Chapter 6

THE SECOND LAW OF THERMODYNAMICS

Thermodynamics: An Engineering Approach

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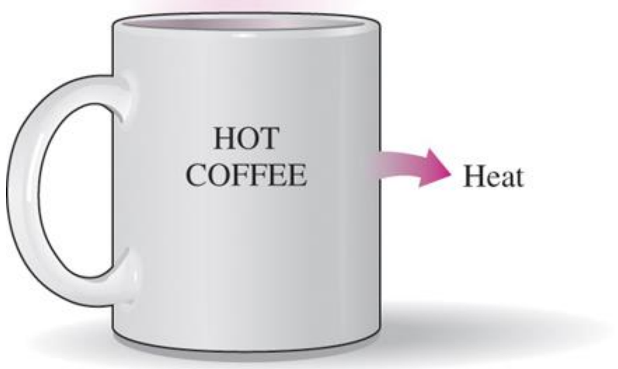
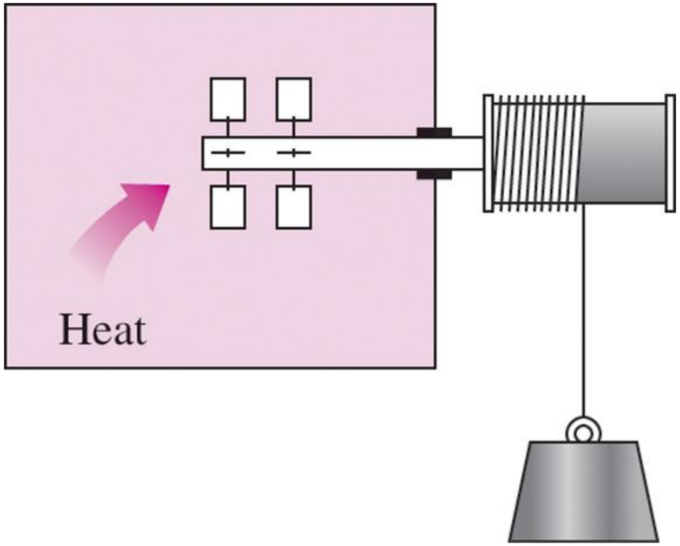
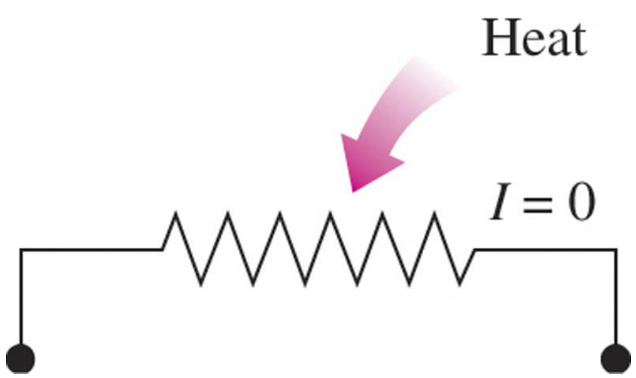
INTRODUCTION TO THE SECOND LAW

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





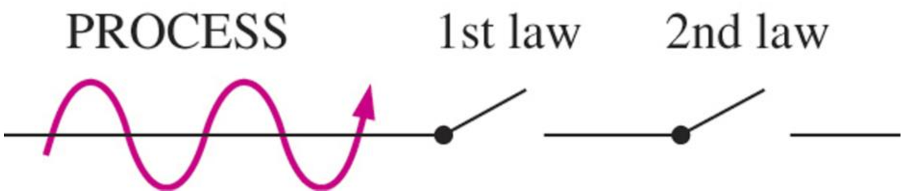
Transferring heat to a paddle wheel will not cause it to rotate.



Transferring heat to a wire will not generate electricity.

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

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

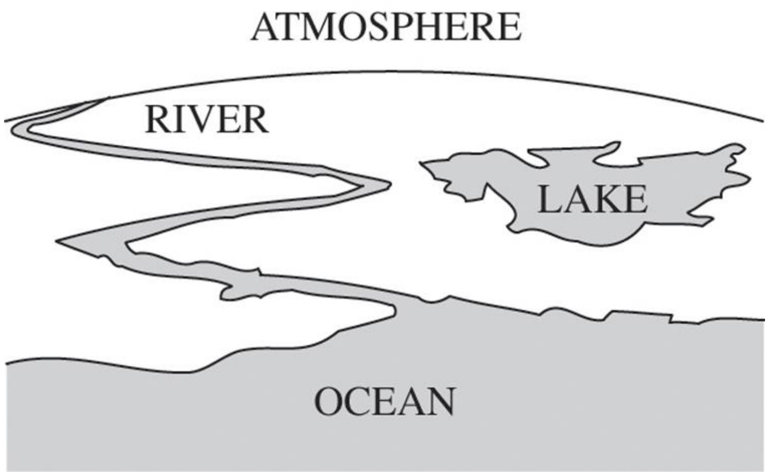


A process must satisfy both the first and second laws of thermodynamics to proceed.

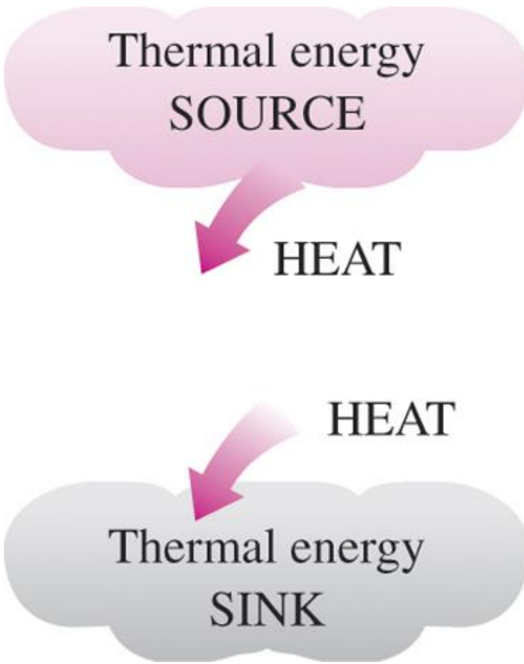
MAJOR USES OF THE SECOND LAW

1) The second law may be used to identify the **direction** of processes.
2) The second law also asserts that energy has **quality** as well as **quantity**.
    1) 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.
    2) 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



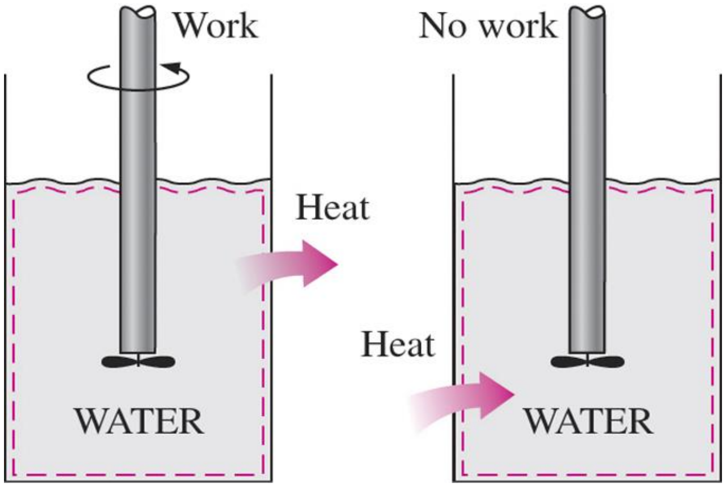
Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.

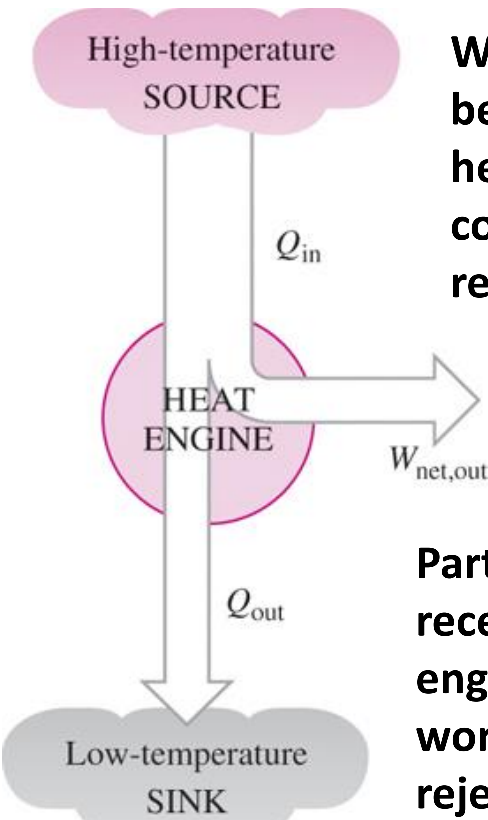


A source supplies energy in the form of heat, and a sink absorbs it.

- 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.
- Large bodies of water (**oceans, lakes, and rivers, atmospheric air** can be modeled accurately as **thermal energy reservoirs** because of their large thermal energy storage capabilities or thermal masses.

HEAT ENGINES





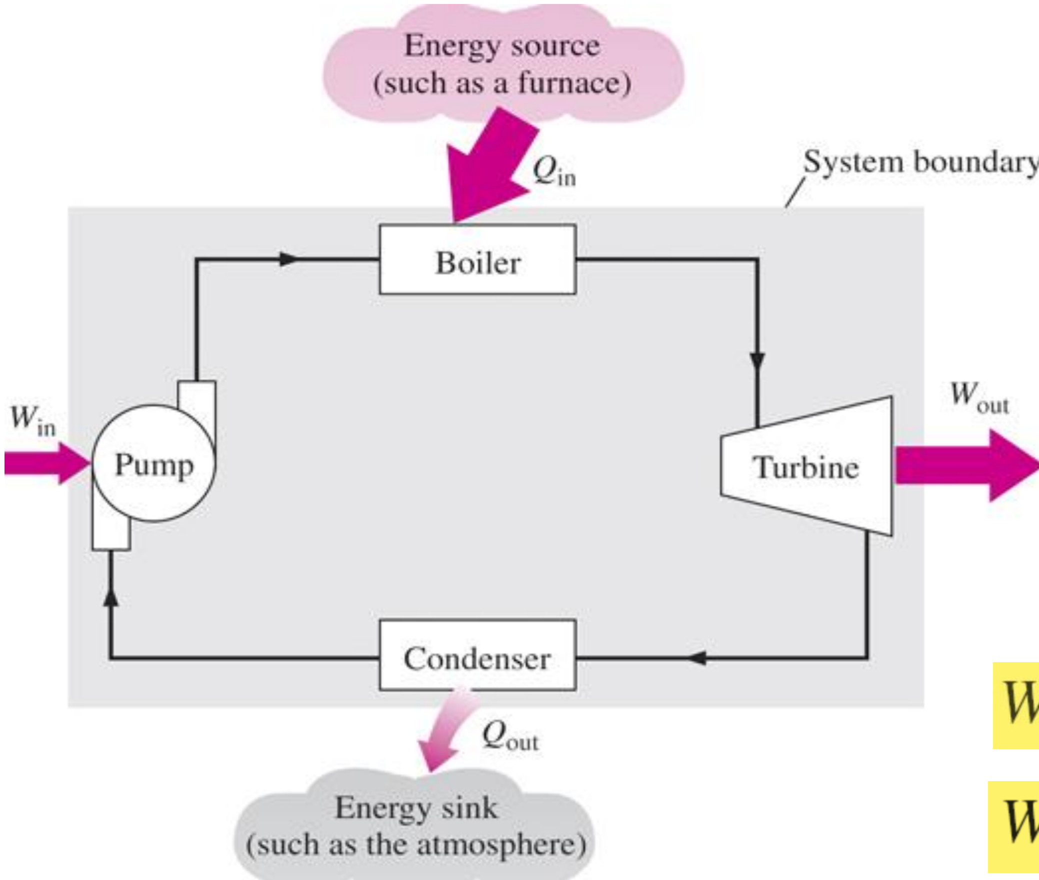
Work can always be converted to heat directly and completely, but the reverse is not true.

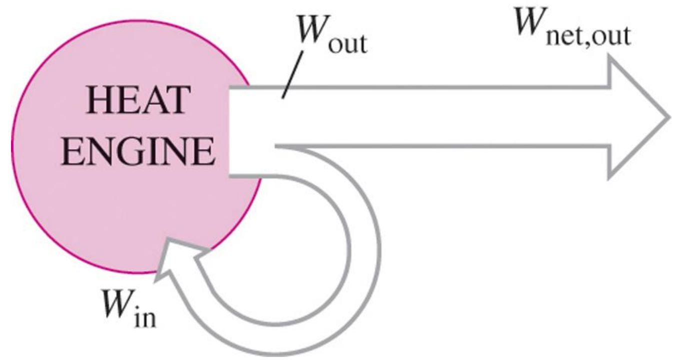
Part of the heat received by a heat engine is converted to work, while the rest is rejected to a sink.

Devices that convert heat to work:

1) They receive heat from a high-temperature source (solar energy, oil furnace, nuclear reactor, etc.).
2) They convert part of this heat to work (usually in the form of a rotating shaft.)
3) They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).
4) **They operate on a cycle**.
5) Heat engines and other cyclic devices usually involve a fluid to and from which heat is transferred while undergoing a cycle. This fluid is called the *working fluid.*

A steam power plant





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

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

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

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

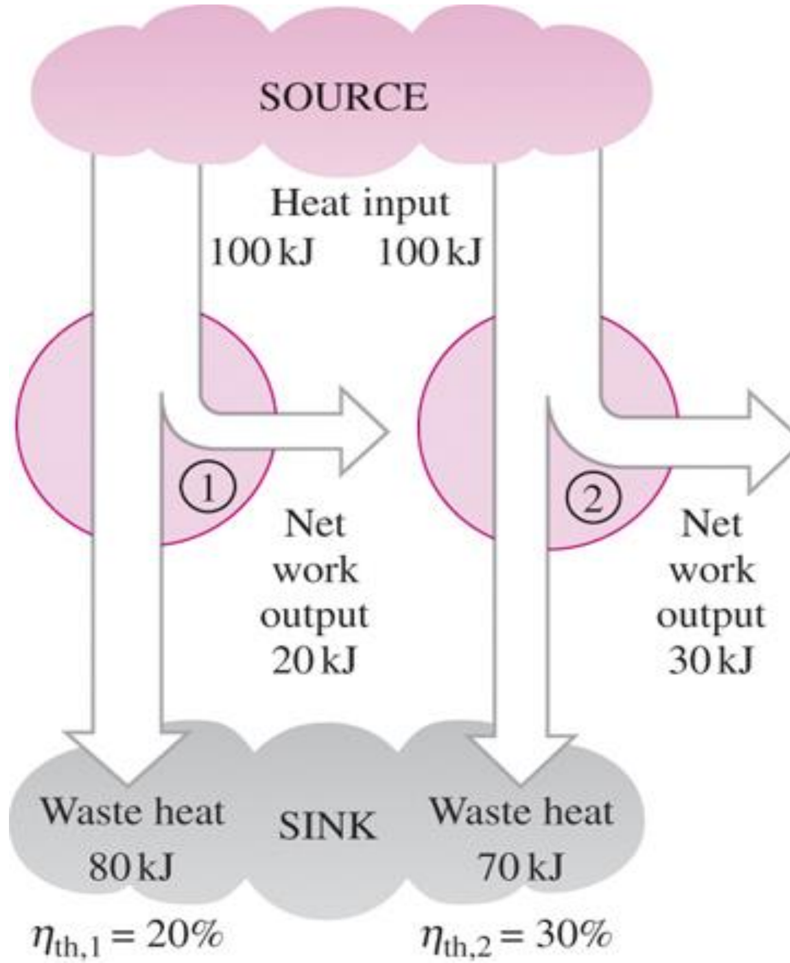
Thermal efficiency

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

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

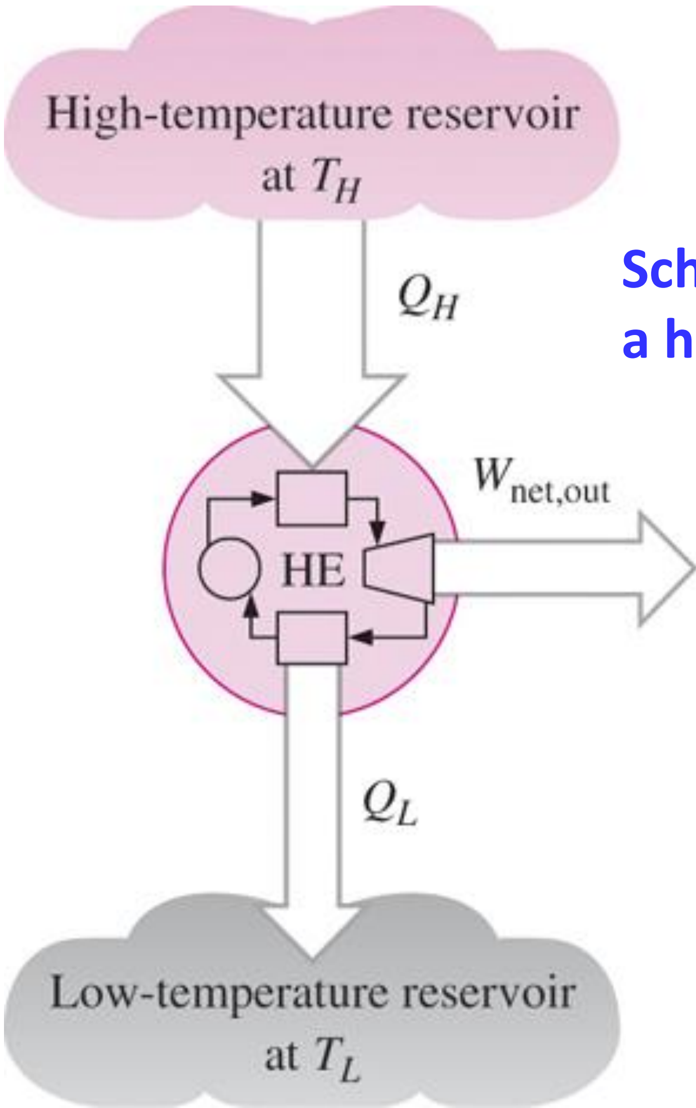
$$\eta_{th} = \frac{W_{net,out}}{Q_{in}}$$

$$\eta_{th} = 1 - \frac{Q_{out}}{Q_{in}}$$

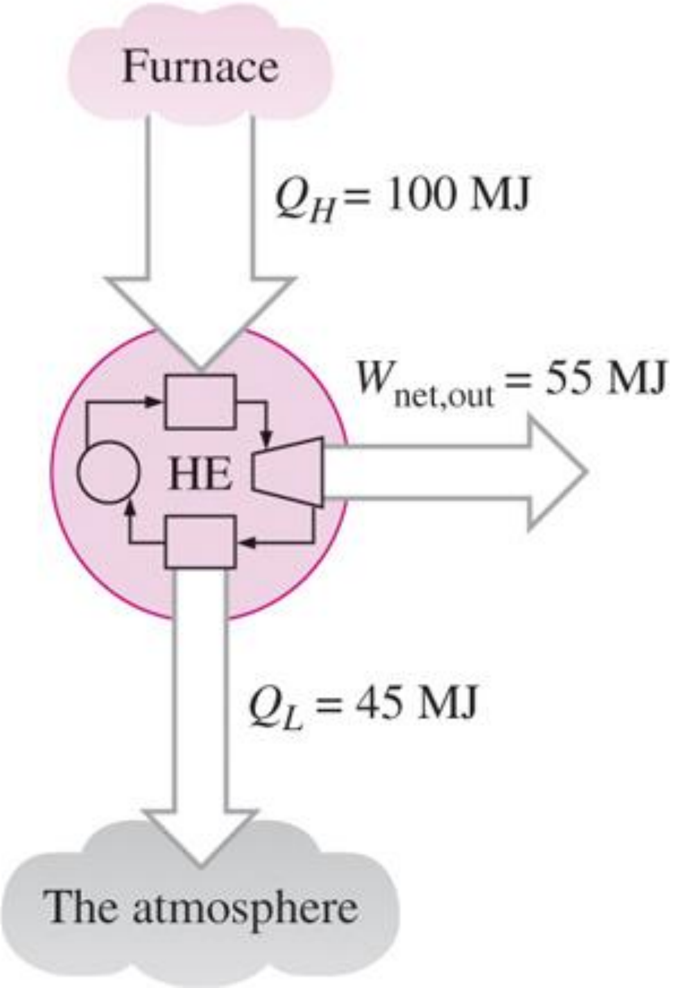


$$W_{net,out} = Q_{in} - Q_{out}$$

Thermal efficiency

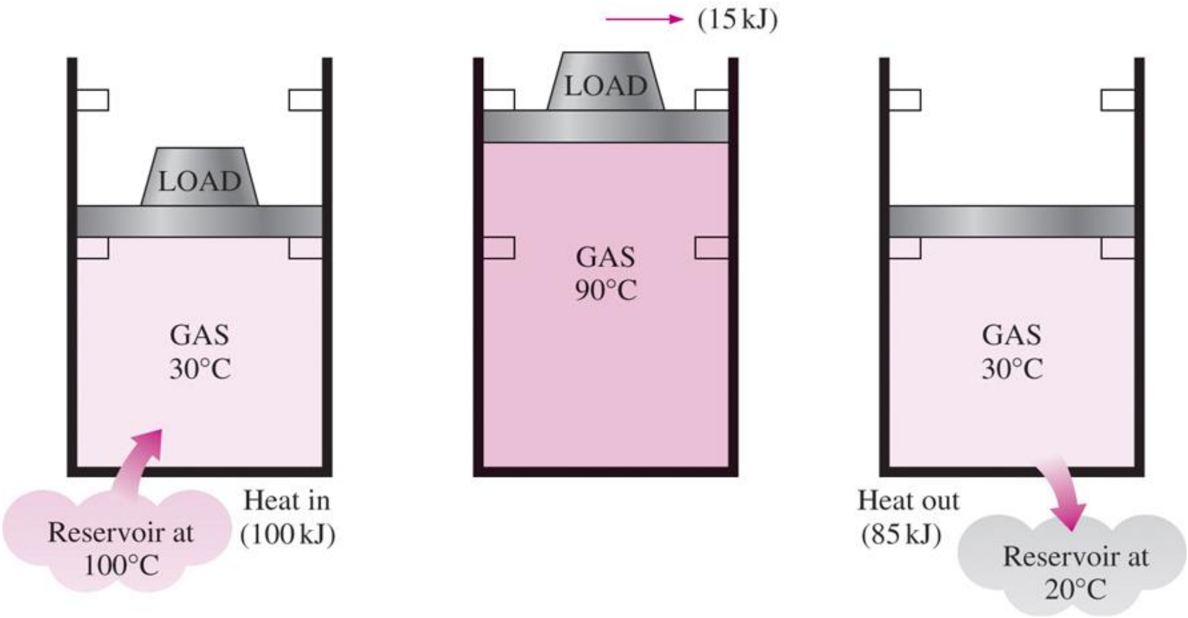


Schematic of a heat engine



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

Can we save Q_{out}?



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

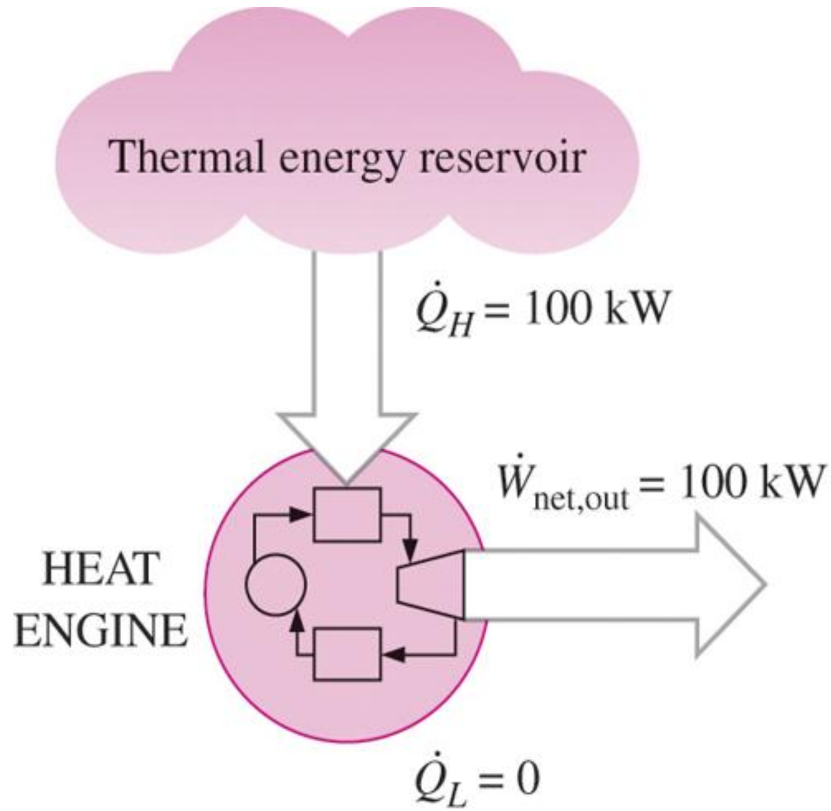
- ❑ Every heat engine *must waste some energy* by transferring it to a low-temperature reservoir in order *to complete the cycle*, even under idealized conditions.

- ❑ 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 NO.
- ❑ The reason is that without a heat rejection process in a condenser, *the cycle cannot be completed.*

Second Law of Thermodynamics: Kelvin–Planck Statement

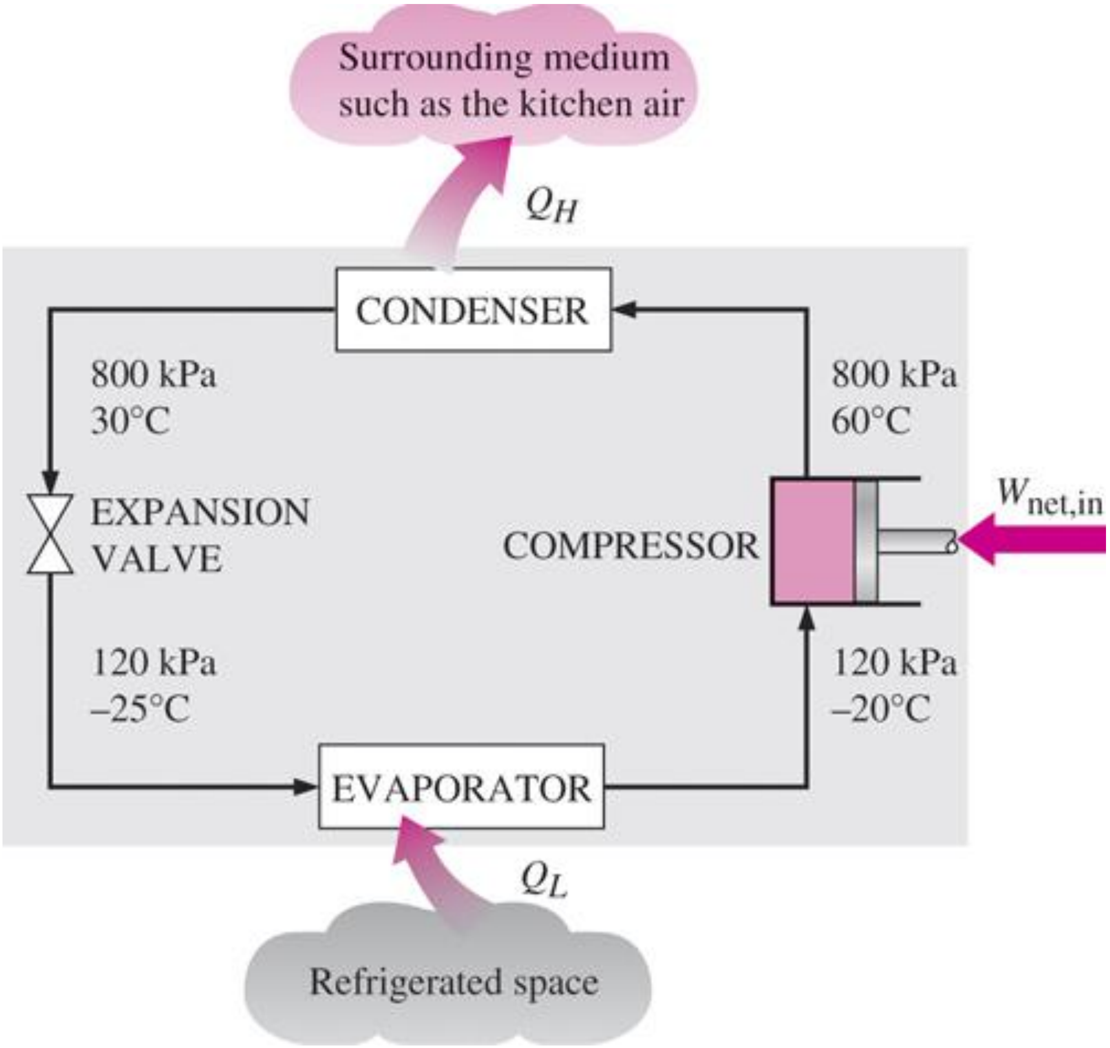
- **It is <u>impossible</u> for any device that operates on a <u>cycle</u> to receive heat from a single reservoir and produce a net amount of work.**

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



A heat engine that <u>violates</u> the Kelvin–Planck statement of the second law.

REFRIGERATORS AND HEAT PUMPS

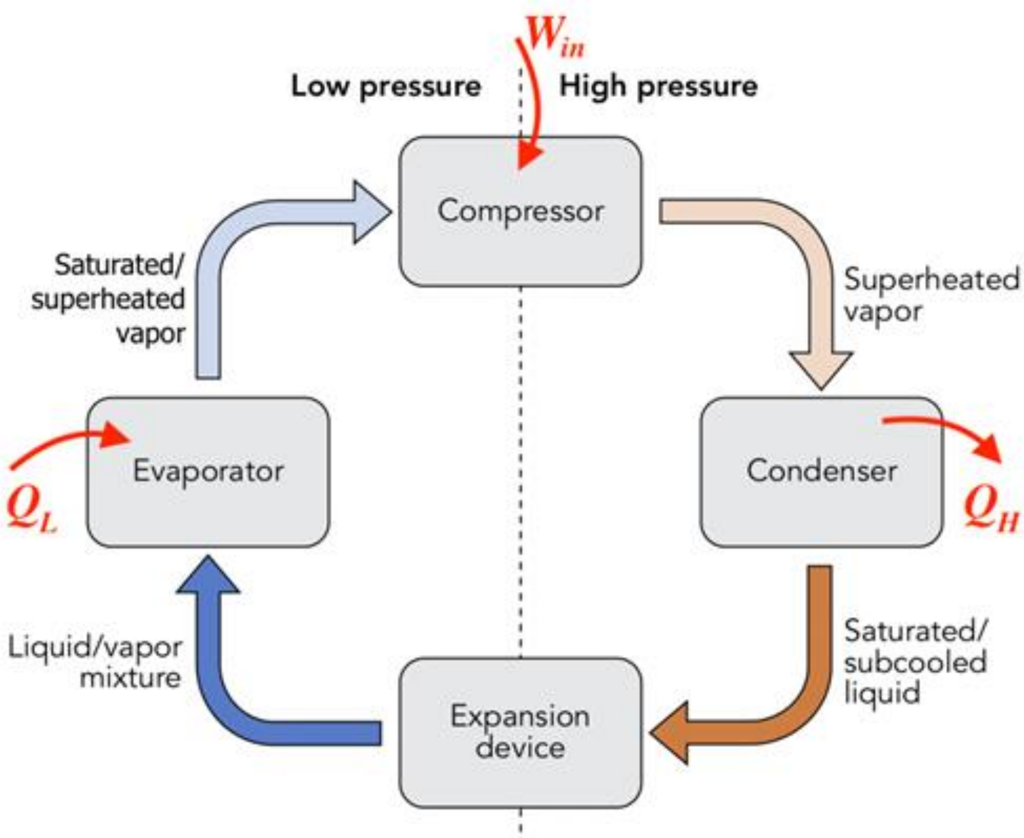


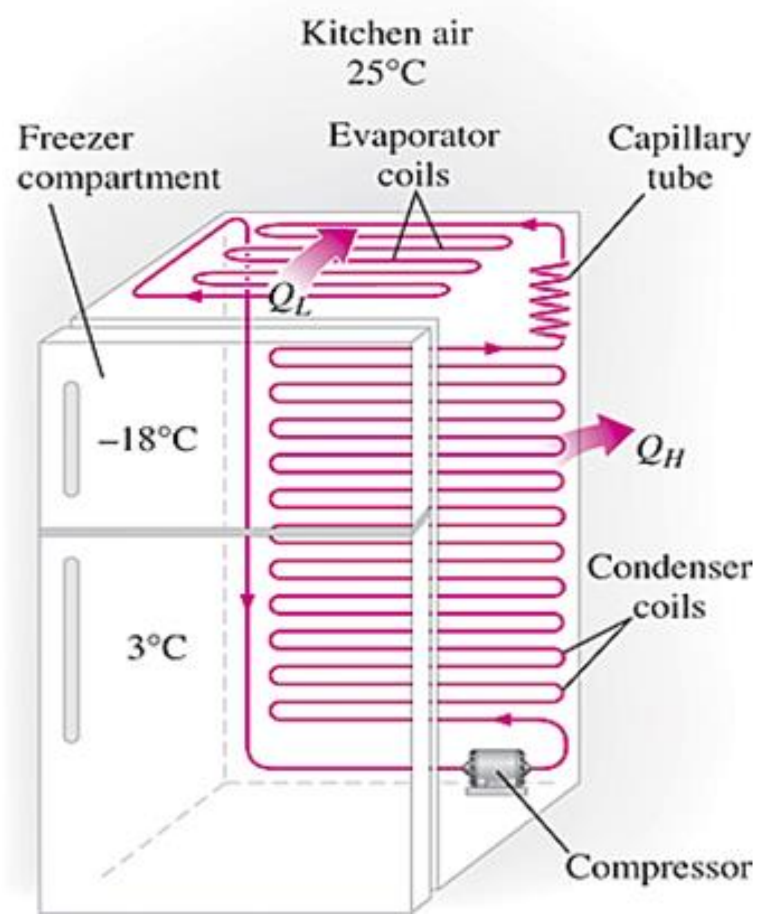
1) The transfer of heat from a low-temperature medium to a high-temperature one requires special devices called refrigerators.
2) Refrigerators, like heat engines, are cyclic devices.
3) The working fluid used in the refrigeration cycle is called a refrigerant.
4) The most frequently used refrigeration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

Basic components of a refrigeration system and typical operating conditions.

REFRIGERATORS AND HEAT PUMPS

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





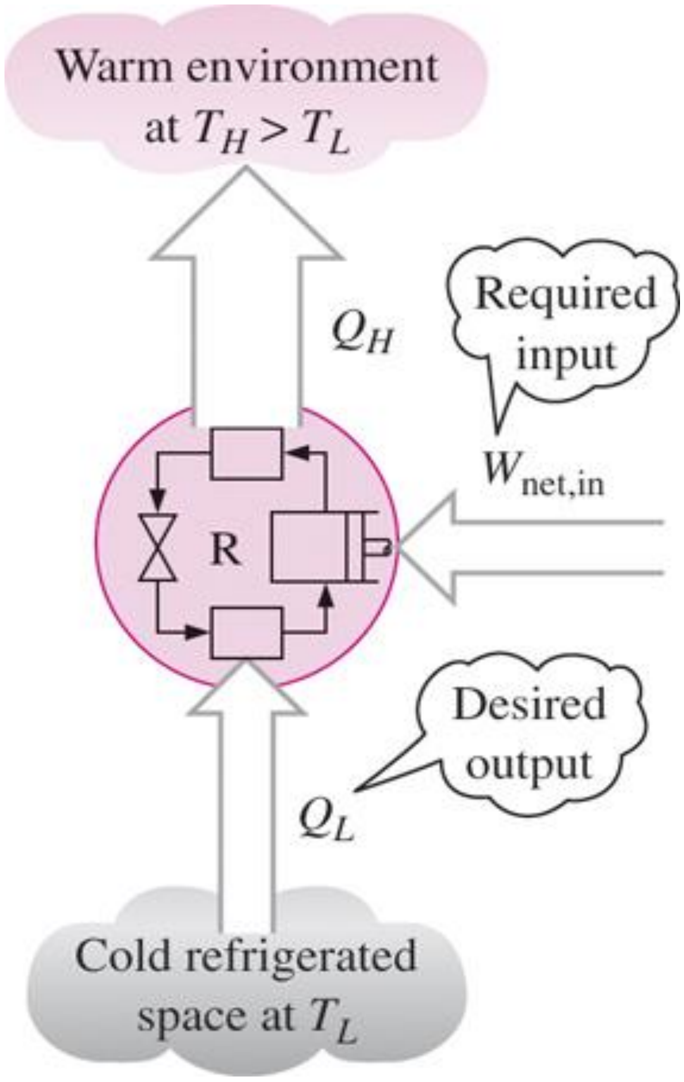
Coefficient of Performance

- The *efficiency* of a refrigerator is expressed in terms of the coefficient of performance (COP).
- The objective of a refrigerator is to remove heat (Q_L) from the refrigerated space.

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

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

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



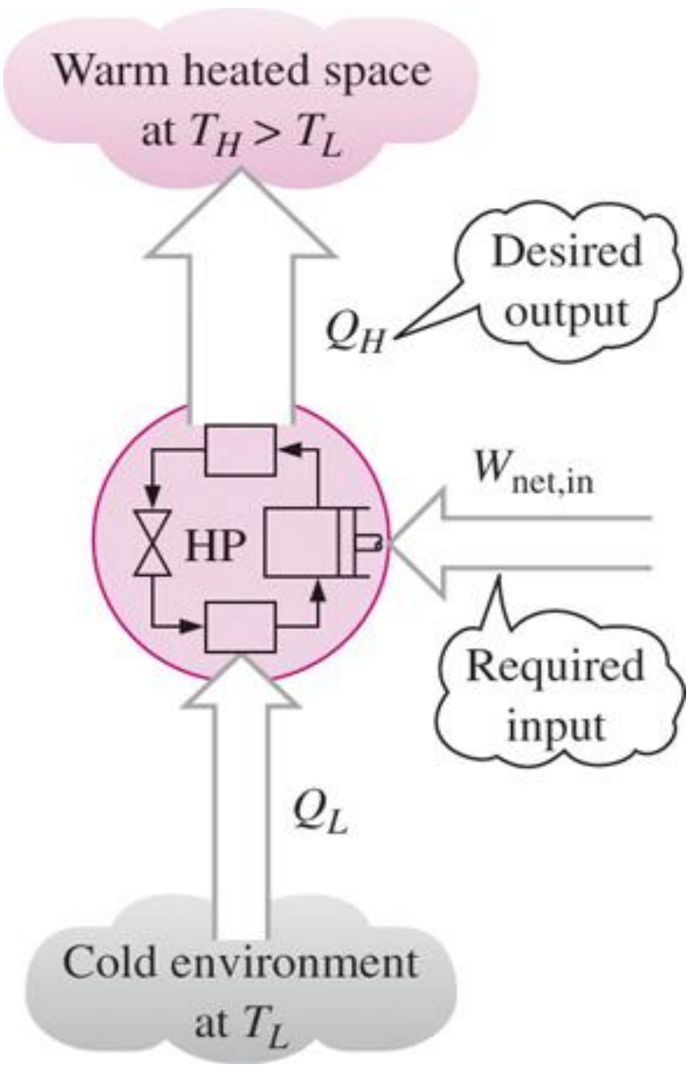
Can the value of COP_R be greater than unity?

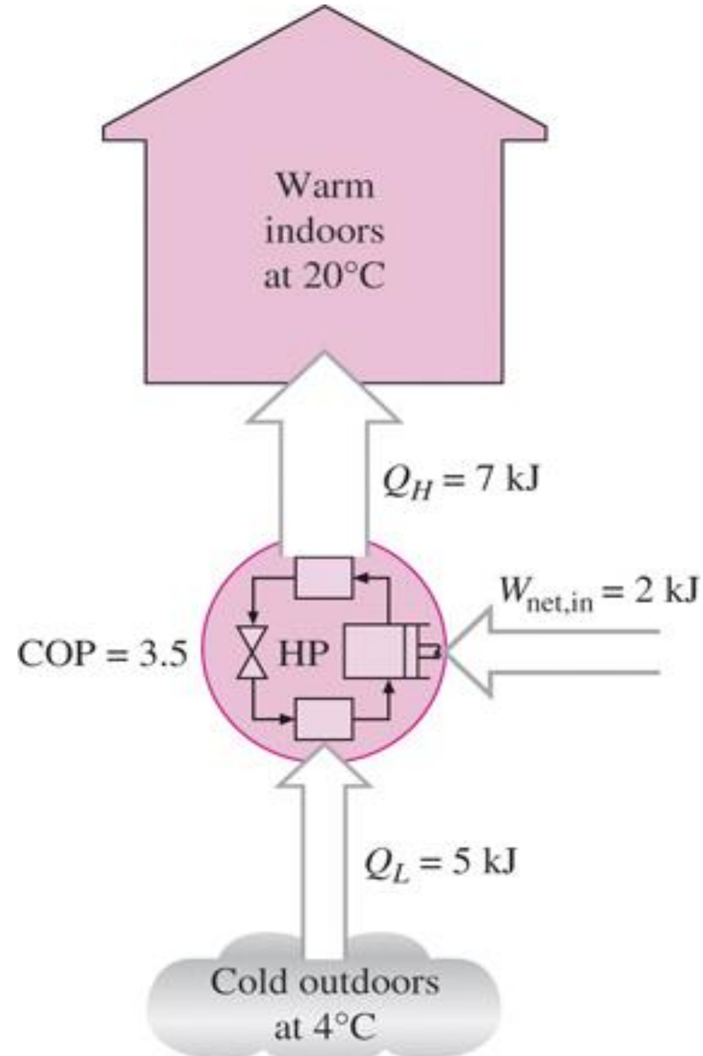
- Refrigerators are designed to consume a power $W_{in} < Q_L$; thus,
- $COP_R > 1$ for a well-designed refrigerator.
- A higher COP_R indicates a better performance.

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

Heat Pumps

- 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.

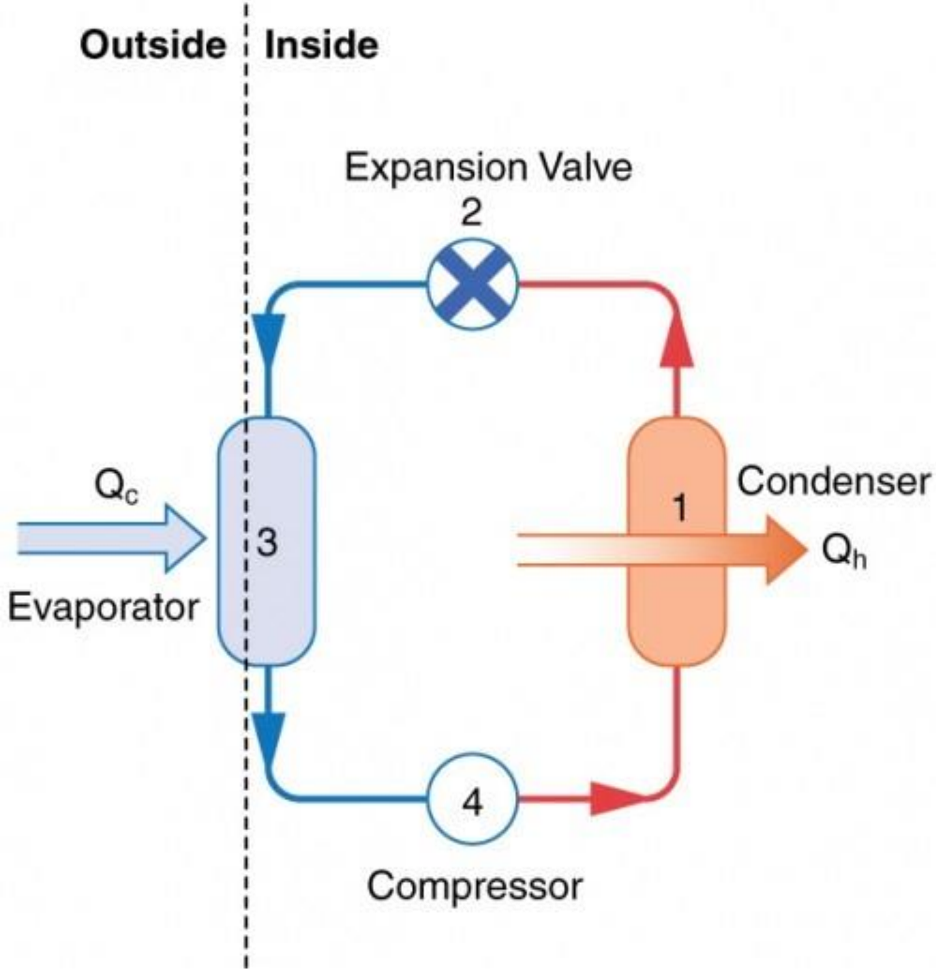




Heat Pumps

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

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



For fixed values of Q_L and Q_H :

$$\text{COP}_{\text{HP}} = \text{COP}_{\text{R}} + 1$$

- ***Can the value of COP_{HP} be lower than unity?***
- ***What does $COP_{HP} = 1$ represent?***

Simple HP components (similar to refrigerator)

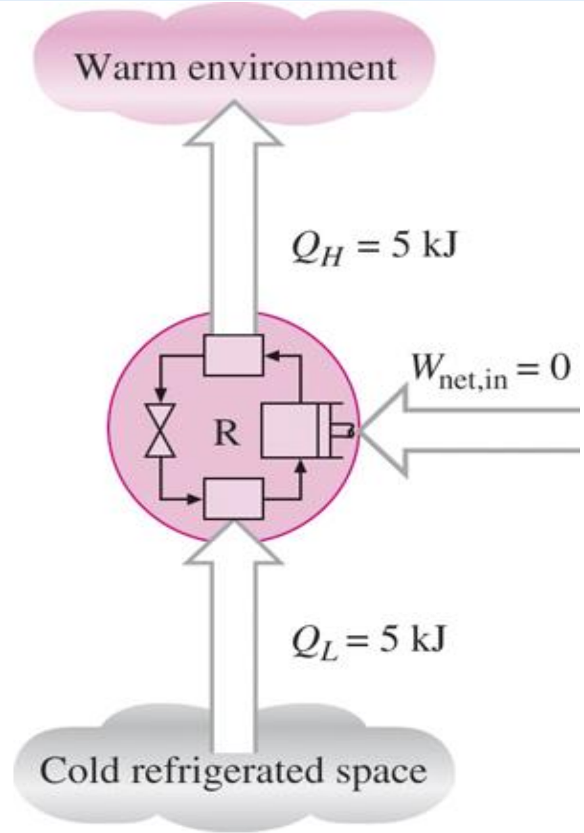
Heat Pumps

1. Most heat pumps in operation today have an average COP of 2 to 3.
2. Most existing heat pumps use the cold outside air as the heat source in winter (***air-source*** HP).
3. In cold climates their efficiency drops considerably when temperatures are below the freezing point.
4. **Air conditioners** are basically refrigerators whose refrigerated space is a room or a building instead of the food compartment.
5. The **COP** of a refrigerator decreases with decreasing refrigeration temperature. Therefore, it is *not economical* to refrigerate to a lower temperature than needed.
6. When installed backward, an air conditioner functions as a heat pump.

Second Law of Thermodynamics: Clausius Statement

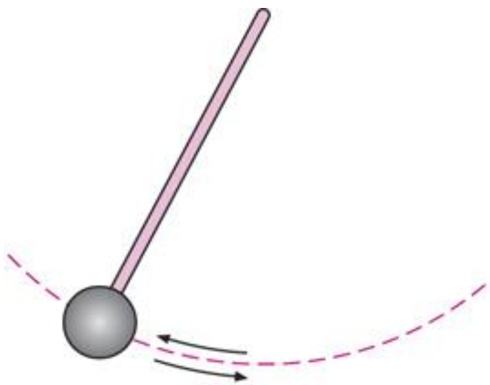
- **It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.**

- It states that a refrigerator cannot operate unless its **compressor** is driven by an external power source, such as an electric motor.
- The net effect on the surroundings involves: *the consumption of some energy in the form of work, AND the transfer of heat from a colder body to a warmer one*.
- No experiment has been conducted and found to contradict **the second law.** This should be taken as sufficient proof of its validity.



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

REVERSIBLE AND IRREVERSIBLE PROCESSES



(*a*) Frictionless pendulum

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

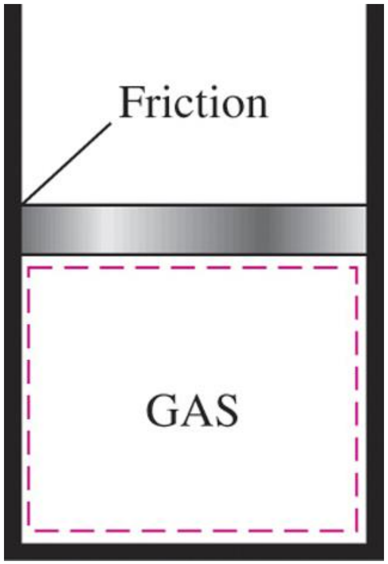
(a), (b) Two familiar reversible processes.

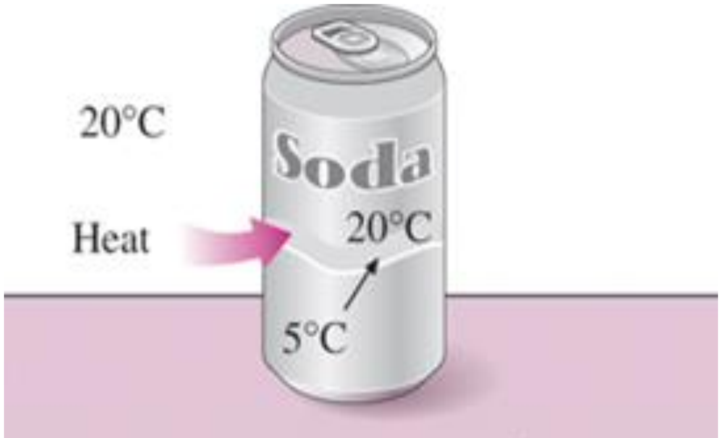
- **Reversible process:** A process that can be reversed *without leaving any trace on the surroundings.*
- **Irreversible process:** A process that is not reversible (*will leave traces*).

- All the processes occurring in nature are **irreversible.**
- *Why are we interested in* **reversible** processes?
  1. *they are easy to analyze,*
  2. *they serve as idealized models (theoretical limits) to which actual processes can be compared.*
- Some processes are <u>*more*</u> irreversible than others.

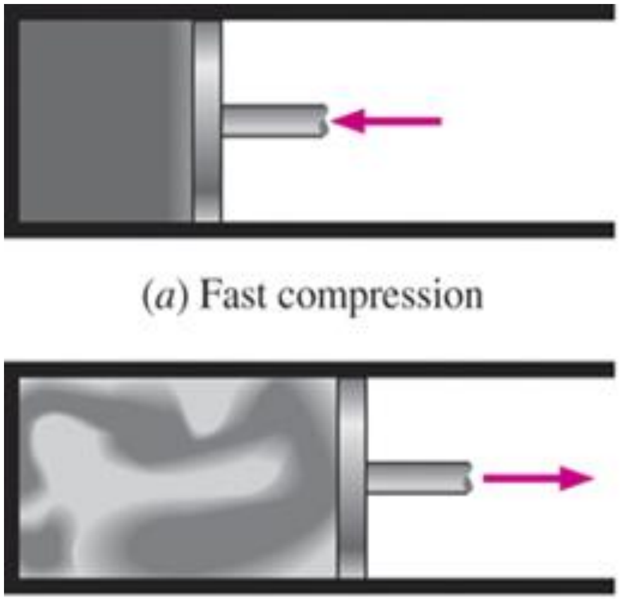
Irreversibilities

- The factors that cause a process to be irreversible are called <u>*irreversibilities.*</u>
- They include ***friction, 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.**



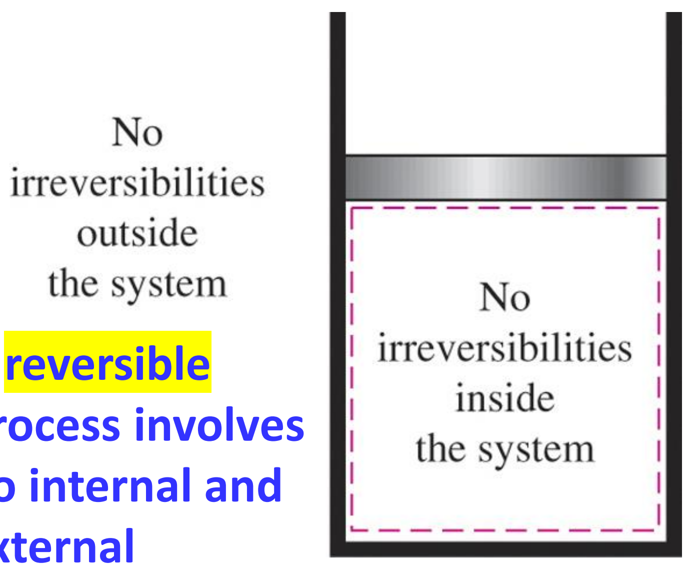


(*a*) An irreversible heat transfer process

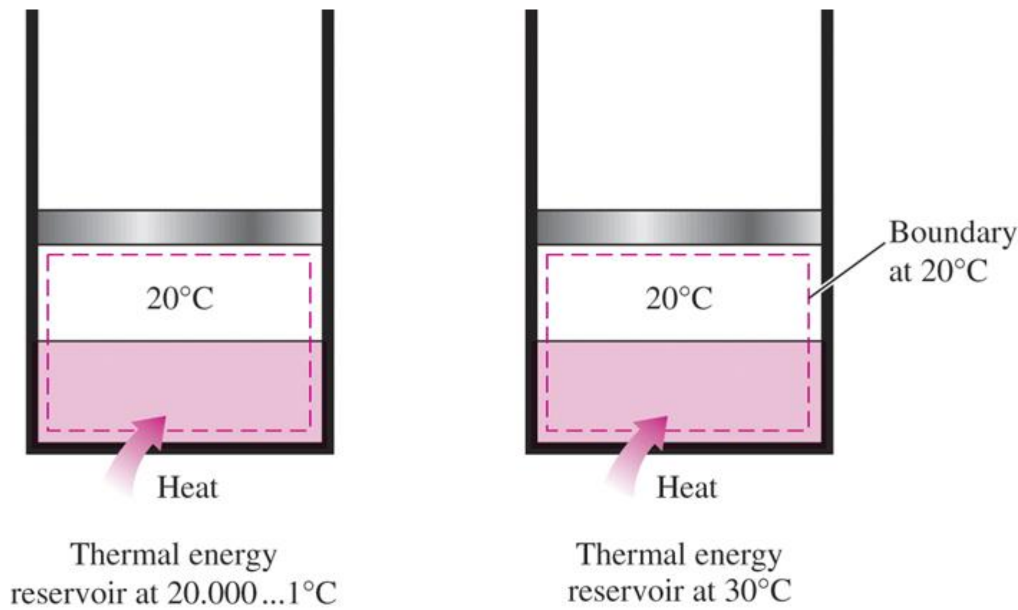

(*a*) Fast compression
(*b*) Fast expansion

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.



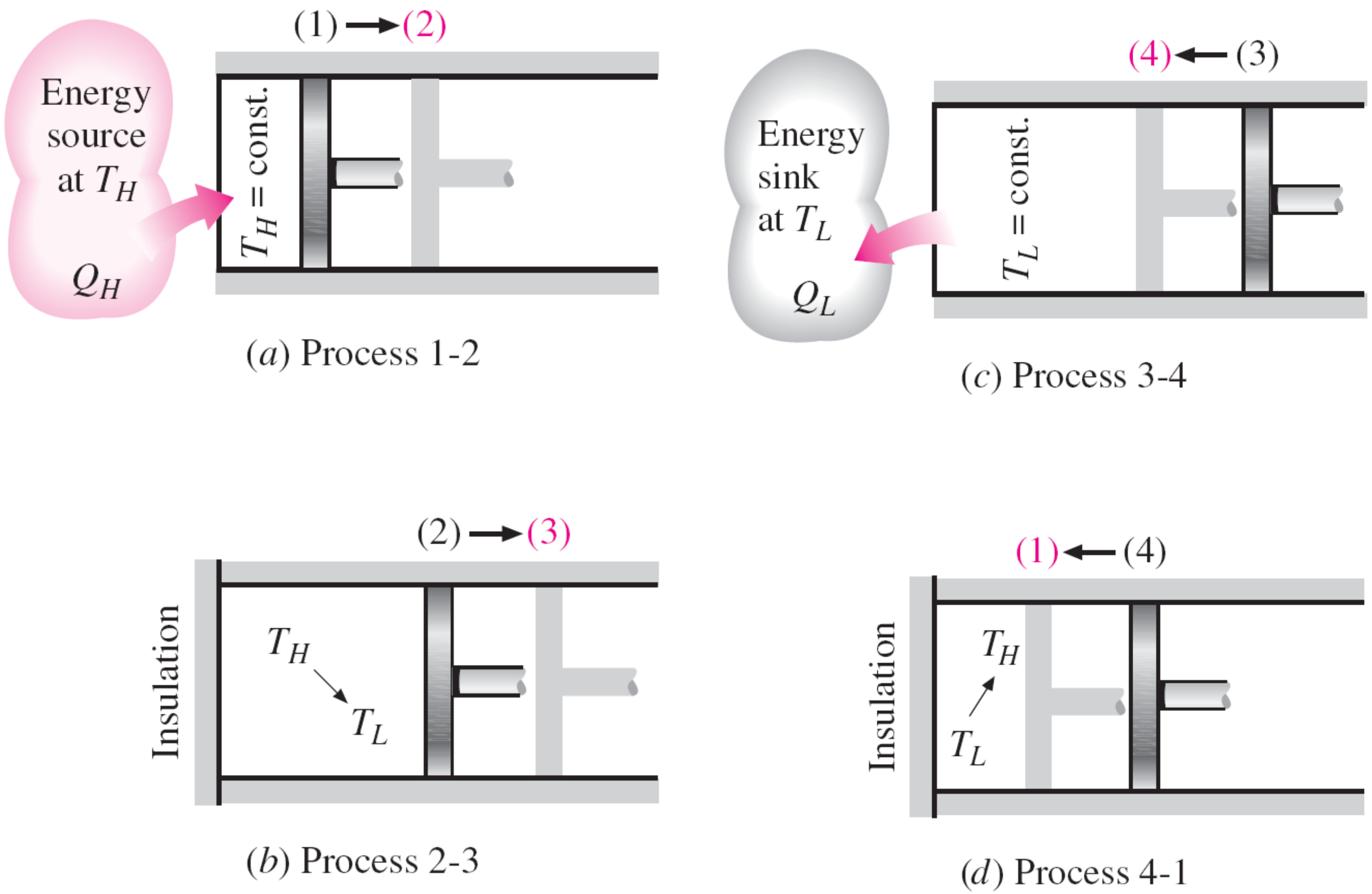
A reversible process involves no internal and external irreversibilities.



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

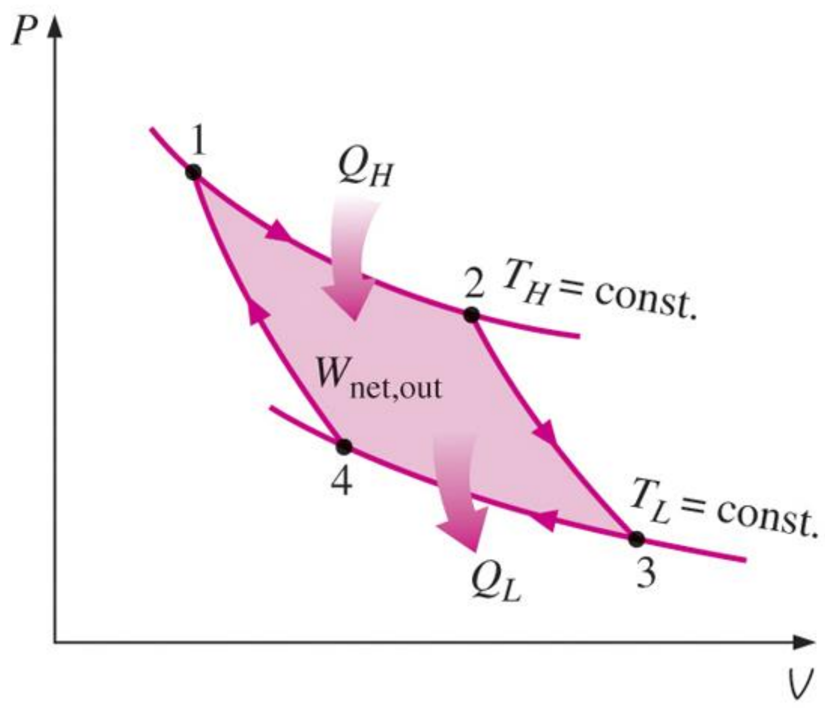
Totally and internally reversible heat transfer processes.

THE CARNOT CYCLE

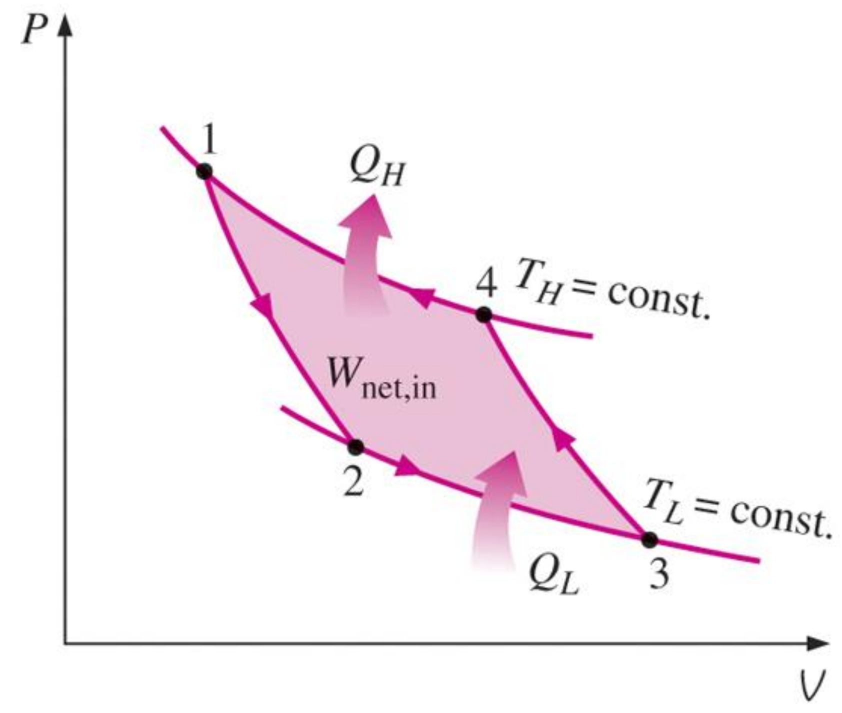


Execution of the Carnot cycle in a closed system.

- Reversible Isothermal Expansion (**process 1-2**, T_H = constant)
- Reversible Adiabatic Expansion (**process 2-3**, temperature drops from T_H to T_L)
- Reversible Isothermal Compression (**process 3-4**, T_L = constant)
- Reversible Adiabatic Compression (**process 4-1**, temperature rises from T_L to T_H)



P-V* diagram of the *Carnot cycle.



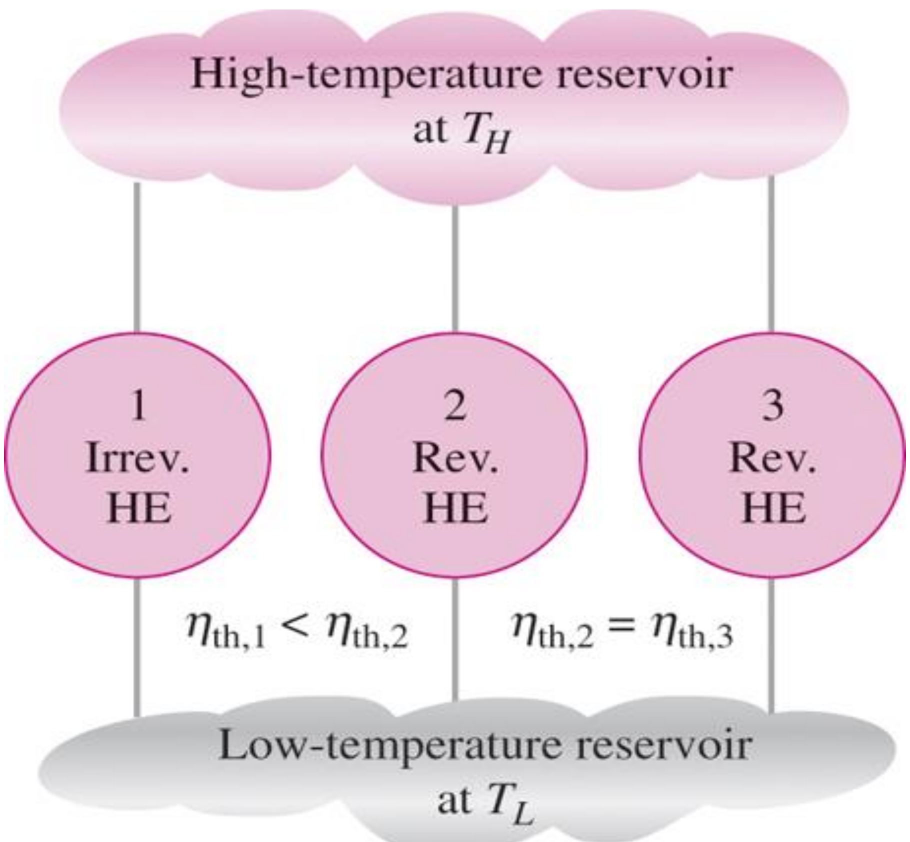
P-V* diagram of the *reversed Carnot cycle.

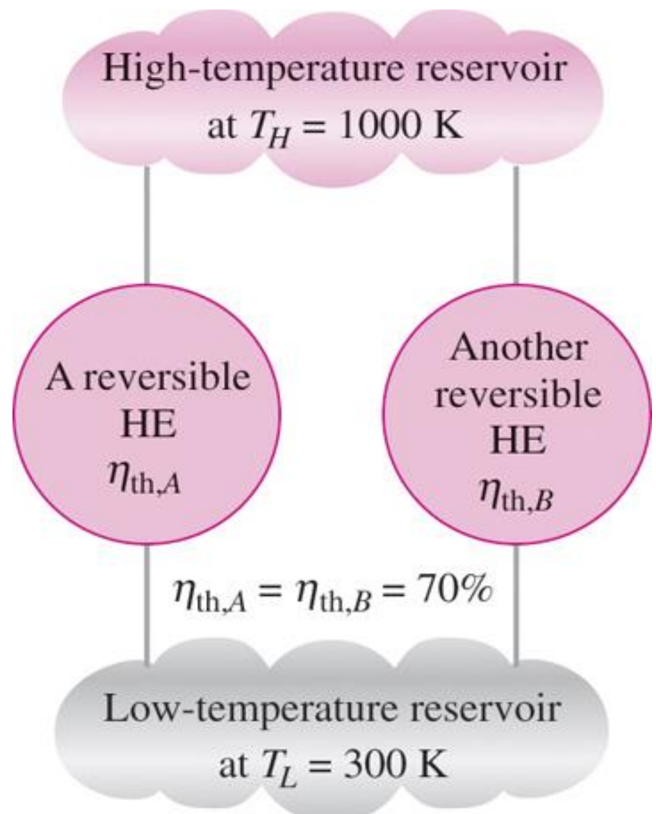
The Reversed Carnot Cycle

- ❑ The Carnot heat-engine cycle is a totally **reversible** cycle.
- ❑ Therefore, all the processes that comprise it can be *reversed*, in which case it becomes the **Carnot refrigeration cycle**.

THE CARNOT PRINCIPLES

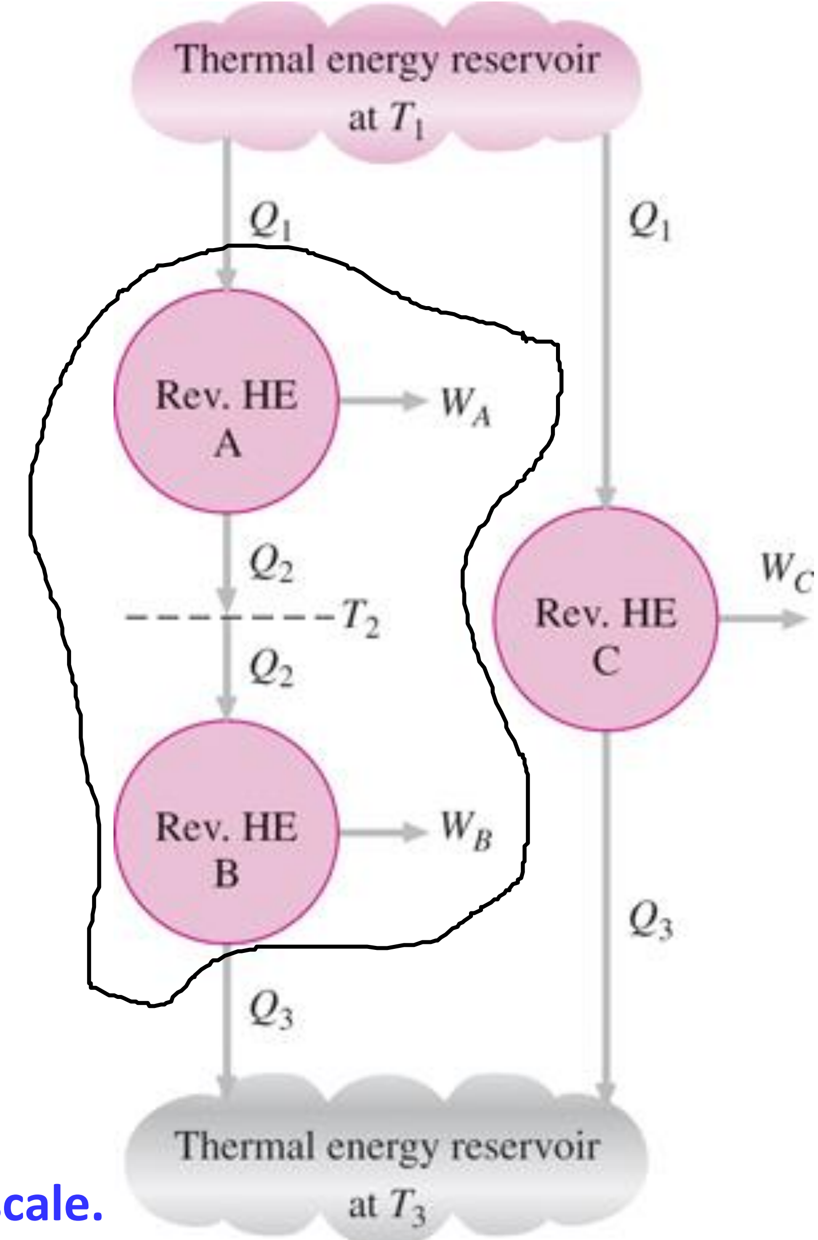
- **FIRST:** The efficiency of an *irreversible* heat engine is always less than the efficiency of a **reversible** one operating between the same two reservoirs.
- **SECOND:** The efficiencies of all **reversible** heat engines operating between the same two reservoirs are <u>the same.</u>





THE THERMODYNAMIC TEMPERATURE SCALE

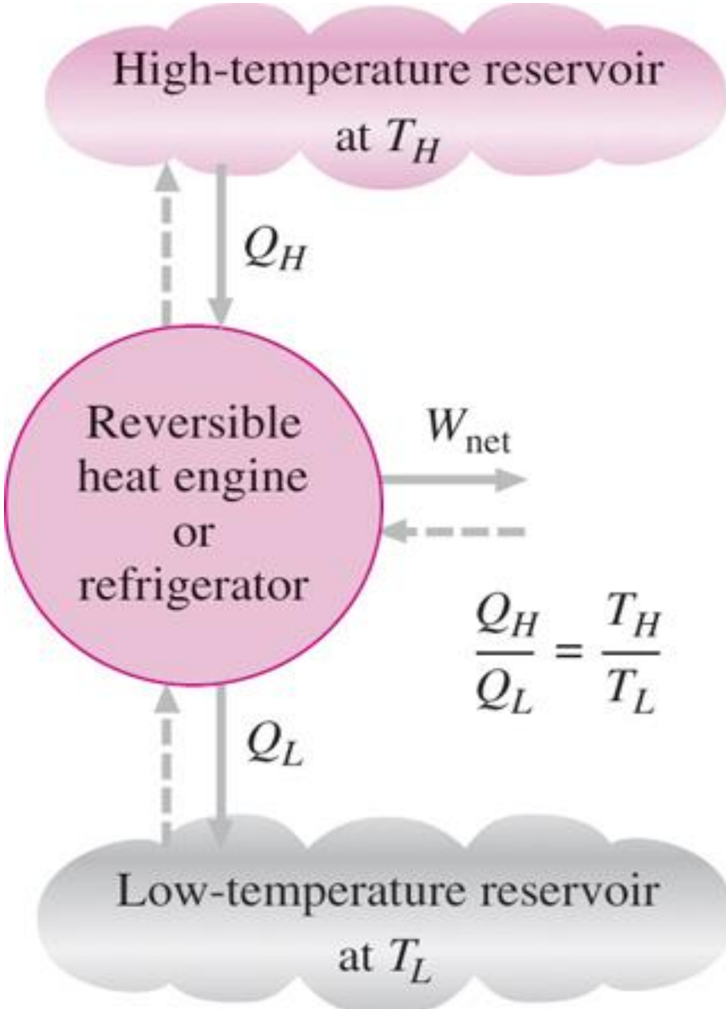
- A temperature scale that is *independent of the properties of the substances* that are used to measure temperature is called the ***thermodynamic temperature scale***.
- Such a temperature scale offers great conveniences in thermodynamic calculations. It provided theoretical limits of engineering equipment performance.

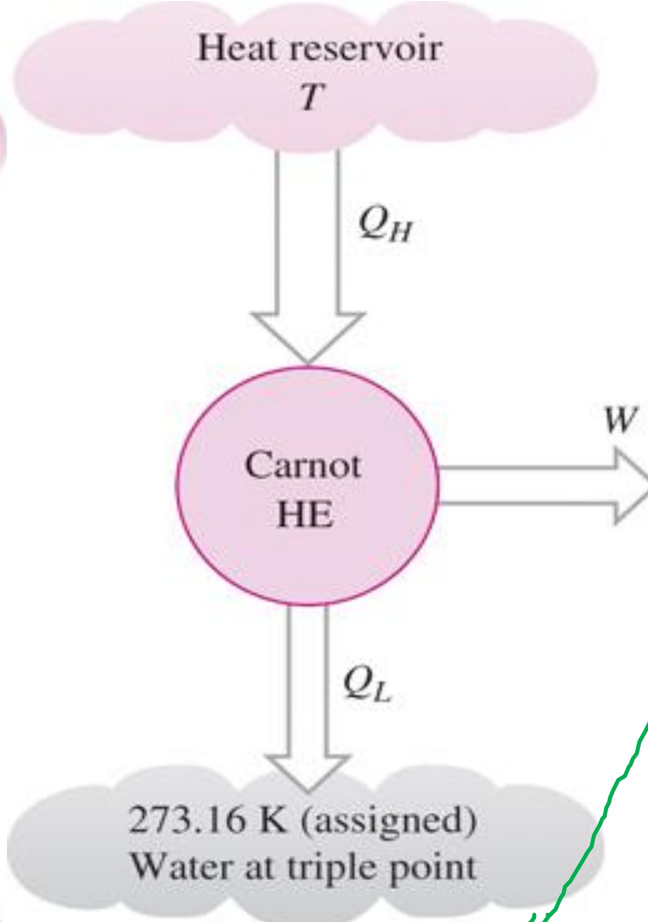


Not function of T2

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

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





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

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

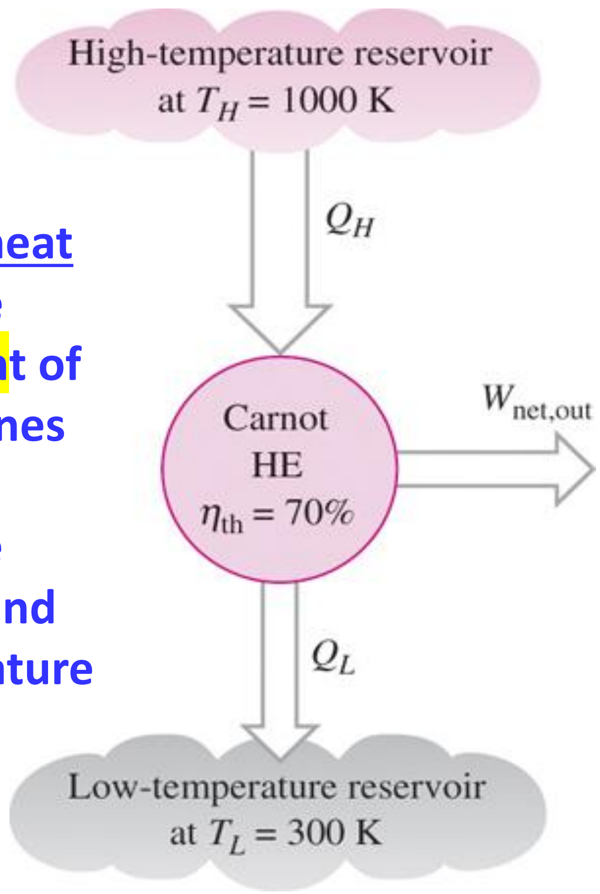
$$T = 273.16 \frac{Q_H}{Q_L}$$

$$T(°C) = T(K) - 273.15$$

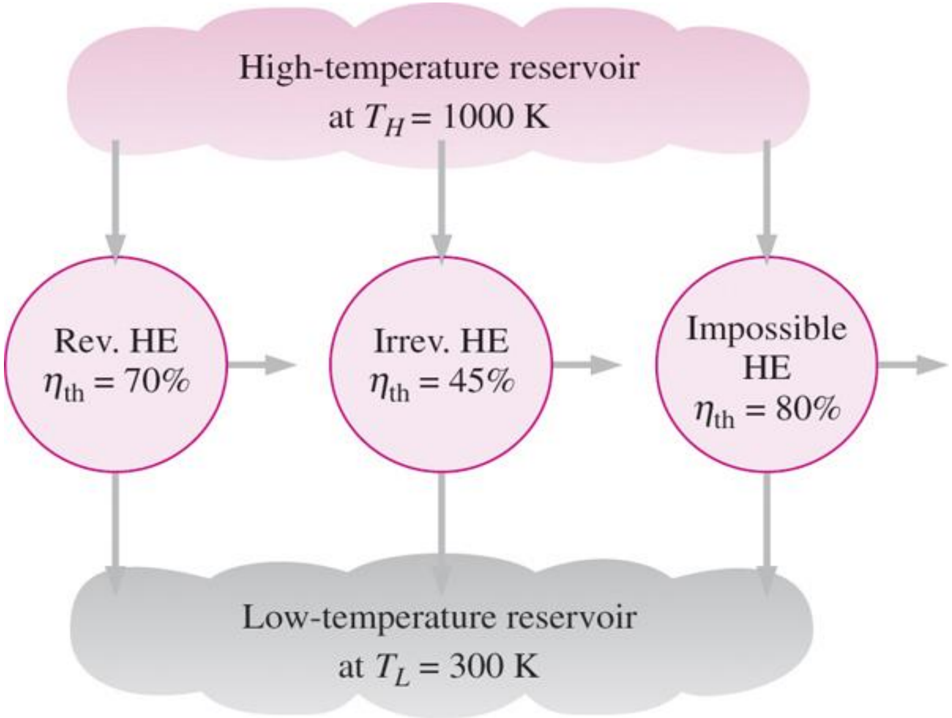
For reversible cycles, the heat transfer ratio Q_H/Q_L can be replaced by the absolute temperature ratio T_H/T_L.

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

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.

Any heat engine

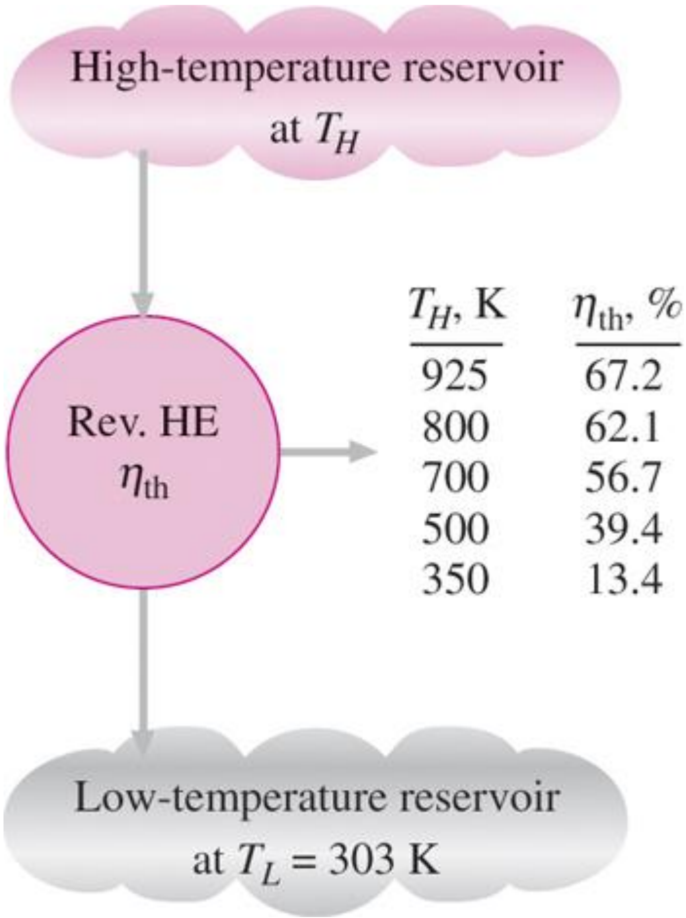
$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

Carnot heat engine

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

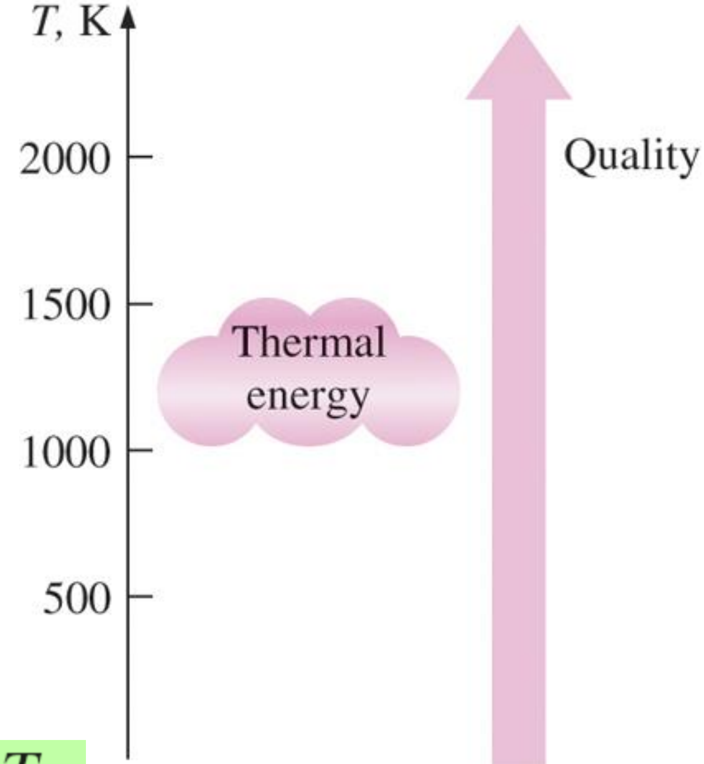
$$\eta_{th} \begin{cases} < \eta_{th,rev} & \text{irreversible heat engine} \\ = \eta_{th,rev} & \text{reversible heat engine} \\ > \eta_{th,rev} & \text{impossible heat engine} \end{cases}$$

The Quality of Energy



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

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

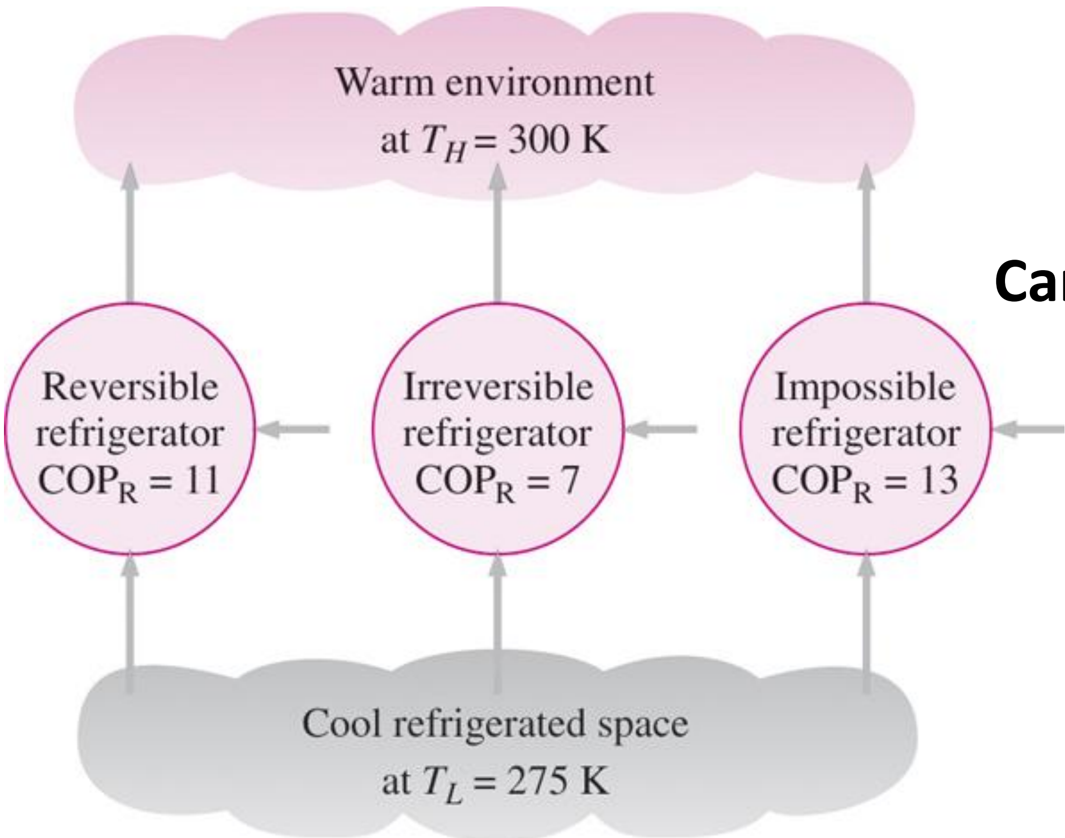


The higher the temperature of the thermal energy, the higher its quality.

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

- **Can we use °C unit for temperature here?**
- ***How do you increase the thermal efficiency of a Carnot heat engine?***
- ***How about for actual heat engines?***

THE CARNOT REFRIGERATOR AND HEAT PUMP



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

Any refrigerator or heat pump

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

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

Carnot refrigerator or heat pump

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

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

How do you increase the COP of a Carnot refrigerator or heat pump?

EXAMPLE 6–1 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.

SOLUTION The rates of heat transfer to and from a heat engine are given. The net power output and the thermal efficiency are to be determined.

Assumptions Heat losses through the pipes and other components are negligible.

Analysis A schematic of the heat engine is given in Fig. 6–16. The furnace serves as the high-temperature reservoir for this heat engine and the river as the low-temperature reservoir. The given quantities can be expressed as

$$\dot{Q}_H = 80 \text{ MW} \quad \text{and} \quad \dot{Q}_L = 50 \text{ MW}$$

The net power output of this heat engine is

$$\dot{W}_{\text{net,out}} = \dot{Q}_H - \dot{Q}_L = (80 - 50) \text{ MW} = \mathbf{30\ MW}$$

Then the thermal efficiency is easily determined to be

$$\eta_{\text{th}} = \frac{\dot{W}_{\text{net,out}}}{\dot{Q}_H} = \frac{30 \text{ MW}}{80 \text{ MW}} = \mathbf{0.375} \text{ (or } 37.5\%)$$

Discussion Note that the heat engine converts 37.5 percent of the heat it receives to work.

EXAMPLE 6–3 **Heat Rejection by a Refrigerator**

The food compartment of a refrigerator, shown in Fig. 6–23, is maintained at 4°C by removing heat from it at a rate of 360 kJ/min. If the required power input to the refrigerator is 2 kW, determine (*a*) the coefficient of performance of the refrigerator and (*b*) the rate of heat rejection to the room that houses the refrigerator.

SOLUTION The power consumption of a refrigerator is given. The COP and the rate of heat rejection are to be determined.

Assumptions Steady operating conditions exist.

Analysis (*a*) The coefficient of performance of the refrigerator is

$$\text{COP}_\text{R} = \frac{\dot{Q}_L}{\dot{W}_{\text{net,in}}} = \frac{360 \text{ kJ/min}}{2 \text{ kW}}\left(\frac{1 \text{ kW}}{60 \text{ kJ/min}}\right) = 3$$

That is, 3 kJ of heat is removed from the refrigerated space for each kJ of work supplied.

(*b*) The rate at which heat is rejected to the room that houses the refrigerator is determined from the conservation of energy relation for cyclic devices,

$$\dot{Q}_H = \dot{Q}_L + \dot{W}_{\text{net,in}} = 360 \text{ kJ/min} + (2 \text{ kW})\left(\frac{60 \text{ kJ/min}}{1 \text{ kW}}\right) = 480 \text{ kJ/min}$$

Discussion Notice that both the energy removed from the refrigerated space as heat and the energy supplied to the refrigerator as electrical work eventually show up in the room air and become part of the internal energy of the air. This demonstrates that energy can change from one form to another, can move from one place to another, but is never destroyed during a process.

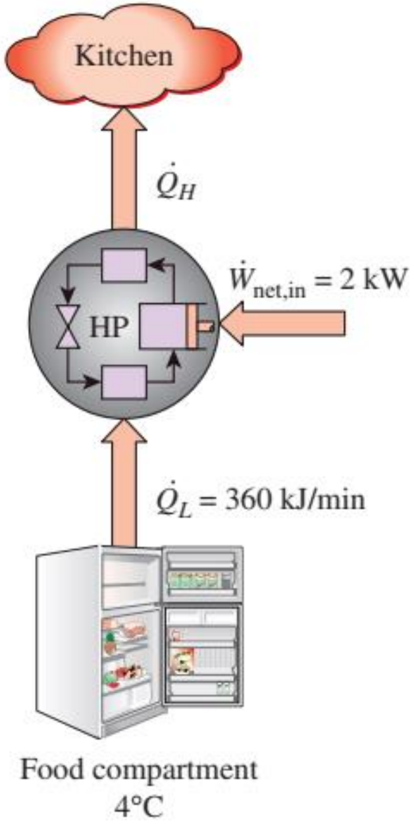


FIGURE 6–23
Schematic for Example 6–3.

EXAMPLE 6–5 **Analysis of a Carnot Heat Engine**

A Carnot heat engine, shown in Fig. 6–47, 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.

SOLUTION The heat supplied to a Carnot heat engine is given. The thermal efficiency and the heat rejected are to be determined.

Analysis (*a*) The Carnot heat engine is a reversible heat engine, and so its efficiency can be determined from Eq. 6–18 to be

$$\eta_{\text{th,rev}} = 1 - \frac{T_L}{T_H} = 1 - \frac{(30 + 273)\text{ K}}{(652 + 273)\text{ K}} = \mathbf{0.672}$$

That is, this Carnot heat engine converts 67.2 percent of the heat it receives to work.

(*b*) The amount of heat rejected Q_L by this reversible heat engine is easily determined from Eq. 6–16 to be

$$Q_{L,\text{rev}} = \frac{T_L}{T_H} Q_{H,\text{rev}} = \frac{(30 + 273)\text{ K}}{(652 + 273)\text{ K}}(500\text{ kJ}) = \mathbf{164\ kJ}$$

Discussion Note that this Carnot heat engine rejects to a low-temperature sink 164 kJ of the 500 kJ of heat it receives during each cycle.

EXAMPLE 6–6 A Carnot Refrigeration Cycle Operating in the Saturation Dome

A Carnot refrigeration cycle is executed in a closed system in the saturated liquid–vapor mixture region using 0.8 kg of refrigerant-134a as the working fluid (Fig. 6–51). The maximum and the minimum temperatures in the cycle are 20 and −8°C, respectively. It is known that the refrigerant is saturated liquid at the end of the heat rejection process, and the net work input to the cycle is 15 kJ. Determine the fraction of the mass of the refrigerant that vaporizes during the heat addition process, and the pressure at the end of the heat rejection process.

SOLUTION A Carnot refrigeration cycle is executed in a closed system. The mass fraction of the refrigerant that vaporizes during the heat addition process and the pressure at the end of the heat rejection process are to be determined.

Assumptions The refrigerator operates on the ideal Carnot cycle.

Analysis Knowing the high and low temperatures, the coefficient of performance of the cycle is

$$\mathrm{COP_R} = \frac{1}{T_H/T_L - 1} = \frac{1}{(20 + 273\ \mathrm{K})/(-8 + 273\ \mathrm{K}) - 1} = 9.464$$

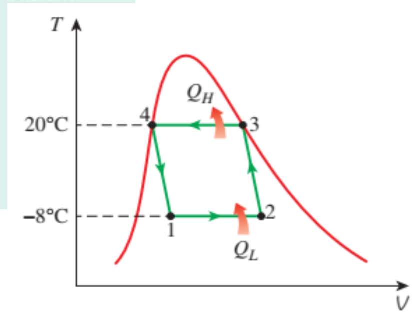


FIGURE 6–51
Schematic for Example 6–6.

The amount of cooling is determined from the definition of the coefficient of performance to be

$$Q_L = \text{COP}_R \times W_{in} = (9.464)(15\ \text{kJ}) = 142\ \text{kJ}$$

The enthalpy of vaporization R-134a at −8°C is h_{fg} = 204.59 kJ/kg (Table A-11). Then the amount of refrigerant that vaporizes during heat absorption becomes

$$Q_L = m_{evap} h_{fg@-8°C} \rightarrow m_{evap} = \frac{142\ \text{kJ}}{204.59\ \text{kJ/kg}} = 0.694\ \text{kg}$$

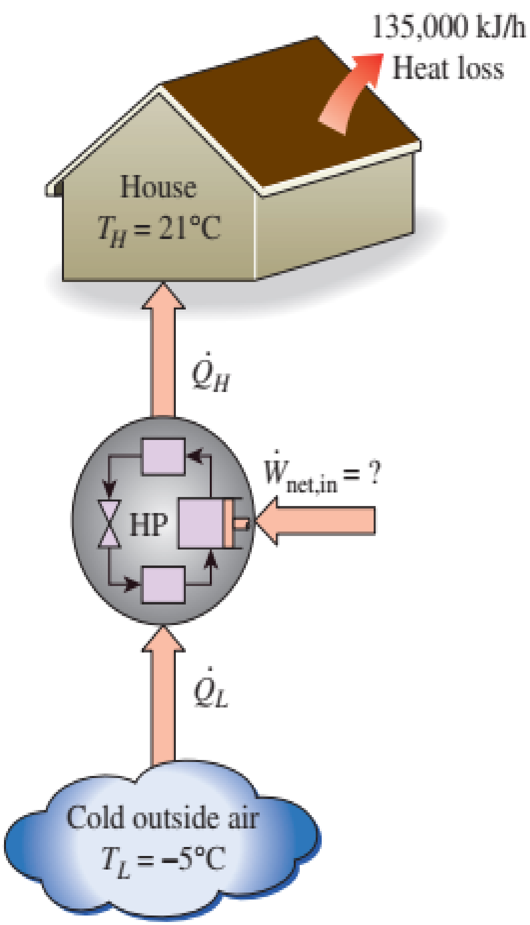
Therefore, the fraction of mass that vaporized during heat addition process to the refrigerant is

$$\text{Mass fraction} = \frac{m_{evap}}{m_{total}} = \frac{0.694\ \text{kg}}{0.8\ \text{kg}} = \mathbf{0.868} \text{ or } \mathbf{86.8\%}$$

The pressure at the end of heat rejection process is simply the saturation pressure at heat rejection temperature,

$$P_4 = P_{sat@20°C} = \mathbf{572.1\ kPa}$$

Discussion Carnot cycle is an idealized refrigeration cycle, thus it cannot be achieved in practice. Practical refrigeration cycles are analyzed in Chap. 11.



EXAMPLE 6–7 Heating a House by a Carnot Heat Pump

A heat pump is to be used to heat a house during the winter, as shown in Fig. 6–52. The house is to be maintained at 21°C at all times. The house is estimated to be losing heat at a rate of 135,000 kJ/h when the outside temperature drops to −5°C. Determine the minimum power required to drive this heat pump.

SOLUTION A heat pump maintains a house at a constant temperature. The required minimum power input to the heat pump is to be determined.

Assumptions Steady operating conditions exist.

Analysis The heat pump must supply heat to the house at a rate of $\dot{Q}_H$ = 135,000 kJ/h = 37.5 kW. The power requirements are minimum when a reversible heat pump is used to do the job. The COP of a reversible heat pump operating between the house and the outside air is

$$\text{COP}_{\text{HP,rev}} = \frac{1}{1 - T_L/T_H} = \frac{1}{1 - (-5 + 273\text{ K})/(21 + 273\text{ K})} = 11.3$$

Then, the required power input to this reversible heat pump becomes

$$\dot{W}_{\text{net,in}} = \frac{\dot{Q}_H}{\text{COP}_{\text{HP}}} = \frac{37.5\text{ kW}}{11.3} = \mathbf{3.32\text{ kW}}$$