphere).

# Example

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 (*a*) the thermal efficiency of this Carnot engine and (*b*) the amount of heat rejected to the sink per cycle.



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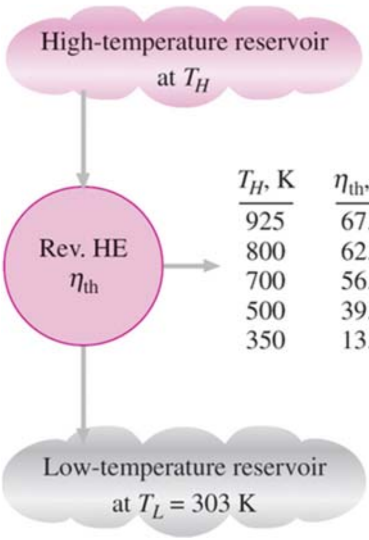
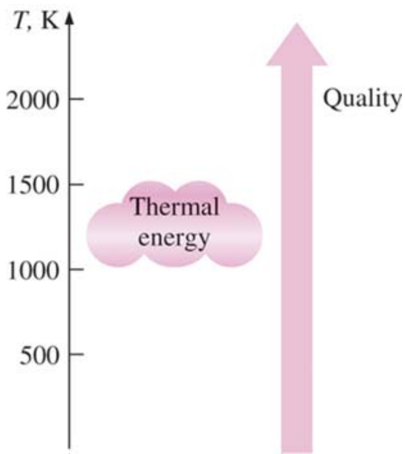
# The Quality (work potential of energy) of Energy




The variation of the thermal efficiency with the source temperature when the sink temperature is held constant

| $T_H$, K | $\eta_{th}$, % |
|---|---|
| 925 | 67.2 |
| 800 | 62.1 |
| 700 | 56.7 |
| 500 | 39.4 |
| 350 | 13.4 |

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




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

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

How do you increase the thermal efficiency of a Carnot heat engine? How about for actual heat engines? as $T_H$ is increased, or as $T_L$ is decreased.



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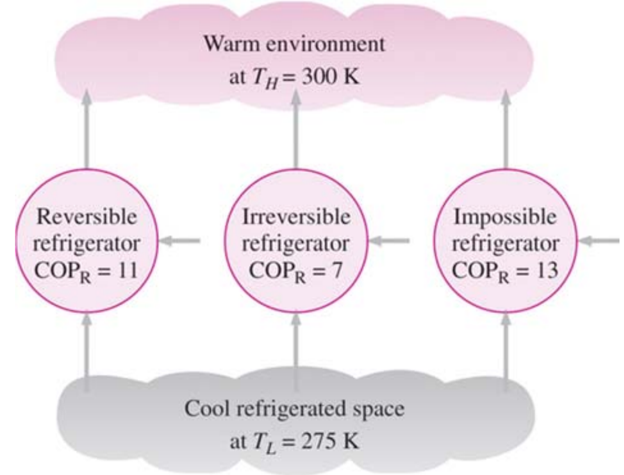
# The Carnot Refrigerator and Heat Pump




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

- All actual refrigerators or heat pumps operating between these temperature limits ($T_L$ and $T_H$) have lower coefficients of performance

- Any refrigerator or heat pump

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

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

- Carnot refrigerator or heat pump

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

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

- These are the highest coefficients of performance that a refrigerator or a heat pump operating between the temperature limits of $T_L$ and $T_H$ can have.



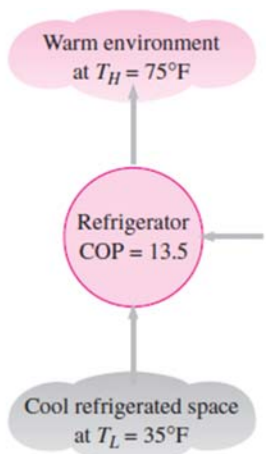
# The Carnot Refrigerator and Heat Pump

- The coefficients of performance of actual and reversible refrigerators operating between the same temperature limits can be compared as follows:

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

## Example

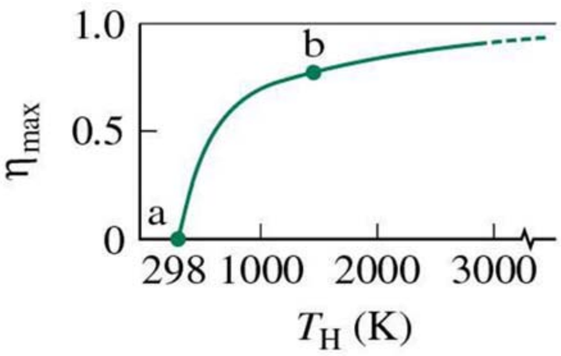
An inventor claims to have developed a refrigerator that maintains the refrigerated space at 35°F while operating in a room where the temperature is 75°F and that has a COP of 13.5. Is this claim reasonable?



## Maximum Performance

### Heat Engines

$$\eta_{\max} = 1 - \frac{T_C}{T_H}$$




### Refrigerators & Heat Pumps

$$\beta_{\max} = \frac{T_C}{T_H - T_C}$$

$$\gamma_{\max} = \frac{T_H}{T_H - T_C}$$

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

$$\beta_{\text{real}} = \frac{Q_L}{Q_H - Q_L} \le \frac{T_L}{T_H - T_L}$$

$$\gamma_{\text{real}} = \frac{Q_H}{Q_H - Q_L} \le \frac{T_H}{T_H - T_L}$$



## Ideal-Gas Temperature Scale; Carnot's Equations

- The cycle traversed by an ideal gas serving as the working fluid in a Carnot engine

It consists of four *reversible* steps:

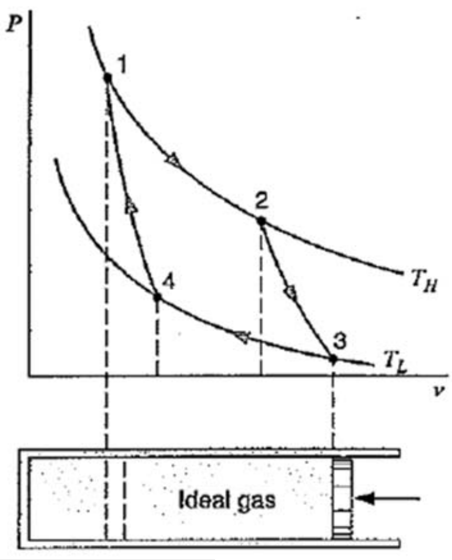
- 4 to 1: Adiabatic compression until the temperature rises from $T_C$ to $T_H$.
- 1 to 2: Isothermal expansion to arbitrary point $c$ with absorption of heat $|Q_H|$.
- 2 to 3: Adiabatic expansion until the temperature decreases to $T_C$.
- 3 to 4: Isothermal compression to the initial state with rejection of heat $|Q_C|$.

- Remember that

$$\delta w = P\,dv \qquad Pv = RT \qquad du = C_{v0}\,dT$$

$$\delta q = du + \delta w$$

$$\Rightarrow \quad \delta q = C_{v0}\,dT + \frac{RT}{v}\,dv$$



# Ideal-Gas Temperature Scale; Carnot's Equations

For the isothermal heat addition process 1-2,

$$q_H = {}_1q_2 = 0 + RT_H \ln\frac{v_2}{v_1} \qquad \text{I}$$

For the adiabatic expansion process 2-3,

$$0 = \int_{T_H}^{T_L} \frac{C_{v0}}{T}\,dT + R\ln\frac{v_3}{v_2} \qquad \text{II}$$

For the isothermal heat rejection process 3-4,

$$q_L = -{}_3q_4 = -0 - RT_L\ln\frac{v_4}{v_3} = +RT_L\ln\frac{v_3}{v_4} \qquad \text{III}$$

For the adiabatic compression process 4-1

$$0 = \int_{T_L}^{T_H} \frac{C_{v0}}{T}\,dT + R\ln\frac{v_1}{v_4} \qquad \text{IV}$$



# Ideal-Gas Temperature Scale; Carnot's Equations

From II and IV

$$\int_{T_L}^{T_H} \frac{C_{v0}}{T}\,dT = R\ln\frac{v_3}{v_2} = -R\ln\frac{v_1}{v_4}$$

$$\frac{v_3}{v_2} = \frac{v_4}{v_1}, \quad \text{or} \quad \frac{v_3}{v_4} = \frac{v_2}{v_1} \qquad \text{V}$$

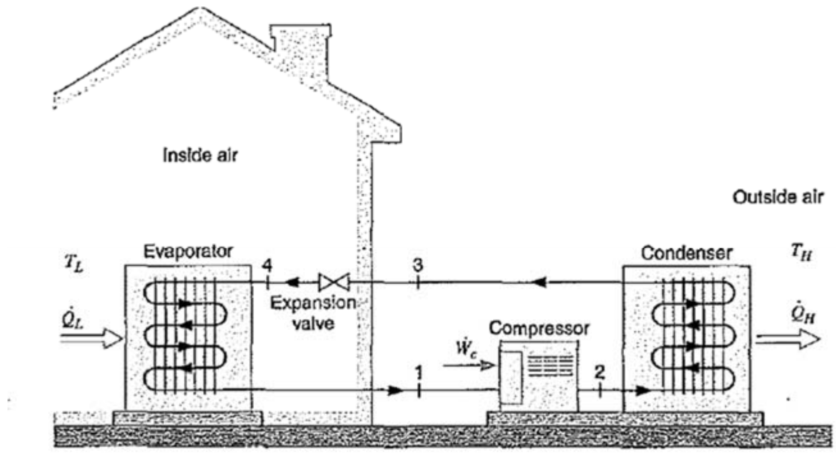
From I , III and IV

$$\frac{q_H}{q_L} = \frac{RT_H\ln\frac{v_2}{v_1}}{RT_L\ln\frac{v_3}{v_4}} = \frac{T_H}{T_L}$$

$$\eta \equiv \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H}$$

# Example

As one mode of operation of an air conditioner is the cooling of a room on a hot day, it works as a refrigerator. A total of 4 kW should be removed from a room at 24°C to the outside atmosphere at 35°C. What is the magnitude of the required work assuming it is a Carnot-cycle refrigerator.



An air conditioner in cooling mode