Thermodynamics: An Engineering Approach
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CHAPTER 6
THE SECOND LAW OF THERMODYNAMICS

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Objectives

- Introduce the second law of thermodynamics
- Identify valid processes as those that satisfy both the first and second laws of thermodynamics
- Discuss thermal energy reservoirs, reversible and irreversible processes, heat engines, refrigerators, and heat pumps
- Describe the Kelvin–Planck and Clausius statements of the second law of thermodynamics
- Discuss the concepts of perpetual-motion machines
- Apply the second law of thermodynamics to cycles
- Apply the second law to develop the absolute thermodynamic temperature scale
- Describe the Carnot cycle, examine the Carnot principles, idealized Carnot heat engines, refrigerators, and heat pumps
- Determine the expressions for the thermal efficiencies and coefficients of performance for reversible heat engines, heat pumps, and refrigerators

INTRODUCTION TO THE SECOND LAW

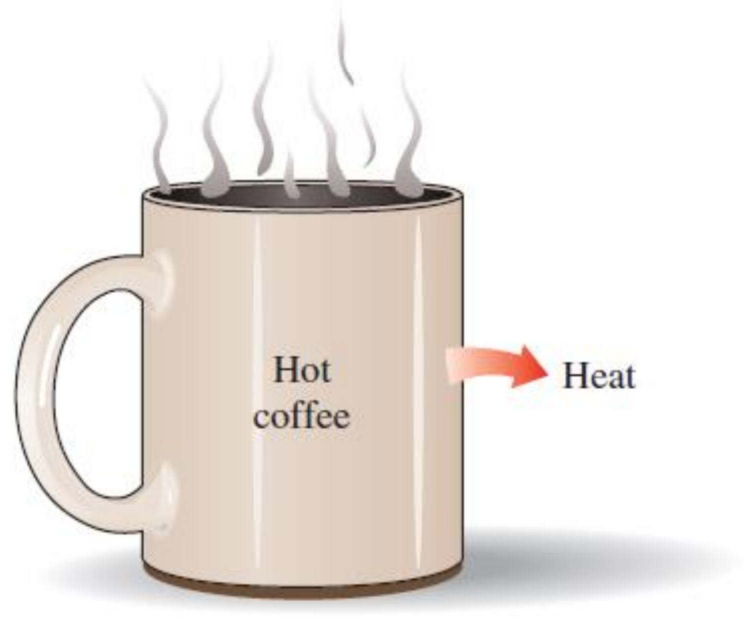


FIGURE 6–1
A cup of hot coffee does not get hotter in a cooler room.

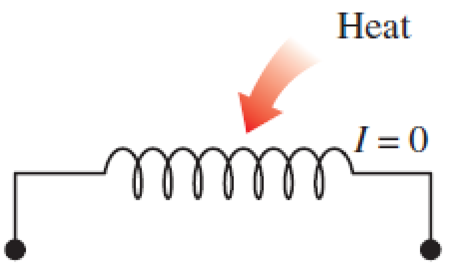


FIGURE 6–2
Transferring heat to a wire will not generate electricity.

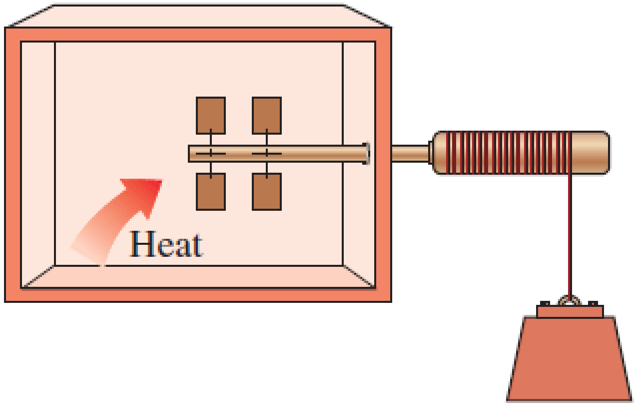


FIGURE 6–3
Transferring heat to a paddle wheel will not cause it to rotate.

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

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.

FIGURE 6–4
Processes occur in a certain direction, and not in the reverse direction.

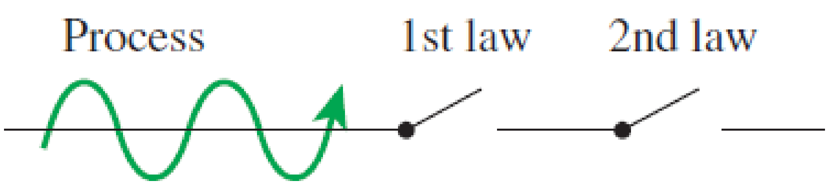


FIGURE 6–5
A process must satisfy both the first and second laws of thermodynamics to proceed.

- First law places no restriction on the direction of the process, and satisfying the first law does not ensure that the process can actually occur
- The direction or whether a process can take place is given by the second law of thermodynamics
- **Thus process can occur only when both first and second laws are satisfied**

THERMAL ENERGY RESERVOIRS

- A hypothetical body with a relatively ***large thermal energy capacity*** (mass × 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

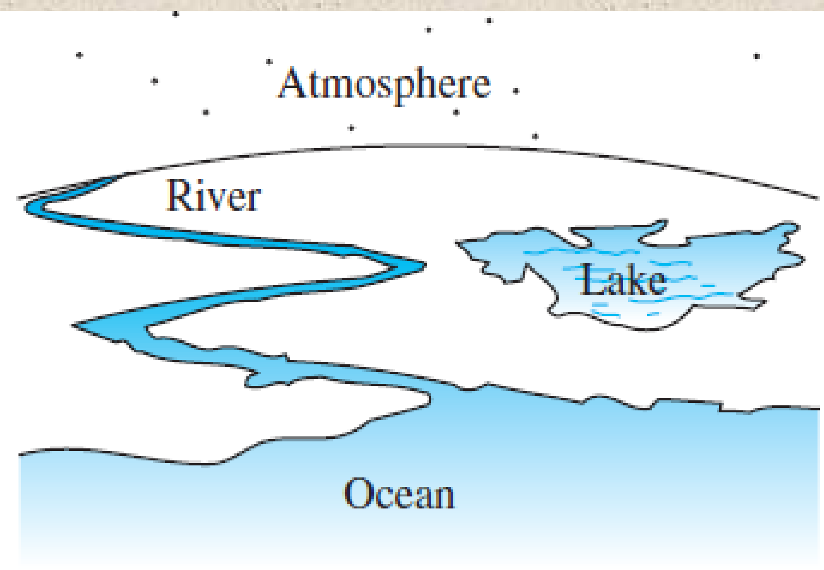


FIGURE 6–6
Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.

THERMAL ENERGY RESERVOIRS

- A two-phase system can also be modeled as a reservoir since it can absorb and release large quantities of heat while remaining at **constant temperature**
- A body does not actually have to be very large to be considered a reservoir. Any physical body with ***large thermal capacity relative to the amount of heat it supplies or absorbs***, can be considered as a thermal energy reservoir (e.g. air in the room can be considered as a reservoir for case of heat dissipation from a TV set)
- Thermal energy reservoirs are often referred to as ***heat reservoirs*** since they supply of absorb energy in the form of heat

THERMAL ENERGY SOURCE AND SINK

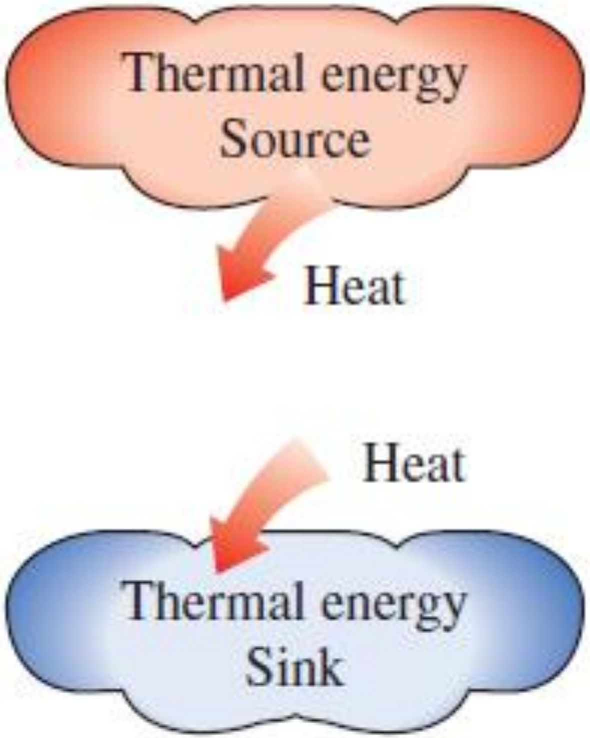


FIGURE 6–7

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

HEAT AND WORK

- Work can be converted to heat directly and completely
- But, converting heat to work requires the use of some special devices called ***heat engines***

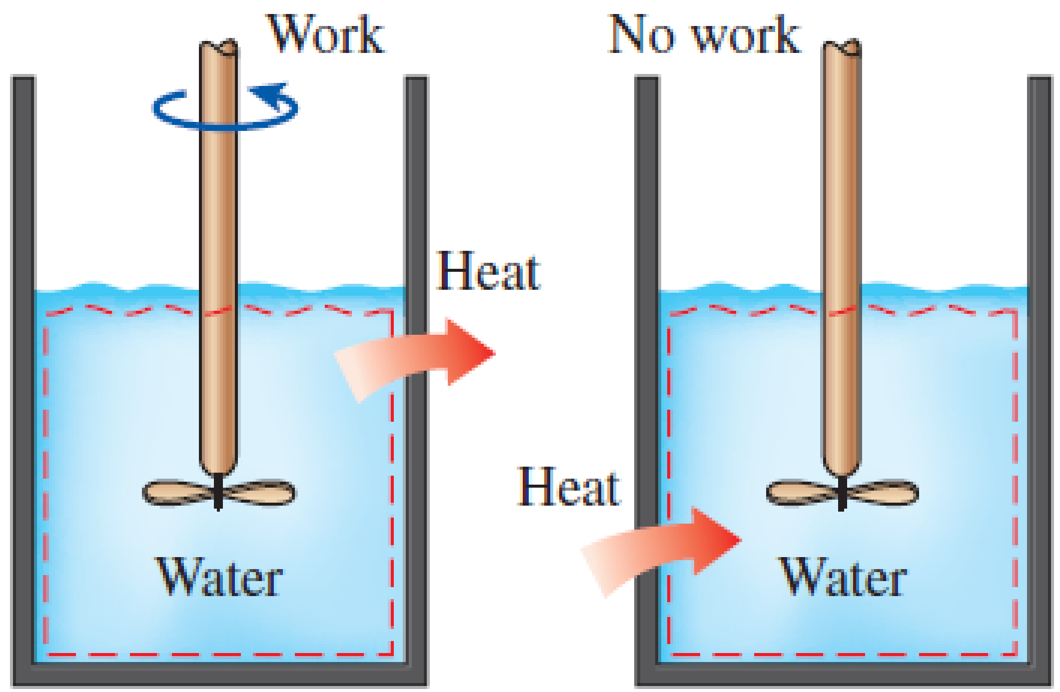


FIGURE 6–8
Work can always be converted to heat directly and completely, but the reverse is not true.

HEAT ENGINES

HEAT ENGINES: The 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

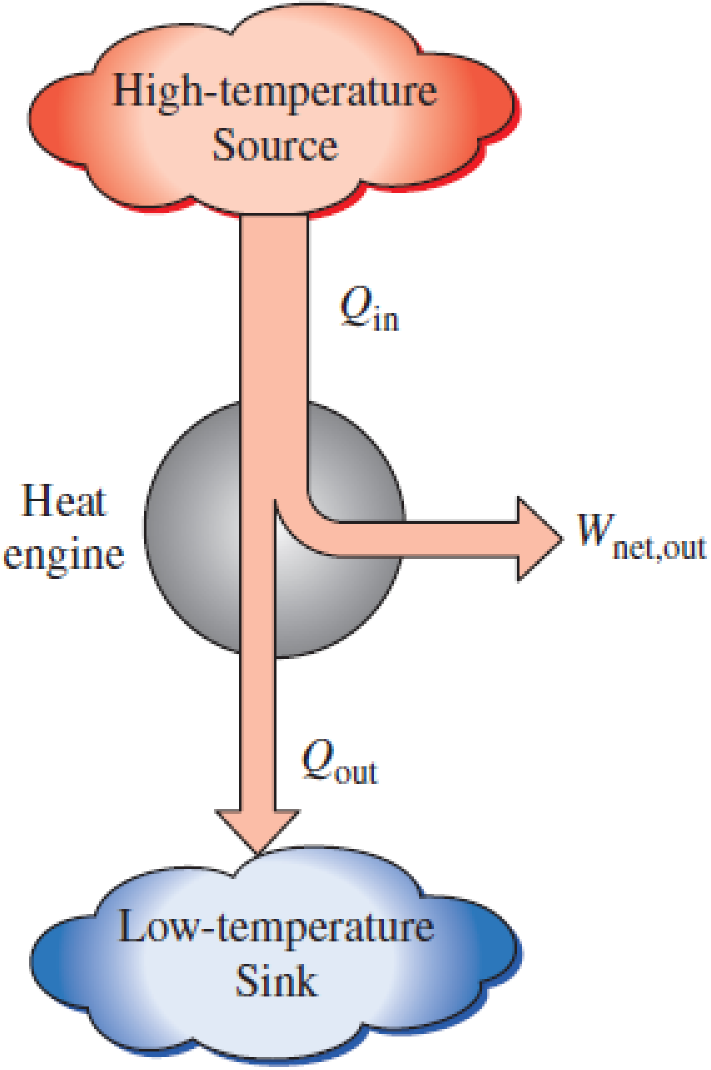
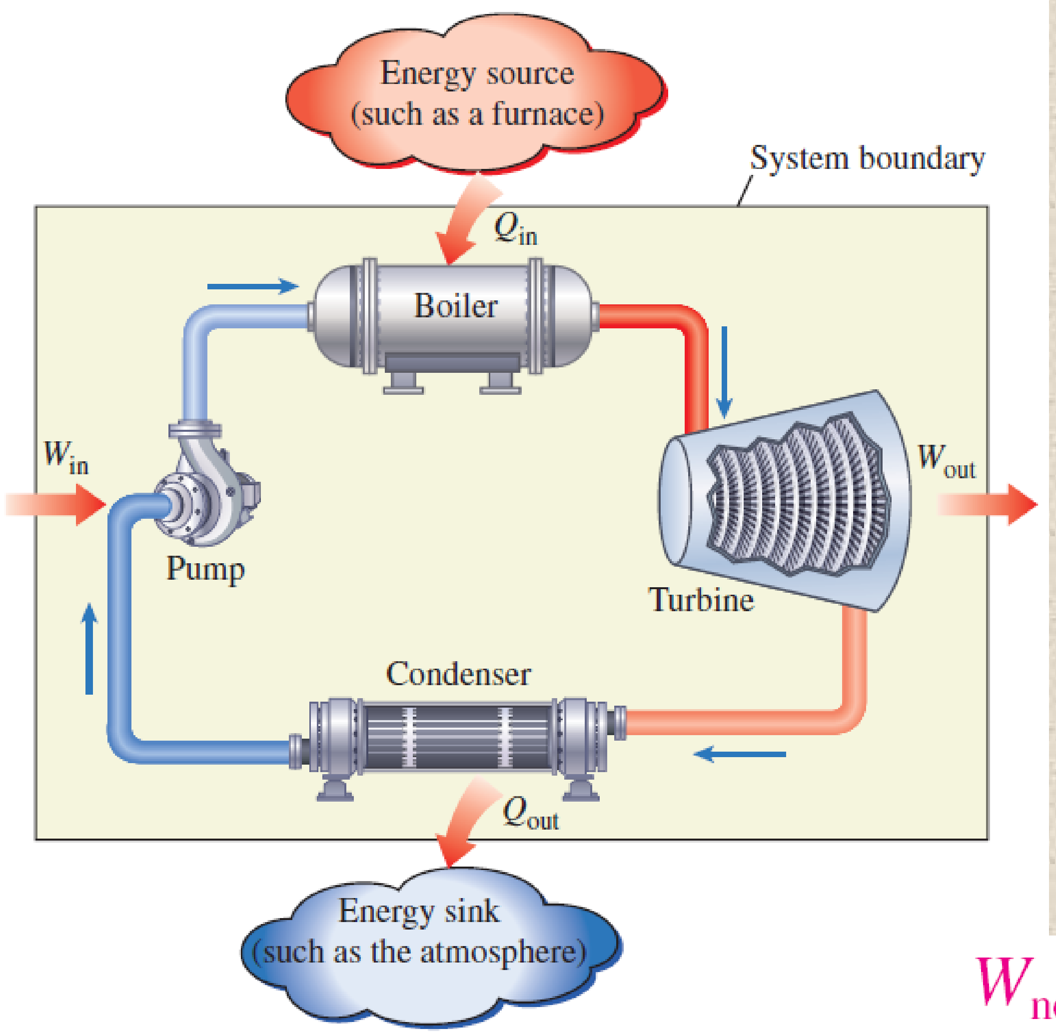


FIGURE 6–9
Part of the heat received by a heat engine is converted to work, while the rest is rejected to a sink.



A steam power plant

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**.

Steam is the working fluid for a steam power plant.

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

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

Net Work Output

- Note that all four components (boiler, turbine, condenser, pump) together with the connecting pipes can be analyzed as a **closed system**
- Under steady conditions, the total energy of this closed system will be constant ($dE/dt = 0$, or $\Delta E = 0$ between two time instances)
- Hence, net work output of the system is also equal to the net heat transfer to the system

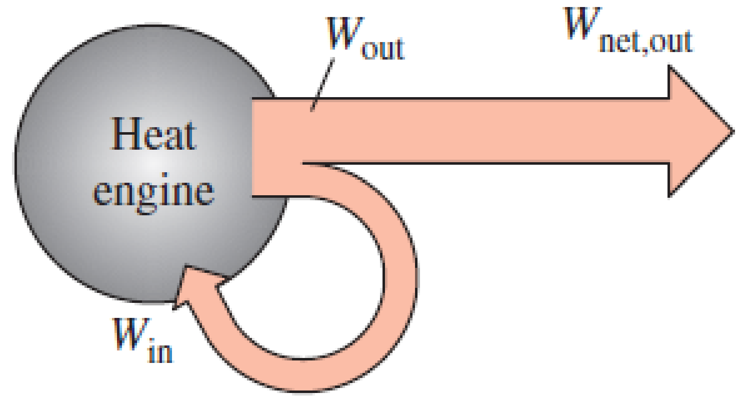


FIGURE 6–11

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

Thermal efficiency

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

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

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

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

- 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

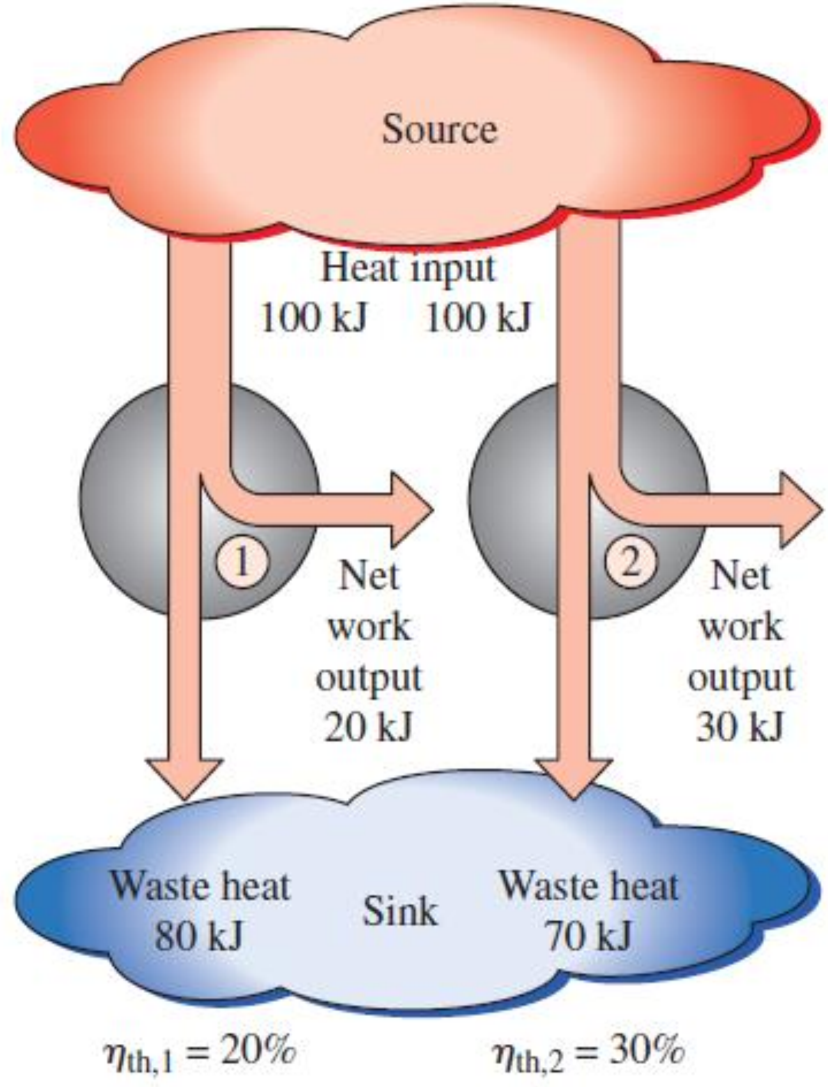


FIGURE 6–12
Some heat engines perform better than others (convert more of the heat they receive to work).

Q_H = magnitude of heat transfer between the cyclic device and the high-temperature medium at temperature T_H

Q_L = magnitude of heat transfer between the cyclic device and the low-temperature medium at temperature T_L

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

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

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

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

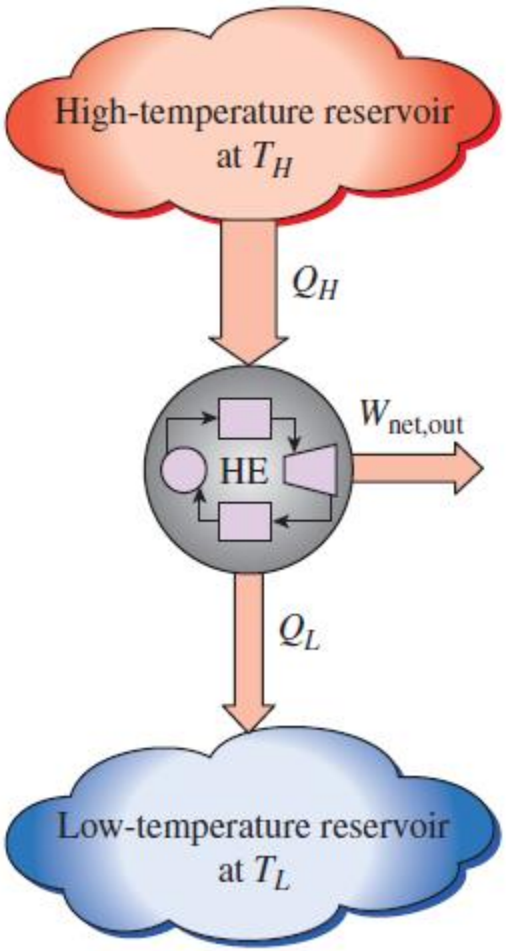


FIGURE 6–13
Schematic of a heat engine.

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

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

- **Note that $\eta_{th} < 1$**
- η_{th} is about 0.25 for spark ignition automobile engine (converts about 25% of chemical energy of gasoline to mechanical work)
- η_{th} is about 0.4 for diesel engines or large gas-turbine plants
- η_{th} is about 0.6 for large combined gas-steam power plants

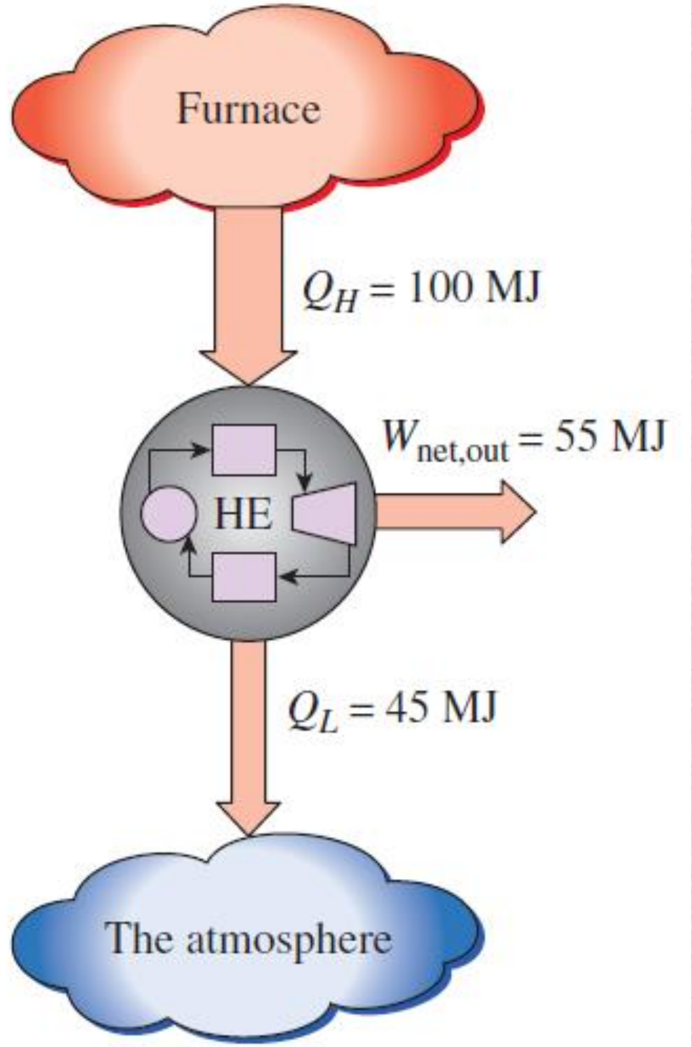
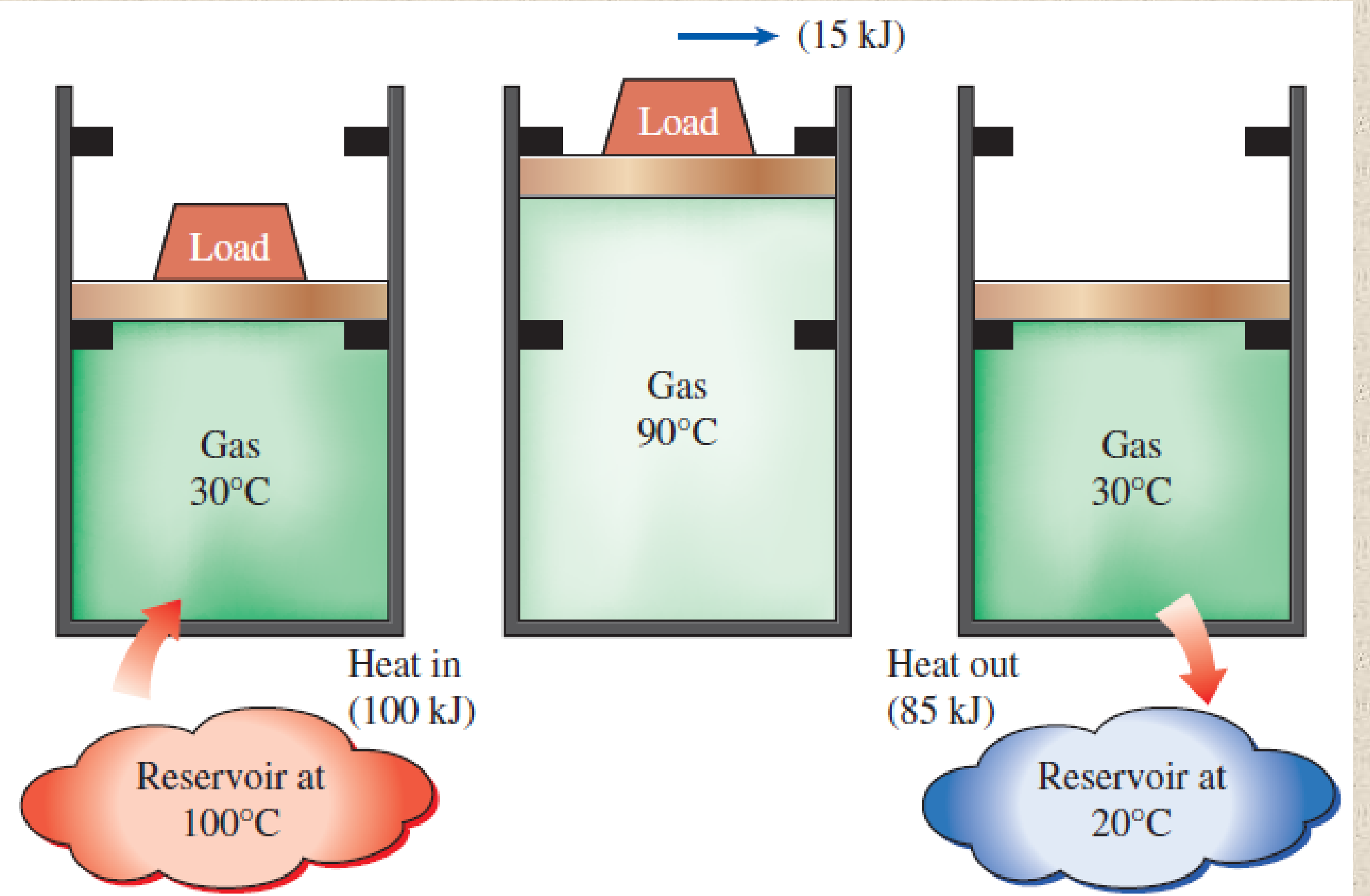


FIGURE 6–14
Even the most efficient heat engines reject almost one-half of the energy they receive as waste heat.

Can we save Q_{out}?

- 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**

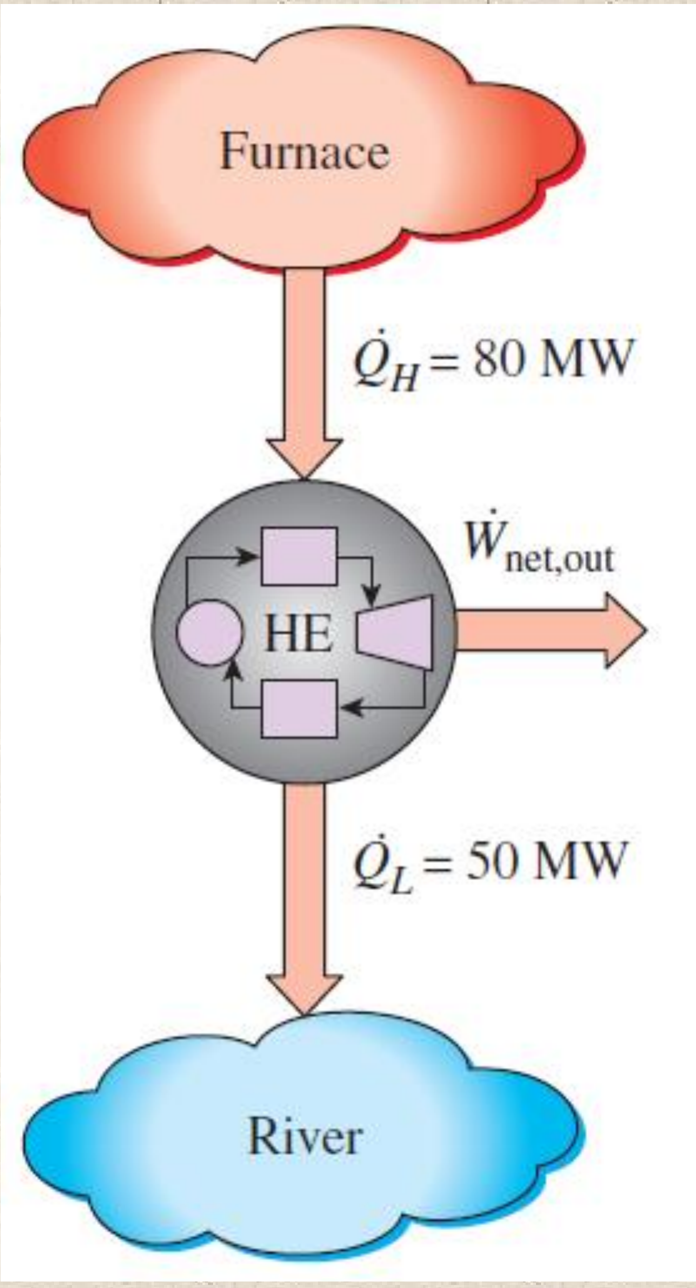


Every heat engine must ***waste*** some energy by transferring it to a low-temperature reservoir in order to complete the cycle, even under idealized conditions.

FIGURE 6–15
A heat-engine cycle cannot be completed without rejecting some heat to a low-temperature sink.

- The amount of heat supplied to the gas (100 kJ) is greater than the work done (15 kJ) since part of the heat supplied is used to raise the temperature of the gas (from 30 °C to 90 °C)
- ***Heat is always transferred from a high-temperature medium to a low-temperature one***, and never the other way round
- Therefore we cannot cool this gas from 90 °C to 30 °C by transferring heat to a reservoir at 100 °C
- Instead we have to bring the system into contact with a low-temperature reservoir, say 20 °C, so that gas ***can return to its initial state*** by rejecting its 85 kJ of excess energy as heat to this reservoir (called waste heat)
- *Heat engine must waste some energy by transferring it to a low temperature reservoir in order to complete the cycle, even under idealized conditions*

Example: Net Power Production of a Heat Engine



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

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

The Second Law of Thermodynamics: Kelvin–Planck Statement

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

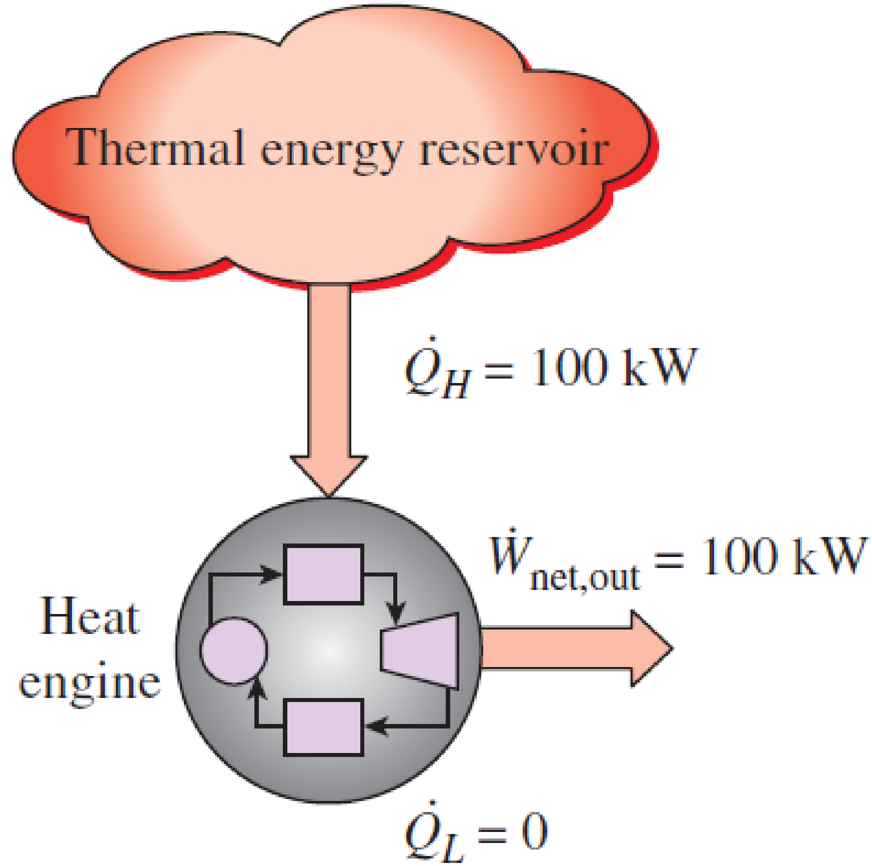


FIGURE 6–18
A heat engine that violates the Kelvin–Planck statement of the second law.

The Second Law of Thermodynamics: Kelvin–Planck Statement

- The heat engine must exchange heat with a low-temperature sink as well as a high-temperature source in order to keep operating
- *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

REFRIGERATORS

- We know that ***heat is transferred in the direction of decreasing temperature***, that is from high-temperature mediums to low temperature ones
- However, 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***

REFRIGERATORS

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

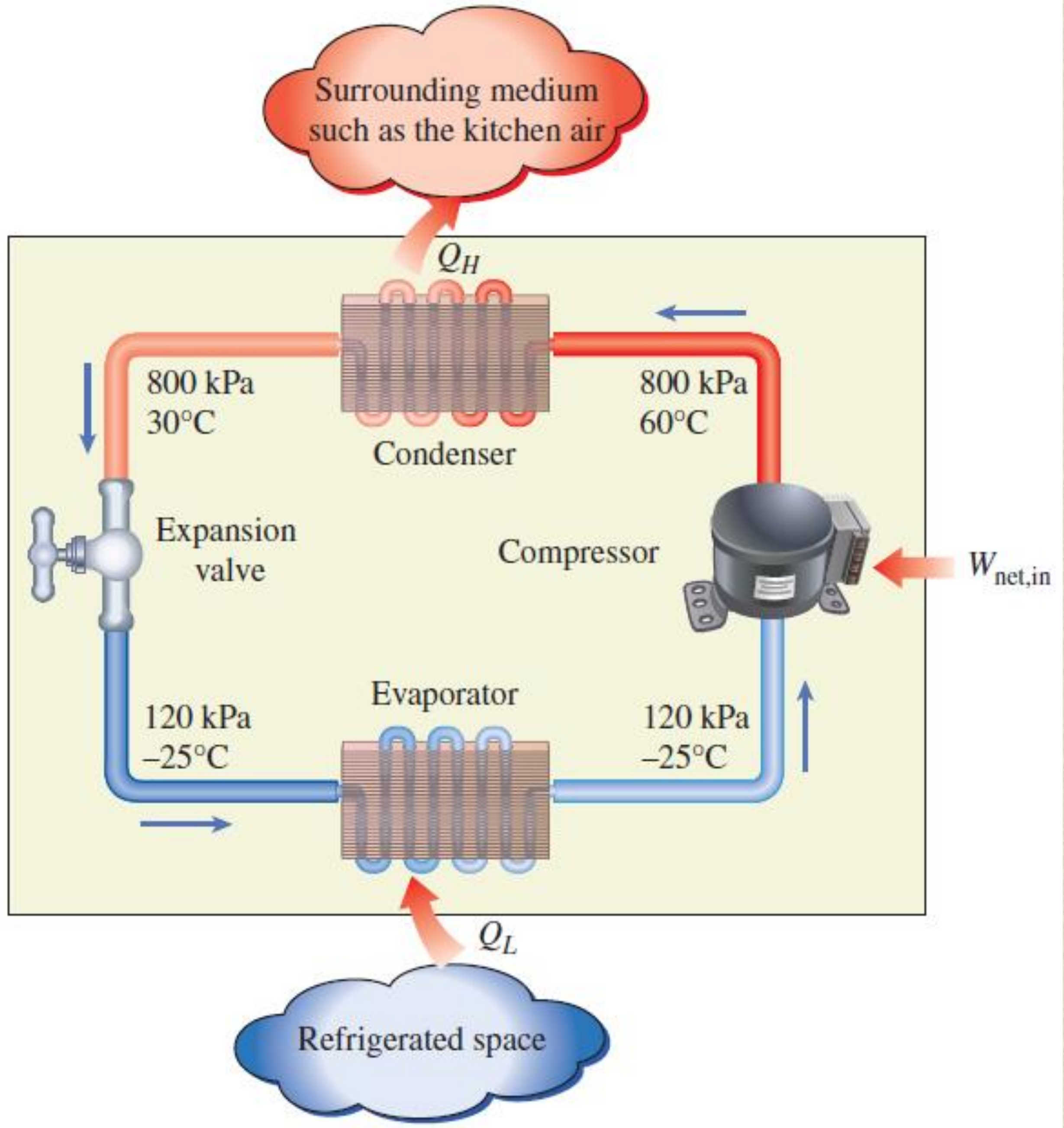


FIGURE 6–19
Basic components of a refrigeration system and typical operating conditions.

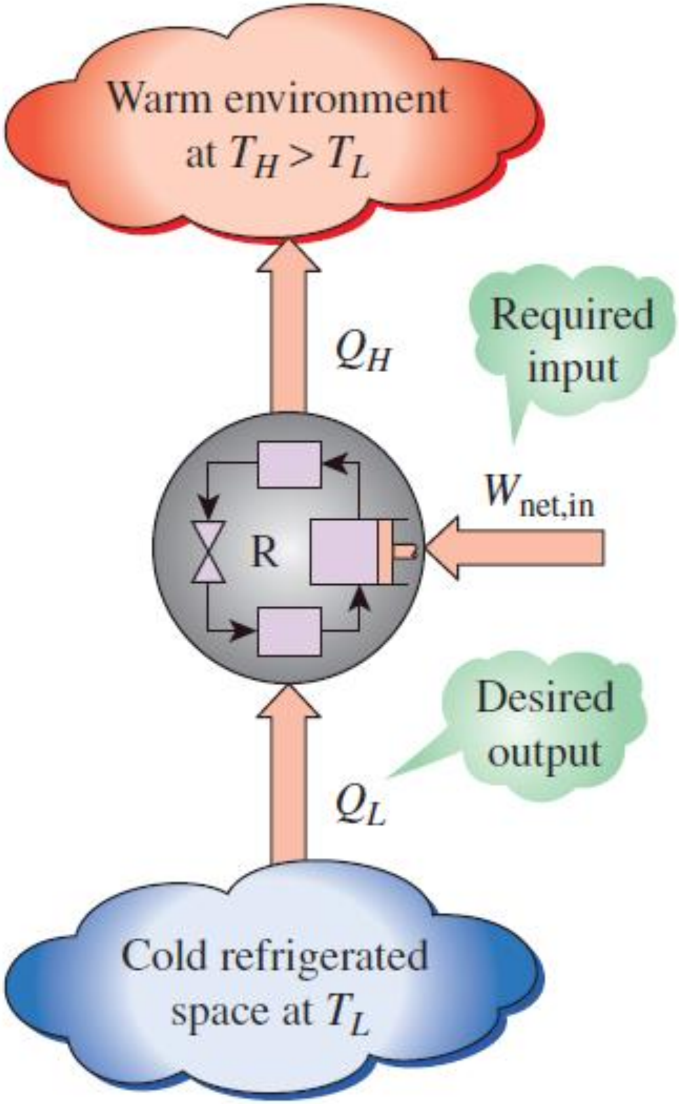


FIGURE 6–20

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

Coefficient of Performance

The ***efficiency*** of a refrigerator is expressed in terms of the **coefficient of performance (COP)**.

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

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

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

Notice that the value of $\mathrm{COP_R}$ can be greater than unity, equal to unity or less than unity

Air Conditioners

- **Air conditioners** are basically refrigerators whose refrigerated space is a room or a building instead of the food compartment
- The COP of a refrigerator (or air conditioner) decreases with decreasing refrigeration temperature
- Therefore, it is not economical to refrigerate to a lower temperature than needed

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Heat Pumps

- The objective of a refrigerator is to maintain the refrigerated space at a low temperature by removing heat from it
-
- **However, the objective of a heat pump is to maintain a heated space at a high temperature**

- Air conditioner, if installed backwards can act like heat pump

FIGURE 6–23

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

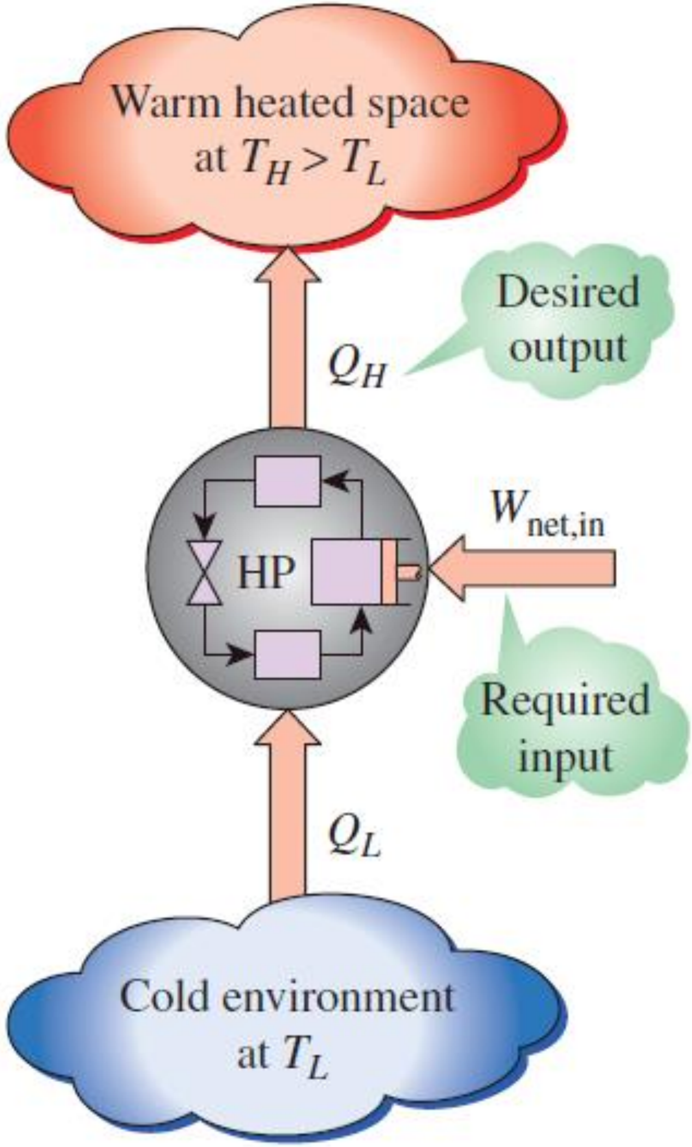


FIGURE 6–21

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

Heat Pumps

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

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

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

COP_{HP} is always greater than unity

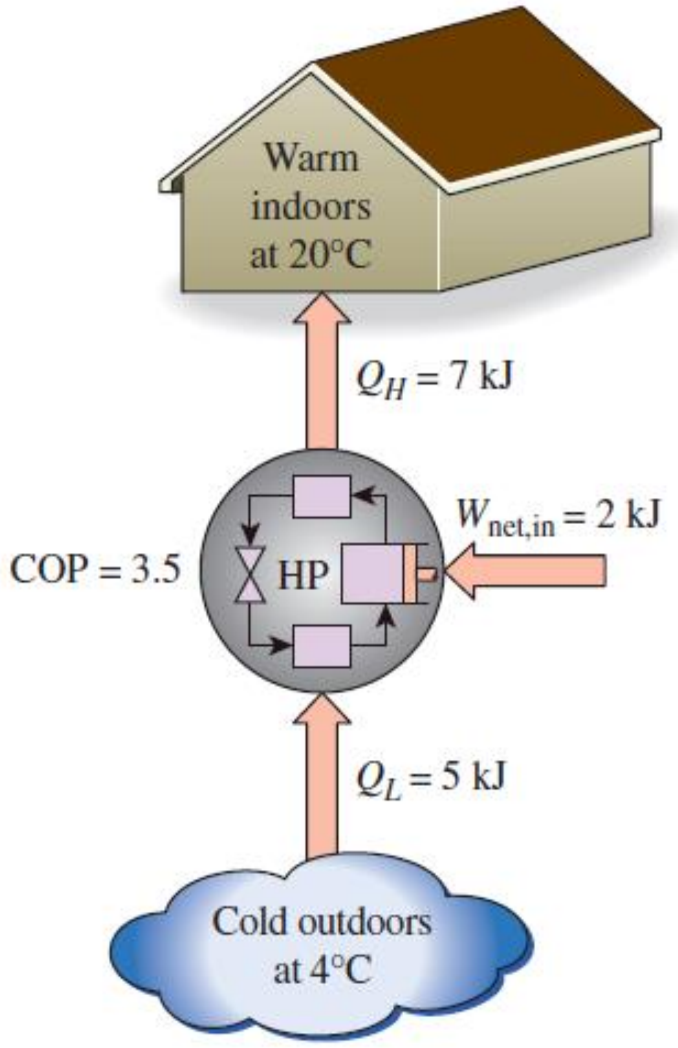


FIGURE 6–22
The work supplied to a heat pump is used to extract energy from the cold outdoors and carry it into the warm indoors.

- 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

The Second Law of Thermodynamics: Clausius Statement

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

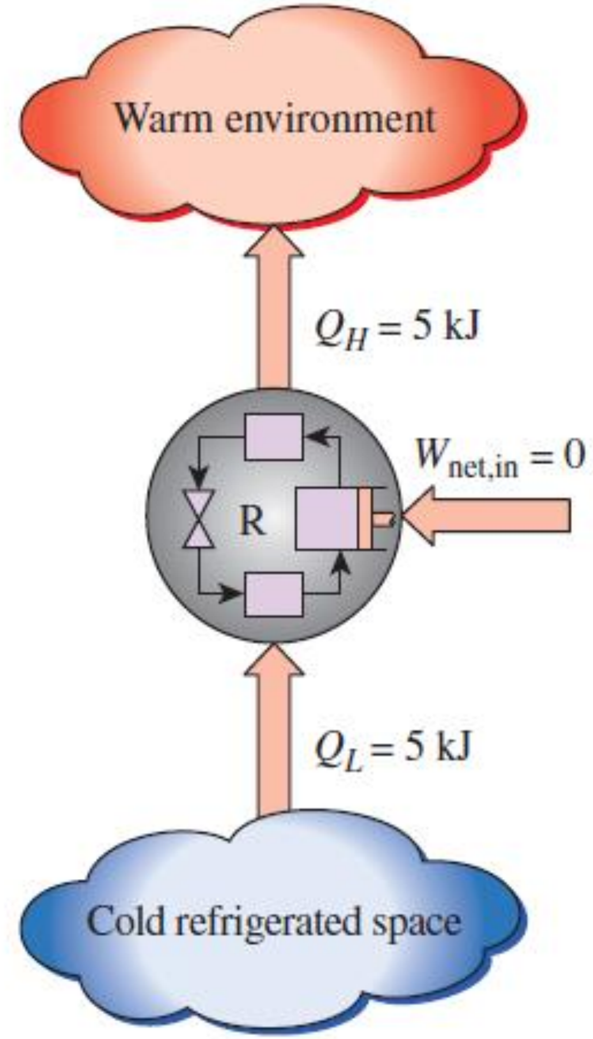


FIGURE 6–25
A refrigerator that violates the Clausius statement of the second law.

The Second Law of Thermodynamics: Clausius Statement

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

The Second Law of Thermodynamics:

Kelvin Planck Statement

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

Clausius Statement

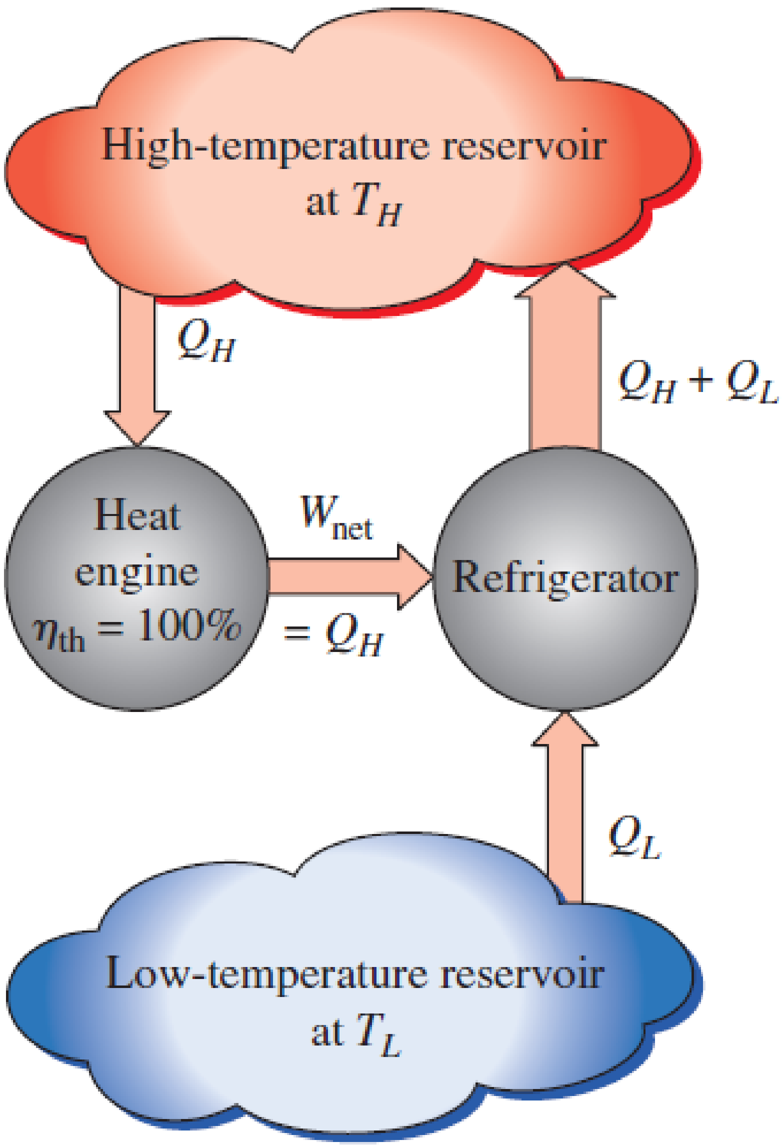
It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.

Equivalence of the two Statements

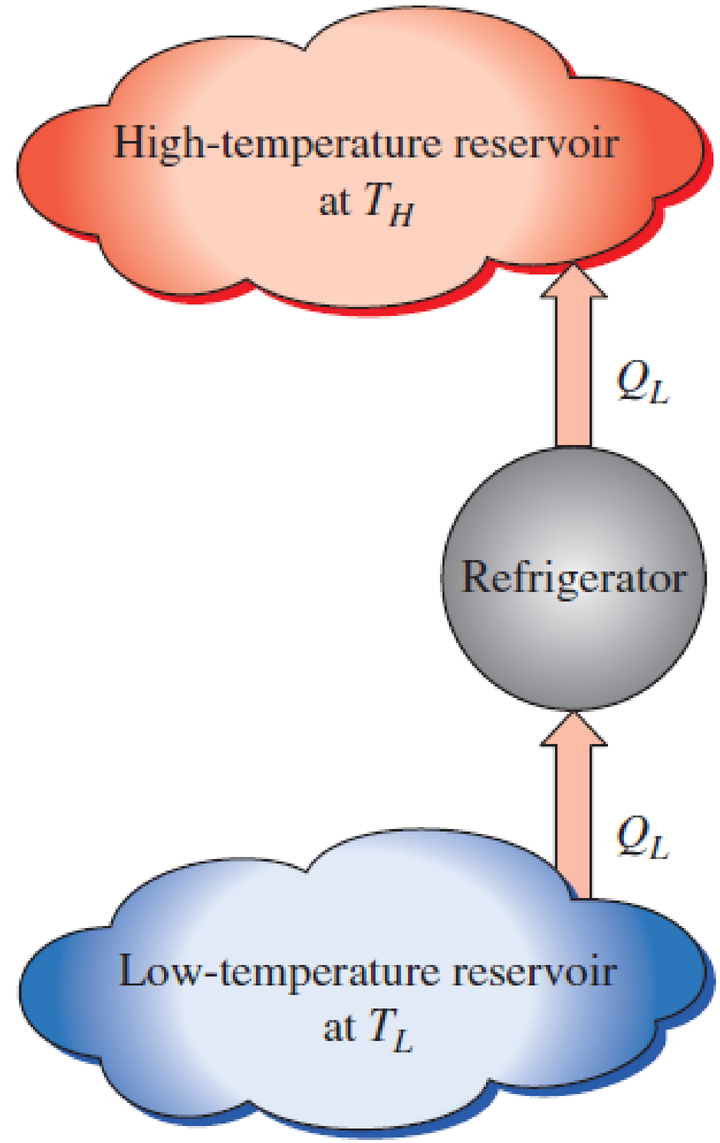
- The Kelvin–Planck and the Clausius statements are equivalent in their consequences, and either statement can be used as the expression of the second law of thermodynamics

- **Any device that violates the Kelvin–Planck statement also violates the Clausius statement, and vice versa**

Equivalence of the two Statements



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



(*b*) The equivalent refrigerator

PERPETUAL-MOTION MACHINES

- **Perpetual-motion machine (PMM):** Any device that violates the first or the second law
- A device that **violates the first law** (by *creating* energy) is called a **PMM1**
- A device that **violates the second law** is called a **PMM2**

Despite numerous attempts, no perpetual-motion machine is known to have worked

If something sounds too good to be true, it probably is

PERPETUAL-MOTION MACHINE – 1

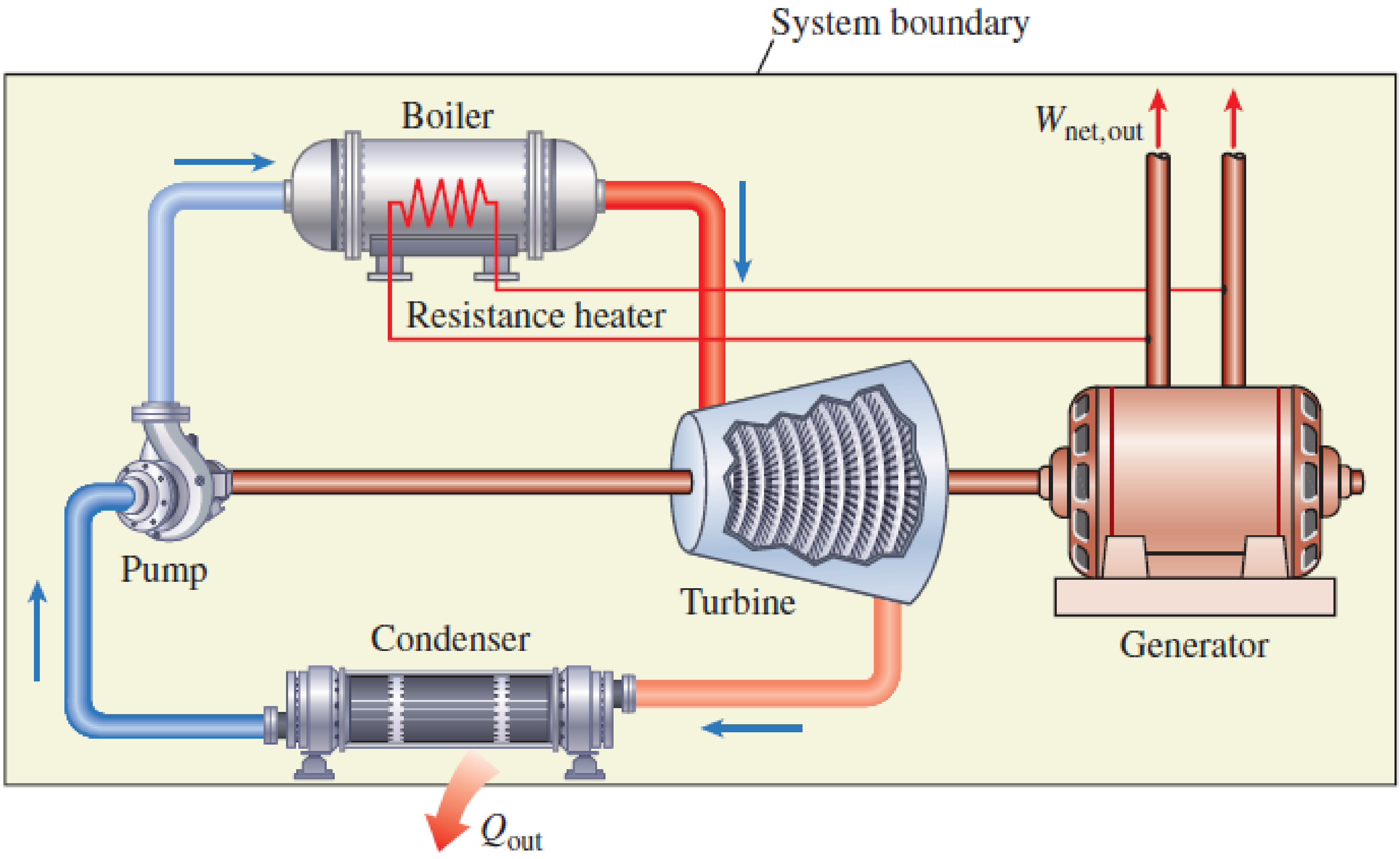


FIGURE 6–27
A perpetual-motion machine that violates the first law of thermodynamics (PMM1).

PERPETUAL-MOTION MACHINE – 2

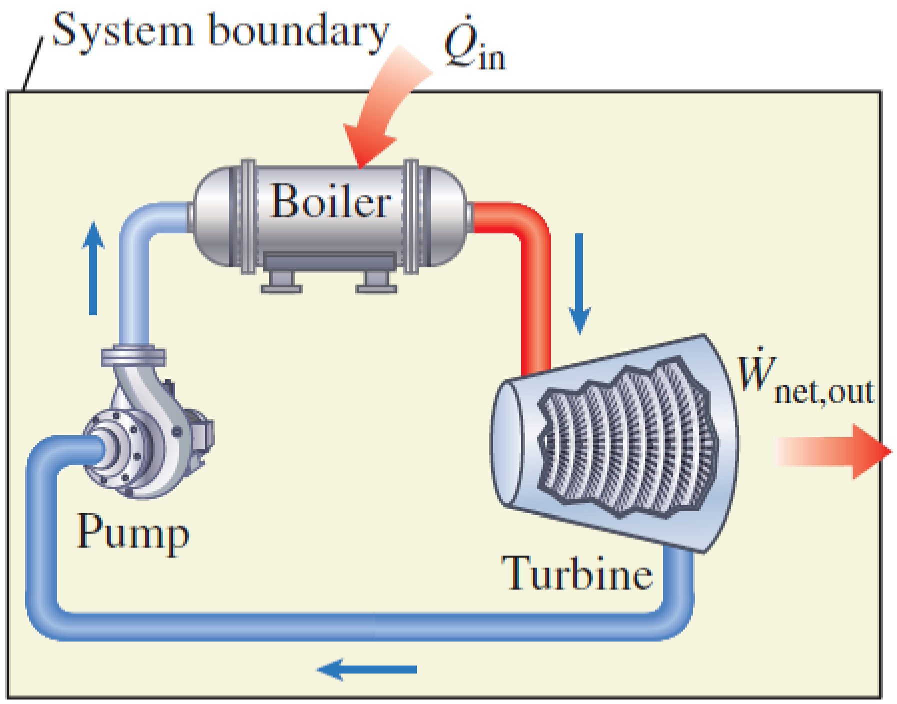


FIGURE 6–28

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

REVERSIBLE AND IRREVERSIBLE PROCESSES

The second law of thermodynamics states that no heat engine can have an efficiency of 100 percent, then what is the highest efficiency that a heat engine can possibly have?

Lets first define an idealized process, called the ***reversible process***

Reversible process: *A process that can be reversed without leaving any trace on the surroundings.* That is ***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 work exchange between the system and the surroundings is zero for the combined (original and reverse) process

Irreversible process: A process that is not reversible

REVERSIBLE AND IRREVERSIBLE PROCESSES

- Note that a system can be restored to its initial state following another process, regardless of whether the original process is reversible or irreversible

- But for reversible processes, this restoration is made without leaving any net change on the surroundings, whereas for irreversible processes, the surroundings usually do some work on the system and therefore does not return to their original state

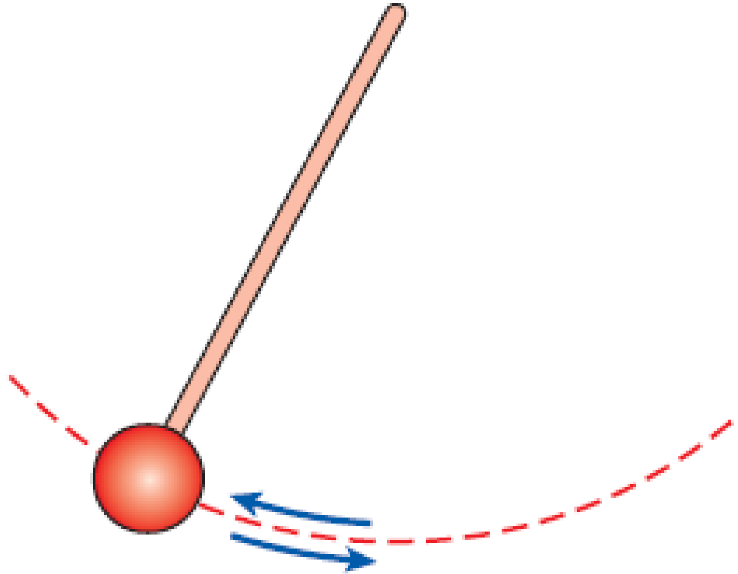
REVERSIBLE AND IRREVERSIBLE PROCESSES

- Reversible processes do not actually occur in nature. They are mere ***idealizations*** of actual processes
- Reversible processes can be approximated by actual devices, but they can never be achieved
- All the processes occurring in nature are irreversible
- ***Why are we interested*** **in reversible processes?**

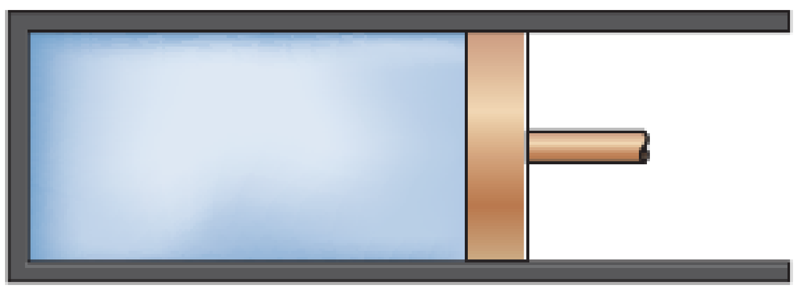
(1) they are easy to analyze since a system passes through a series of equilibrium states during a reversible process

(2) they serve as idealized models (theoretical limits) to which actual processes can be compared

- Some processes are more irreversible than others. We may never be able to have a reversible process, but we can certainly approach it



(*a*) Frictionless pendulum

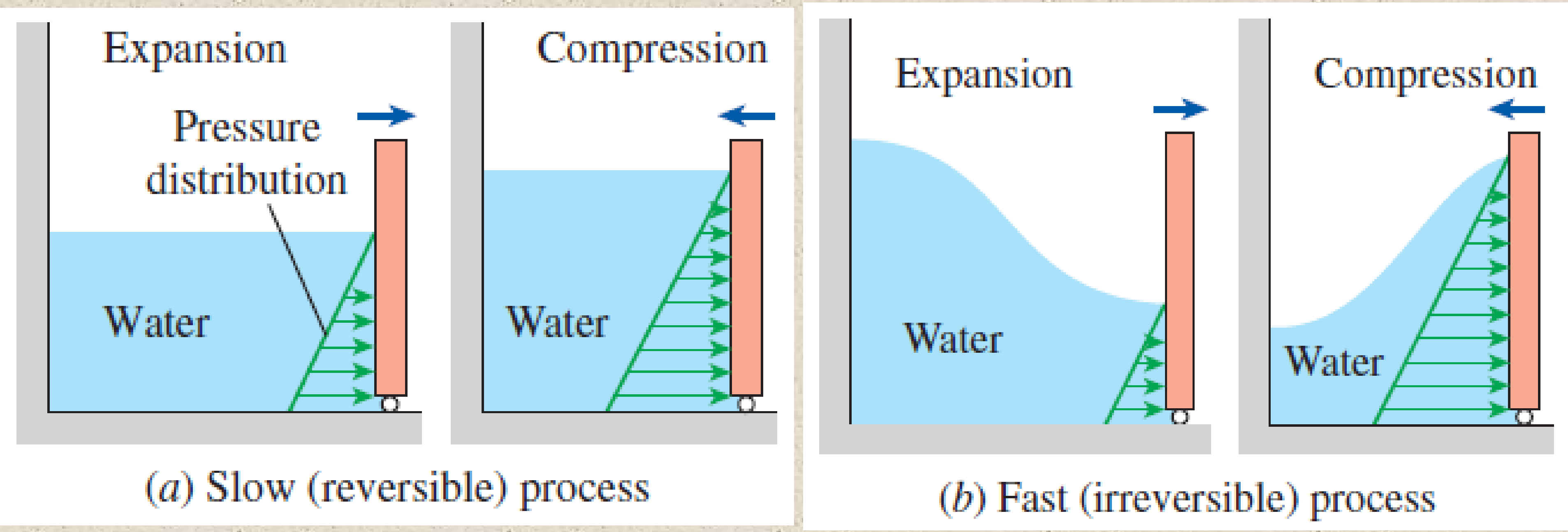


(*b*) Quasi-equilibrium expansion and compression of a gas

FIGURE 6–29

Two familiar reversible processes.

REVERSIBLE AND IRREVERSIBLE PROCESSES



(*a*) Slow (reversible) process

(*b*) Fast (irreversible) process

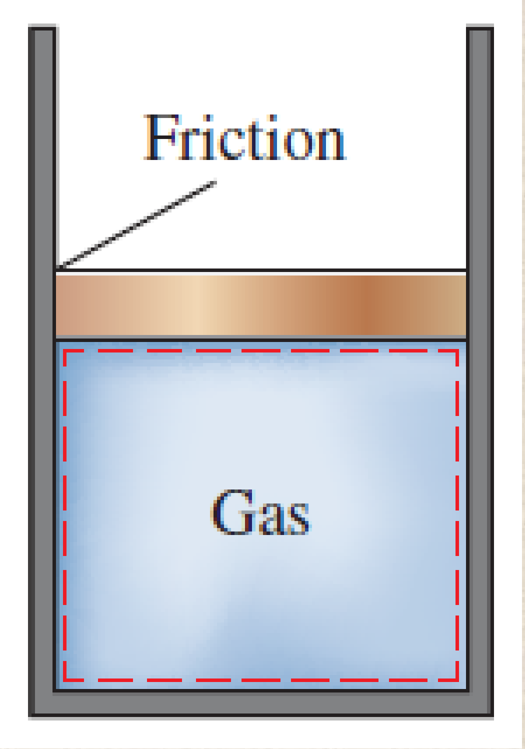
The more closely we approximate a reversible process, the more work delivered by a work-producing device or the less work required by a work-consuming device

Irreversibilities

- The factors that cause a process to be irreversible are called **irreversibilities**
- They include
  - ✓ friction
  - ✓ heat transfer across a finite temperature difference
  - ✓ unrestrained expansion, fast (nonquasi-equilibrium) compression and expansion
  - ✓ mixing of two fluids
  - ✓ electric resistance
  - ✓ inelastic deformation of solids
  - ✓ chemical reactions
- The presence of any of these effects renders a process irreversible

Irreversibilities - Friction

Friction renders a process irreversible

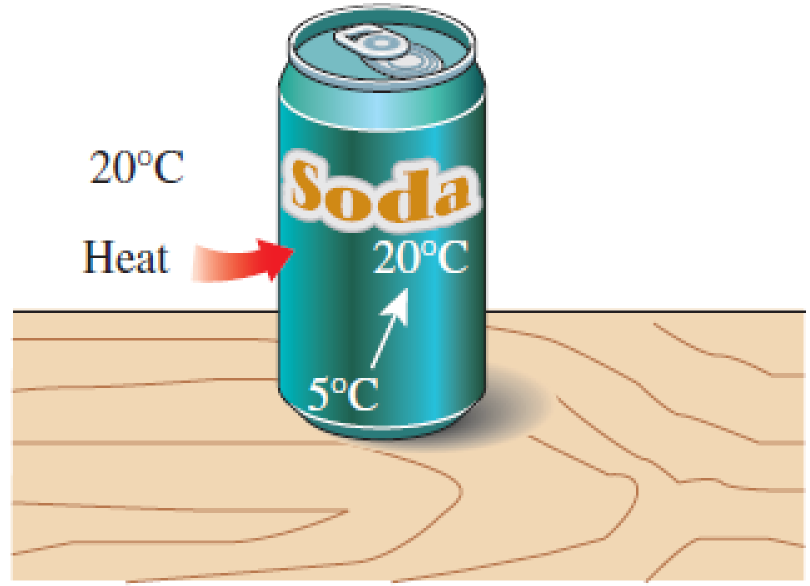


- When two bodies in contact are forced to move relative to each other, a friction force that opposes the motion develops at the interface of these two bodies, and some *work is needed to overcome this friction force*
- *The energy supplied as work is eventually converted to heat* during the process and is transferred to the bodies in contact, as evidenced by a temperature rise at the interface
- When the direction of motion is reversed, the bodies are restored to their original position, but the interface does not cool, and *heat is not converted back to work*.
- Since the system (the moving bodies) and the surroundings cannot be returned to their original states, this process is irreversible

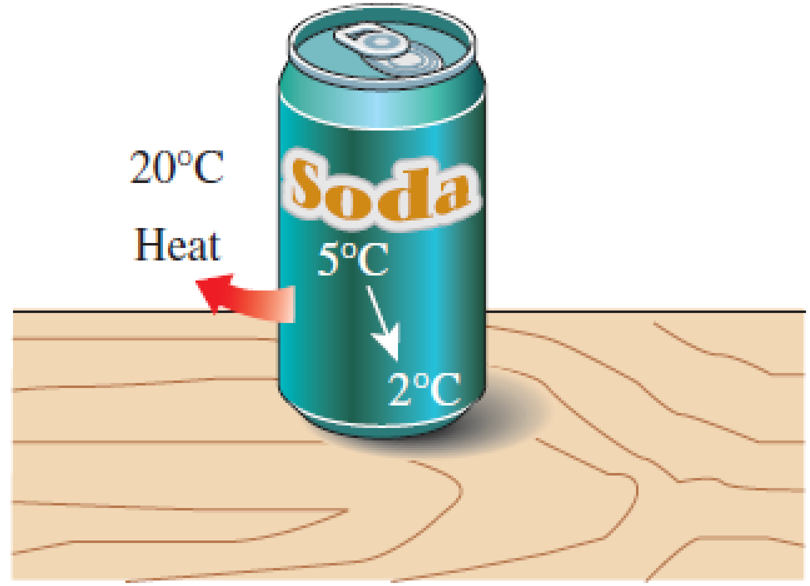
Irreversibilities – Heat transfer across a finite temperature difference

- The only way this process can be reversed and the soda restored to its original temperature is to provide refrigeration, which requires some work input
- At the end of the reverse process, the soda will be restored to its initial state, but the surroundings will not be

(*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

Irreversibilities – Heat transfer across a finite temperature difference

- Heat transfer can occur only when there is a temperature difference between a system and its surroundings
- Therefore, *it is physically impossible to have a reversible heat transfer process*
- But a heat transfer process becomes less and less irreversible as the temperature difference between the two bodies approaches zero
- Then, heat transfer through a differential temperature difference dT can be considered reversible
- As *dT approaches zero, the process can be reversed in direction (at least theoretically) without requiring any refrigeration*

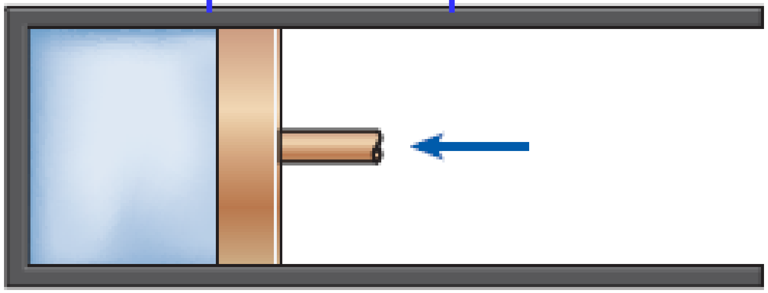
Irreversibilities – Heat transfer across a finite temperature difference

- The smaller the temperature difference between two bodies, the smaller the heat transfer rate will be
- *Any significant het transfer through a small temperature difference requires a very large surface area and a very long time*
- Therefore, even though approaching reversible heat transfer is desirable from a thermodynamic point of view, it is impractical and not economically feasible

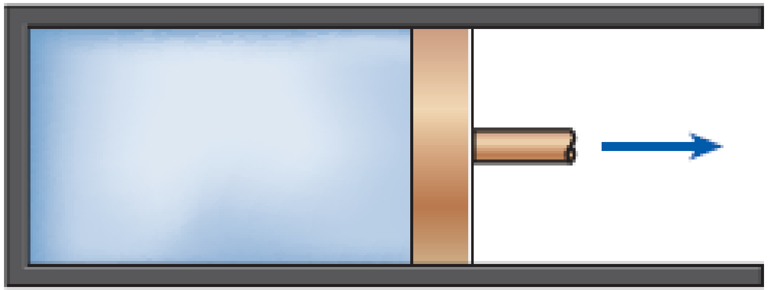
Irreversibilities – Unrestrained expansion / Fast compression/expansion

- In unrestrained expansion, when the membrane is ruptured, the gas fills the entire tank
- Restoring the system (gas) to original state is to compress it to its initial volume while transferring heat from the gas until it reaches its initial temperature
- Amount of heat transferred from the gas equals the amount of work done on the gas by the surroundings, but the heat cannot be converted to work completely to restore the surroundings

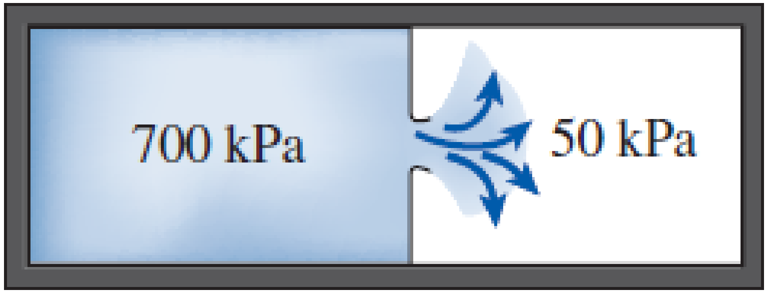
Irreversible compression and expansion processes



(*a*) Fast compression



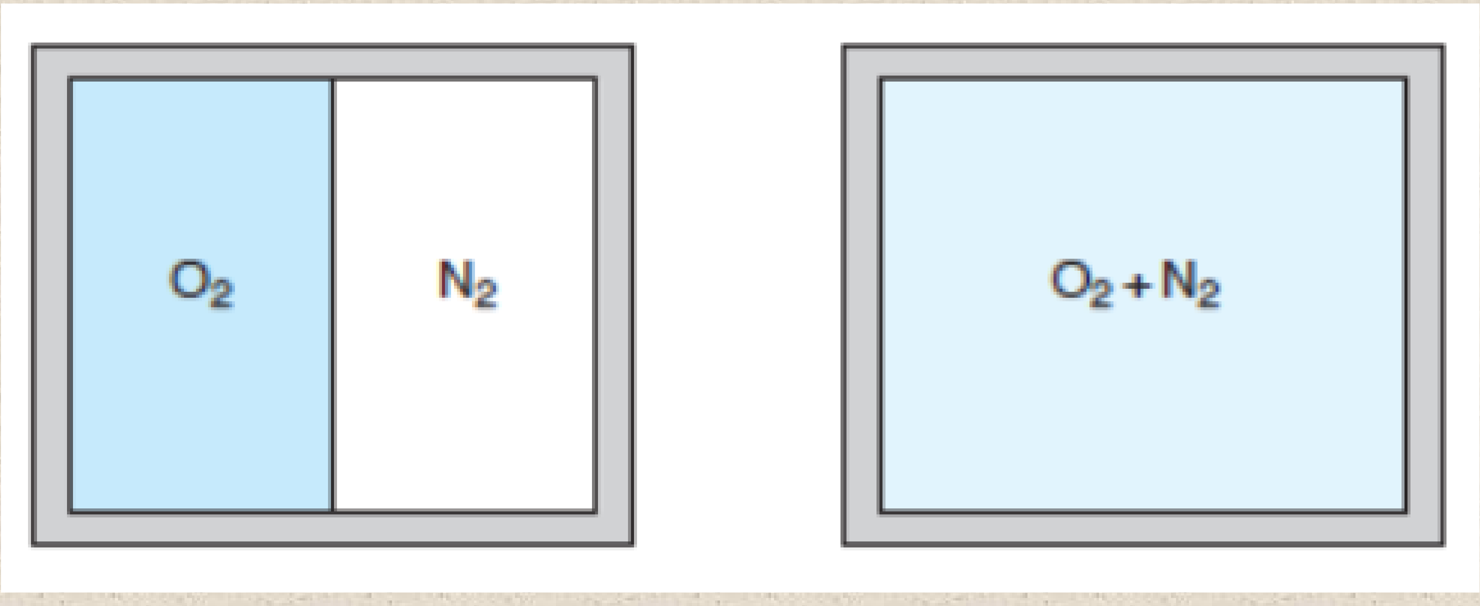
(*b*) Fast expansion



(*c*) Unrestrained expansion

Irreversibilities – Mixing of two fluids

Mixing of two fluids



- To separate gases into its constituents will require work

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 (or simply 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

- **Internally reversible process:** If no irreversibilities occur ***within the boundaries of the system*** during the process
- During an internally reversible process, a system proceeds through a series of equilibrium states, and when the process is reversed system passes through exactly the same equilibrium states while returning to the initial state
- That is the *paths of the forward and reverse processes coincide for an internally reversible process*
- The quasi-equilibrium process is an example of an internally reversible process

Totally Reversible Processes

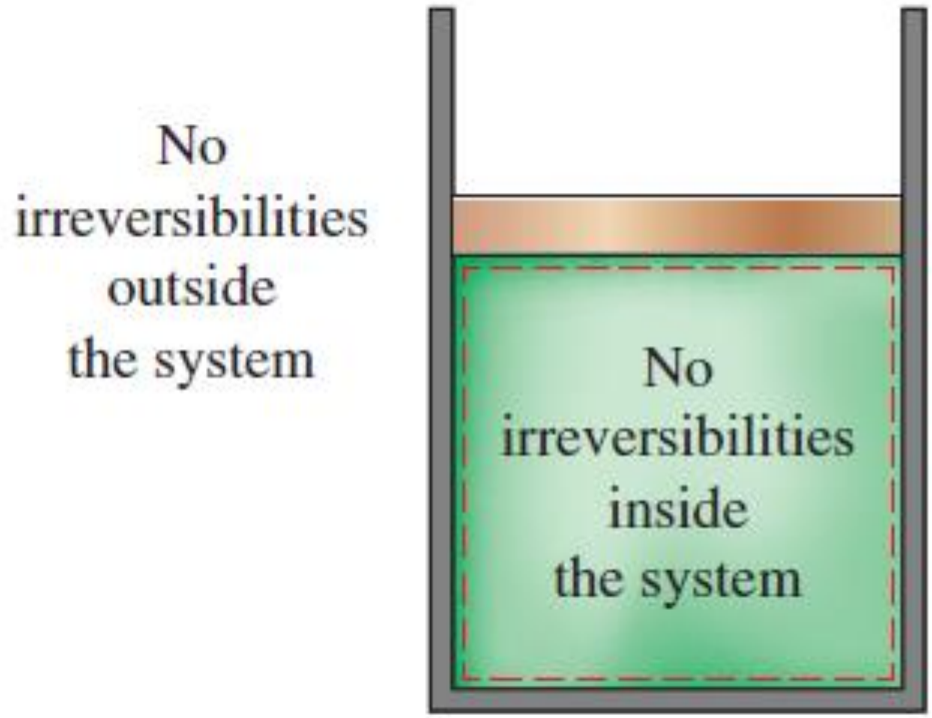
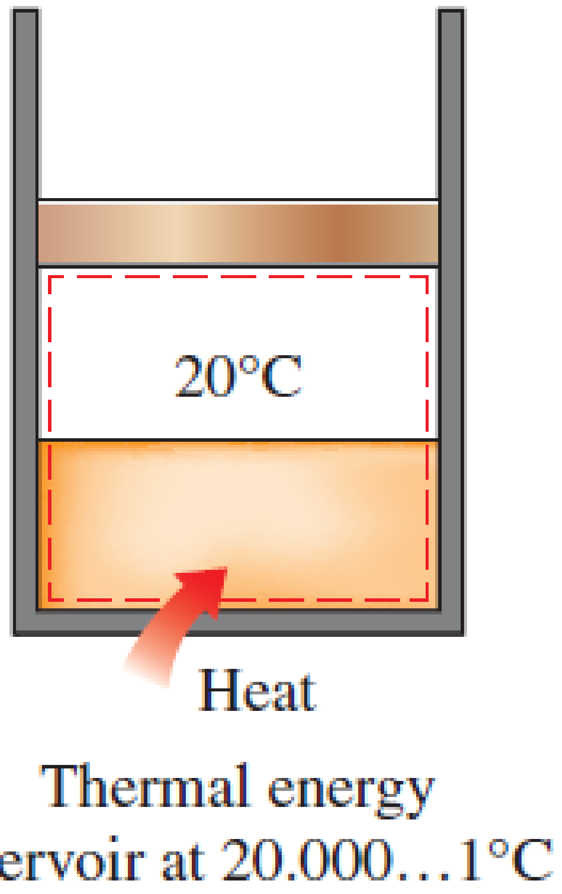


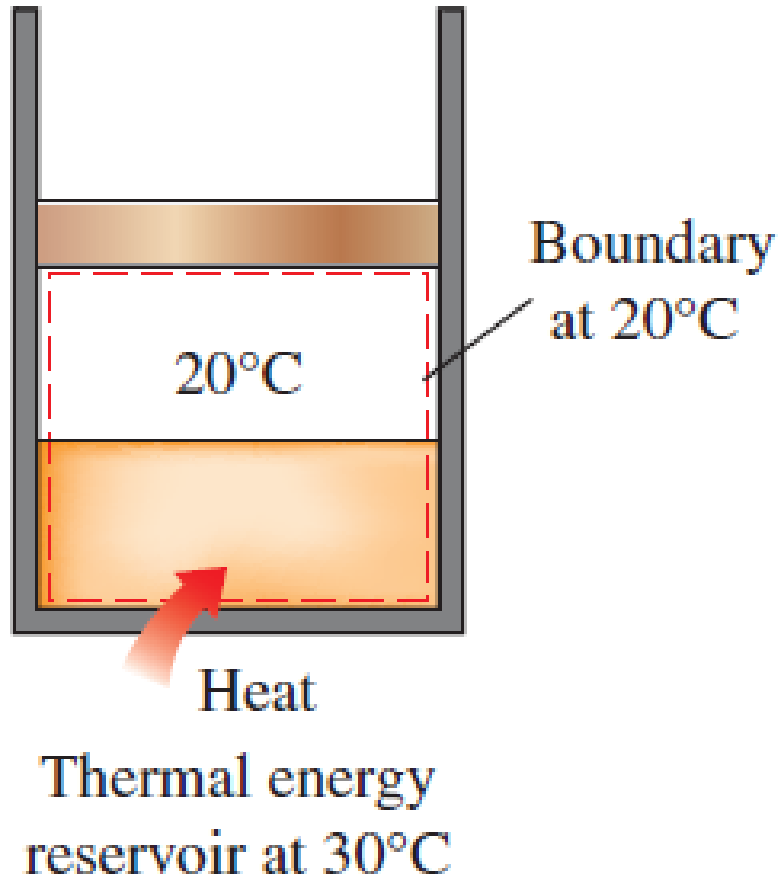
FIGURE 6–34

A reversible process involves no internal and external irreversibilities.

Internally and Externally Reversible Processes



(*a*) Totally reversible



(*b*) Internally reversible

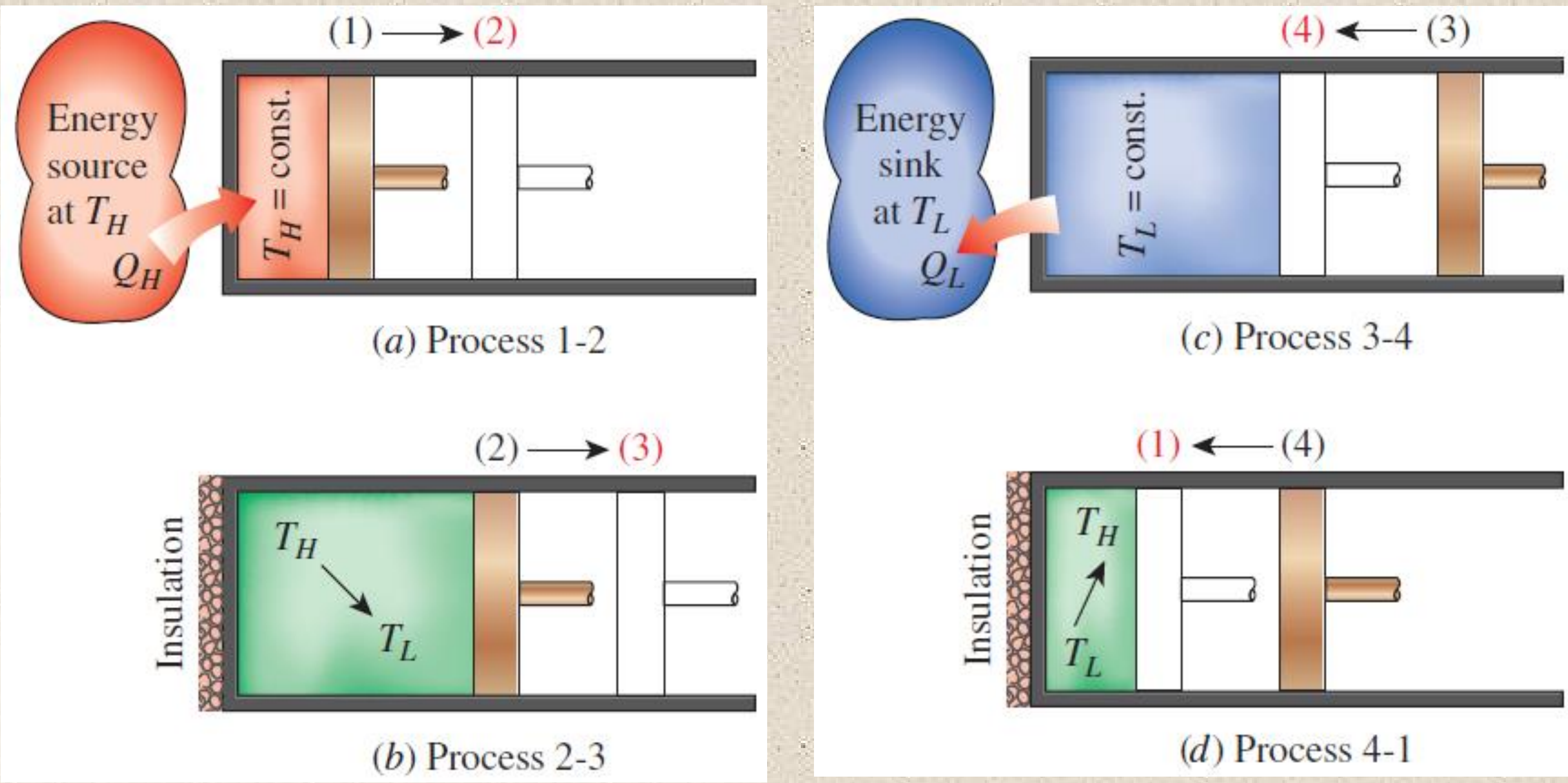
FIGURE 6–35

Totally and internally reversible heat transfer processes.

REVERSIBLE CYCLE

- Heat engines are cyclic devices, i.e. the working fluid of a heat engine returns to its initial state at the end of each cycle
- *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 works is the net work delivered by the heat engines
- The net work, *thus the cycle efficiency, can be maximized by using processes that require least amount of work and deliver the most*, that is, by using reversible processes
- Hence, *most efficient cycles are reversible cycles*, that is, cycles that consist entirely of reversible processes
- Reversible cycles provide upper limits on the performance of real cycles
- Probably the best known reversible cycle is the **Carnot cycle**

THE CARNOT CYCLE



(*a*) Process 1-2

(*b*) Process 2-3

(*c*) Process 3-4

(*d*) Process 4-1

Execution of the Carnot cycle in a closed system

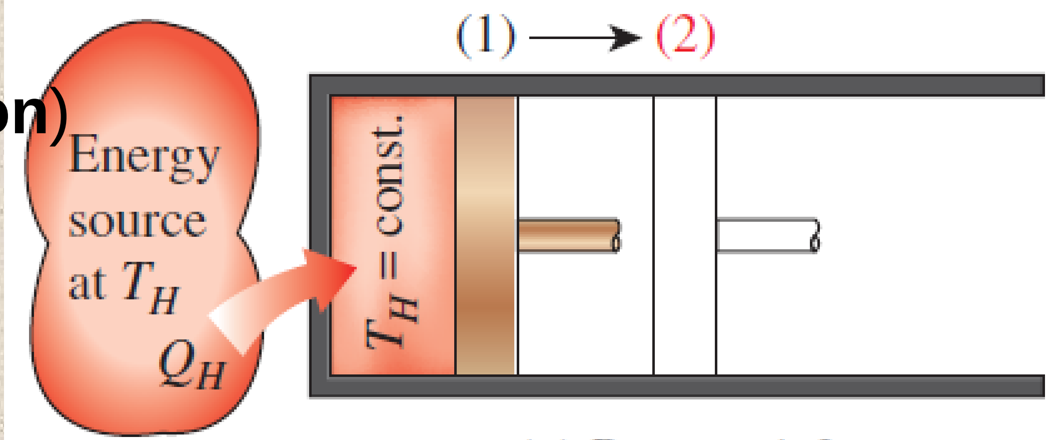
Reversible Isothermal Expansion (with **heat addition**) (process 1-2, T_H = constant)
Reversible Adiabatic Expansion (process 2-3, temperature drops from T_H to T_L)
Reversible Isothermal Compression (with **heat rejection**) (process 3-4, T_L = constant)
Reversible Adiabatic Compression (process 4-1,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

Carnot Cycle

- ***The Carnot heat-engine cycle is a totally reversible cycle***
- Carnot cycle is composed of four reversible processes – two isothermal and two adiabatic
- It can be executed in a closed or a steady flow system
- Being a reversible cycle, the *Carnot engine is the most efficient engine operating between two specified temperature limits*
- Even though the Carnot engine cannot be achieved in reality, the efficiency of actual cycles can be improved by attempting to approximate the Carnot cycle more closely

Reversible Isothermal Expansion (with **heat addition**) (process 1-2, T_H = constant)

Note that this is a *quasi-equilibrium process and the piston is frictionless*



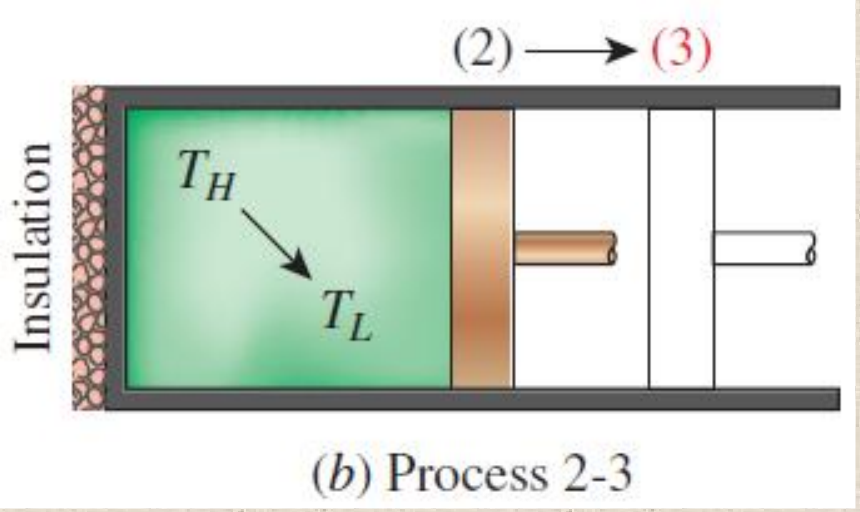
(*a*) Process 1-2

Initially (state 1), the temperature of the gas is T_H and the cylinder head is in close contact with a source at temperature T_H

The gas is allowed to *expand slowly*, doing work on the surroundings. As the gas expands, the temperature of the gas tends to decrease. But as soon as the temperature drops by an infinitesimal amount dT, some heat is transferred from the reservoir into the gas, raising the gas temperature to T_H. Thus ***the gas temperature is kept constant at T_H***

*Since the temperature difference between the gas and the reservoir never exceeds a differential amount dT, this is a **reversible heat transfer process**.* This continues till the gas is at state 2

Reversible Adiabatic Expansion (process 2-3, temperature drops from T_H to T_L)



At state 2, the reservoir that was in contact with the cylinder head is removed and replaced by insulation so that the *system becomes adiabatic*

The gas continues to *expand slowly*, doing work on the surroundings until its temperature drops from T_H to T_L (state 3)

The piston is assumed to be frictionless and the process to be quasi-equilibrium, so ***the process is reversible***

Reversible Isothermal Compression (with **heat rejection**) (process 3-4, T_L = constant)

Note that this is a *quasi-equilibrium process and piston is frictionless*

(c) Process 3-4

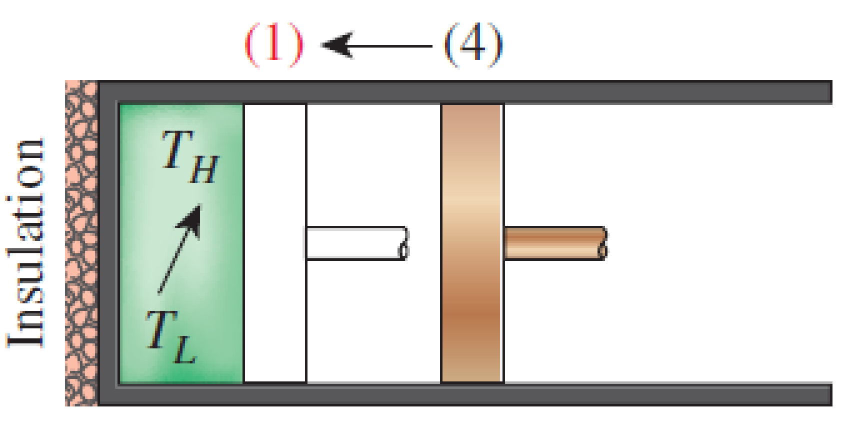
At state 3, the insulation at the cylinder head is removed, and the cylinder is brought in contact with a sink at temperature T_L

Now the piston is pushed inward by an external force, doing work on the gas

As gas is compressed its temperature tends to rise, but as a soon as it rises by an infinitesimal amount dT, heat is transferred from the gas to the sink, causing the gas temperature to drop to T_L. **Thus the gas temperature remains constant at T_L**

*Since the temperature difference between the gas and the sink never exceeds a differential amount dT, this is a **reversible heat transfer process**.* This continues until piston reaches state 4

Reversible Adiabatic Compression (process 4-1, temperature rises from T_L to T_H)



(*d*) Process 4-1

State 4 is such that when the low-temperature reservoir is removed, the insulation is put back on the cylinder head, and the *gas is compressed in a reversible manner*, the gas returns to its initial state (state 1) which completes the cycle

*The piston is assumed to be frictionless and the process to be quasi-equilibrium, so **the process is reversible***

Carnot Cycle

- Area under the curve 1-2-3 is the *work done by the gas* during the expansion part of the cycle
- The area under the curve 3-4-1 is the *work done on the gas* during the compression part of the cycle
- *The area enclosed by the path of the cycle (area 1-2-3-4-1) is the difference between these two areas and represents the* ***net work done during the cycle***

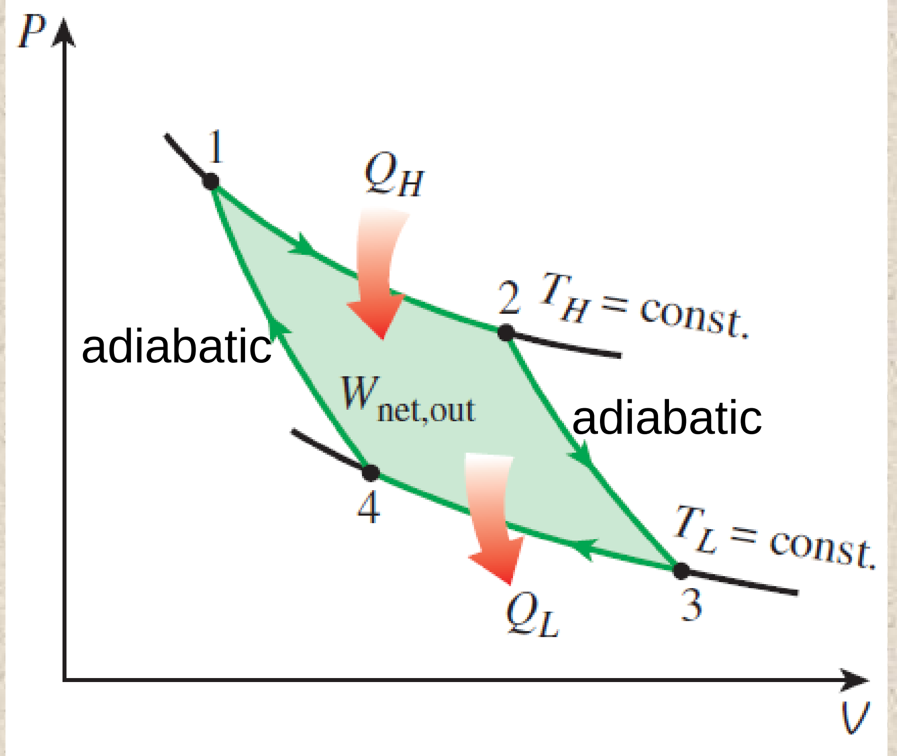


FIGURE 6–37

P-*V* diagram of the Carnot cycle.

Can we save Q_L?

- In an effort to save Q_L if we do not reject Q_L and compress the gas adiabatically at state 3, we would end up back at state 2, retracing the process path 3-2. We would not be rejecting any heat as process 3-2 is adiabatic
- After reaching state 2, to complete the cycle (and reach state 1) we need to reject Q_H amount heat isothermally retracing the process path 2-1

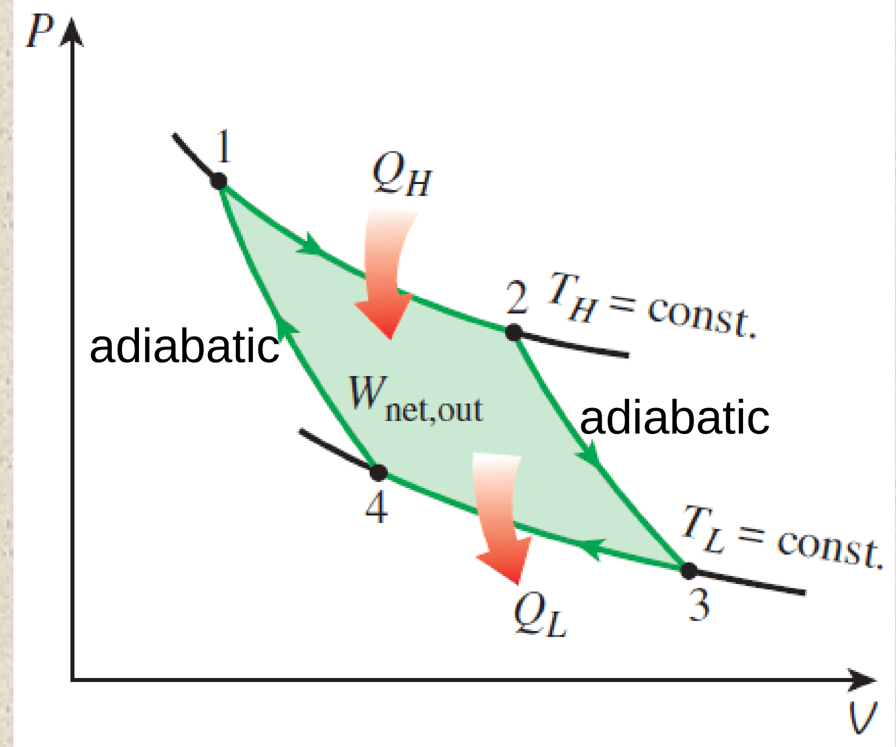


FIGURE 6–37
P-V diagram of the Carnot cycle.

- In this case the *area enclosed by the path of the cycle (area 1-2-3-2-1) will be zero,* hence, we will not be able to obtain any net work output from this engine

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**

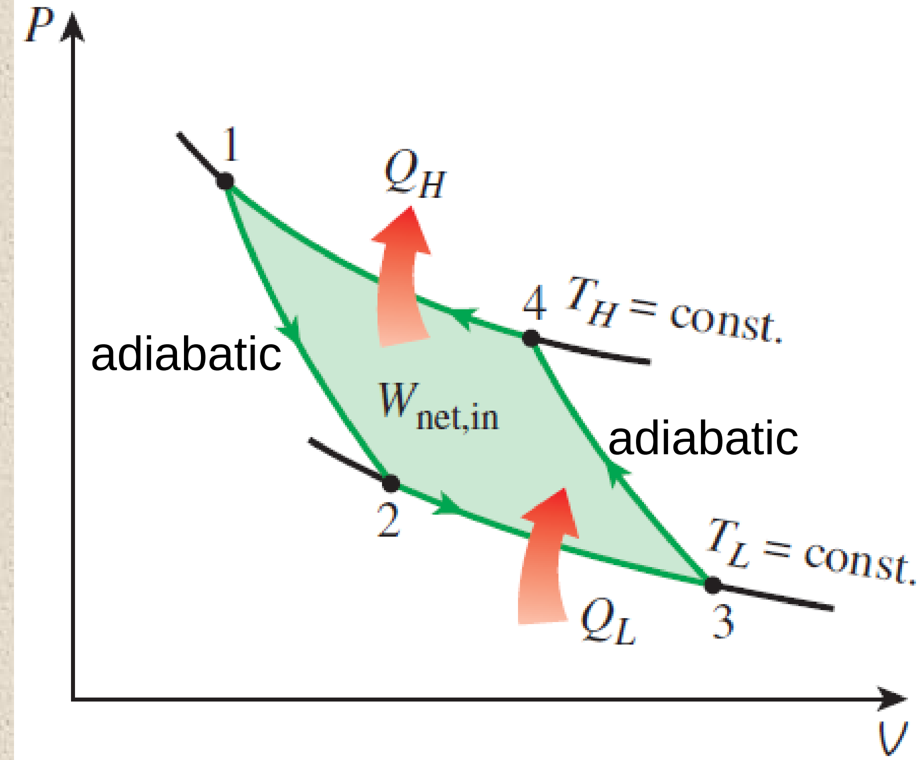


FIGURE 6–38
P-*V* diagram of the reversed Carnot cycle.

THE CARNOT PRINCIPLES

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

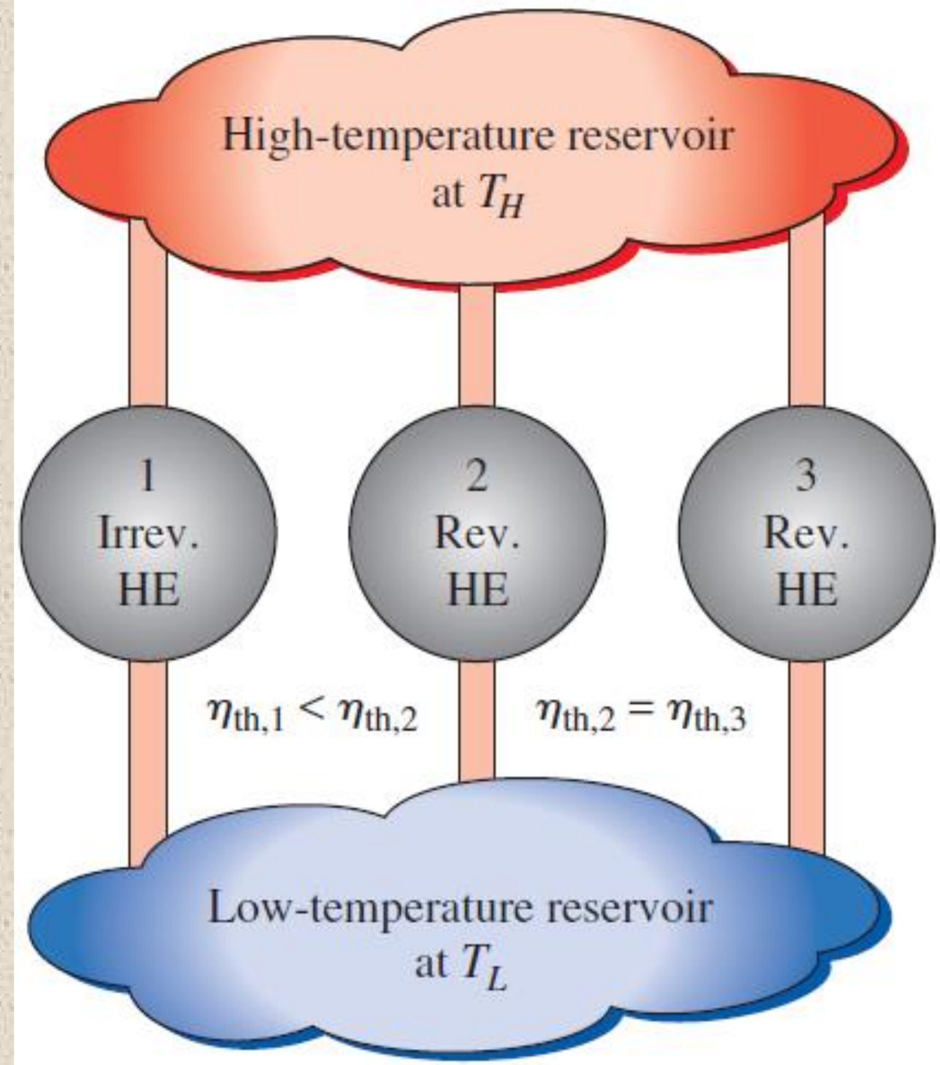
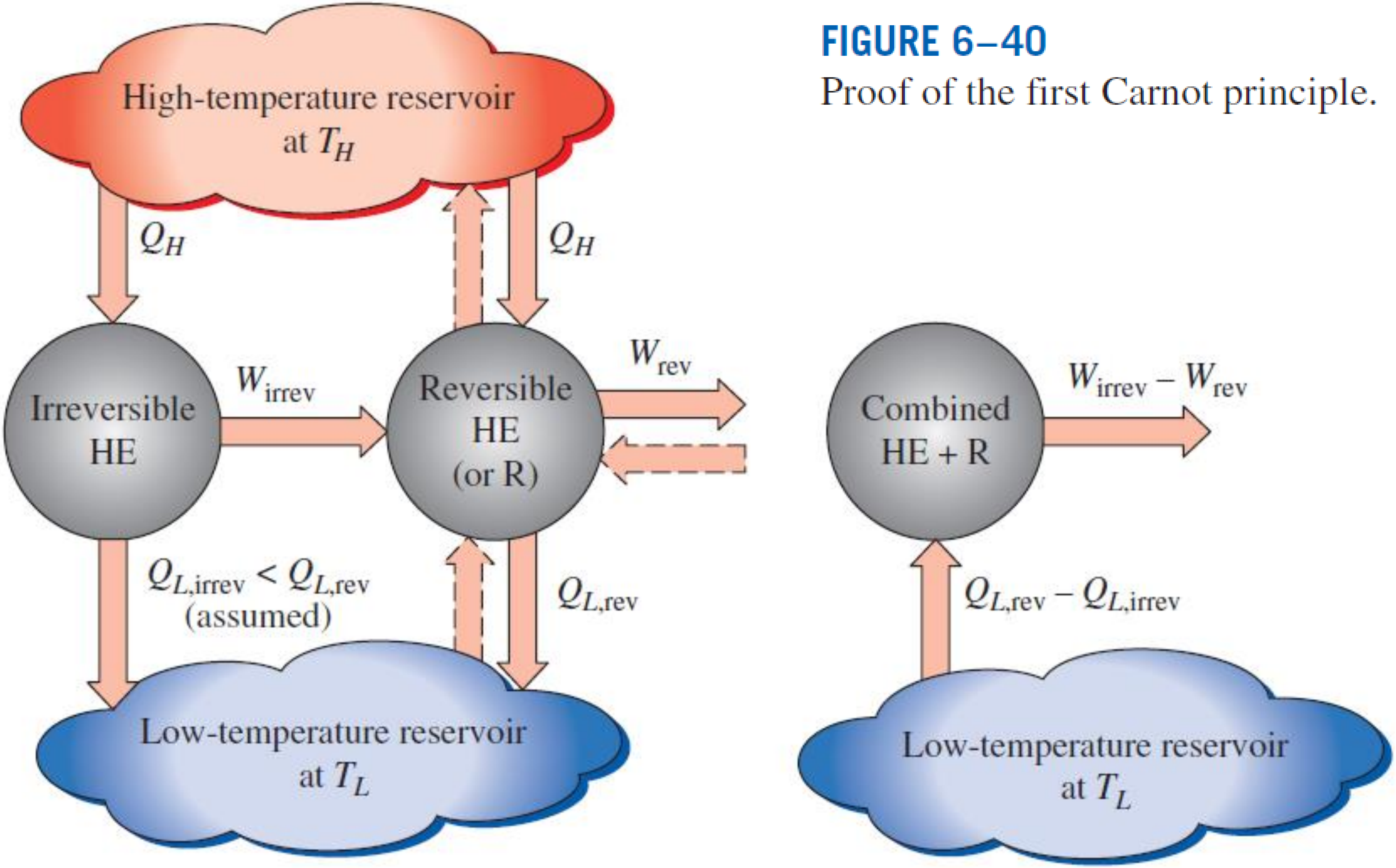


FIGURE 6–39
The Carnot principles.

FIGURE 6–40
Proof of the first Carnot principle.



(*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

PROOF OF CARNOT PRINCIPLES

Consider two heat engines operating between the same reservoirs, one engine is reversible and the other is irreversible

Now 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 of work produced by irreversible one is W_{irrev}

In violation of the first Carnot principle*, we assume that the irreversible heat engine is more efficient than the reversible one (i.e. $\eta_{th,irrev} > \eta_{th,rev}$)* thus, $W_{irrev} > W_{rev}$

Now let the reversible engine be reversed and operate as refrigerator

Now 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*, therefore ***our initial assumption that $\eta_{th,irrev} > \eta_{th,rev}$ is incorrect***

The second Carnot principle can also be proved in a similar manner by replacing the irreversible engine in the previous case by another reversible engine that is more efficient and thus delivers more work than the first reversible engine

Therefore, we conclude that no reversible heat engine can be more efficient than a reversible one operating between the same two reservoirs, regardless of how the cycle is completed or the kind of working fluid used

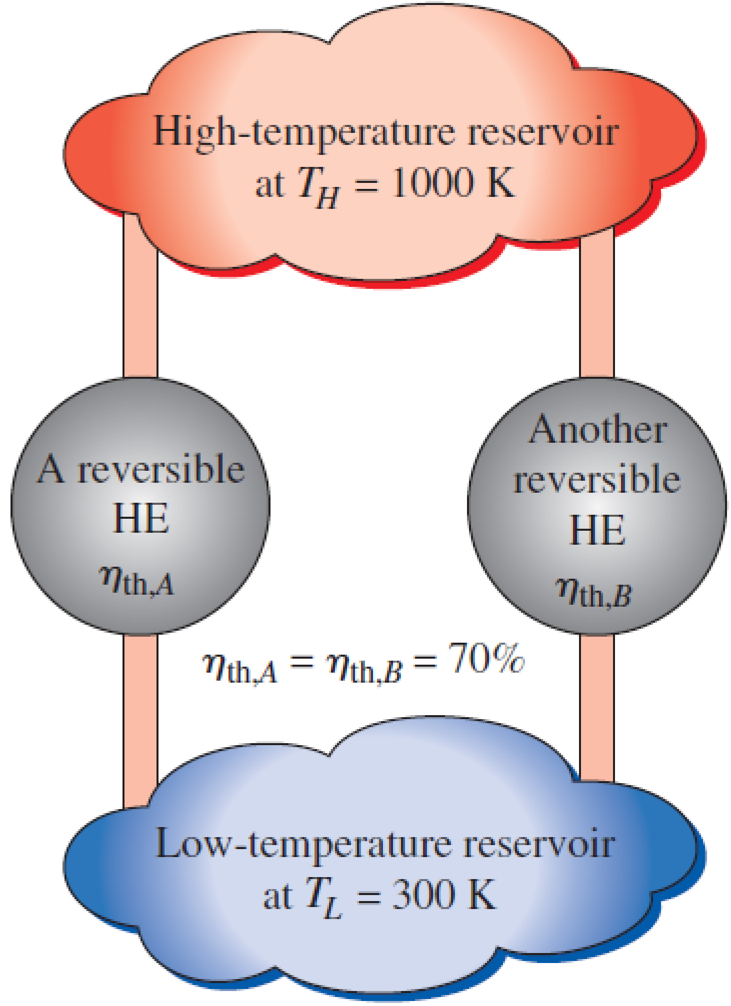


FIGURE 6–41

All reversible heat engines operating between the same two reservoirs have the same efficiency (the second Carnot principle).

THE THERMODYNAMIC TEMPERATURE SCALE

- 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 THERMODYNAMIC TEMPERATURE SCALE

- *The efficiency of a reversible heat engine is independent of the working fluid employed and its properties, the way the cycle is executed, or the type of reversible heat engine used*
- Since energy reservoirs are characterized by their temperature, the *thermal efficiency of reversible heat engines is a function of the reservoir temperatures only*

$$\eta_{\text{th,rev}} = g(T_H, T_L)$$ or $$\frac{Q_H}{Q_L} = f(T_H, T_L)$$

we know

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

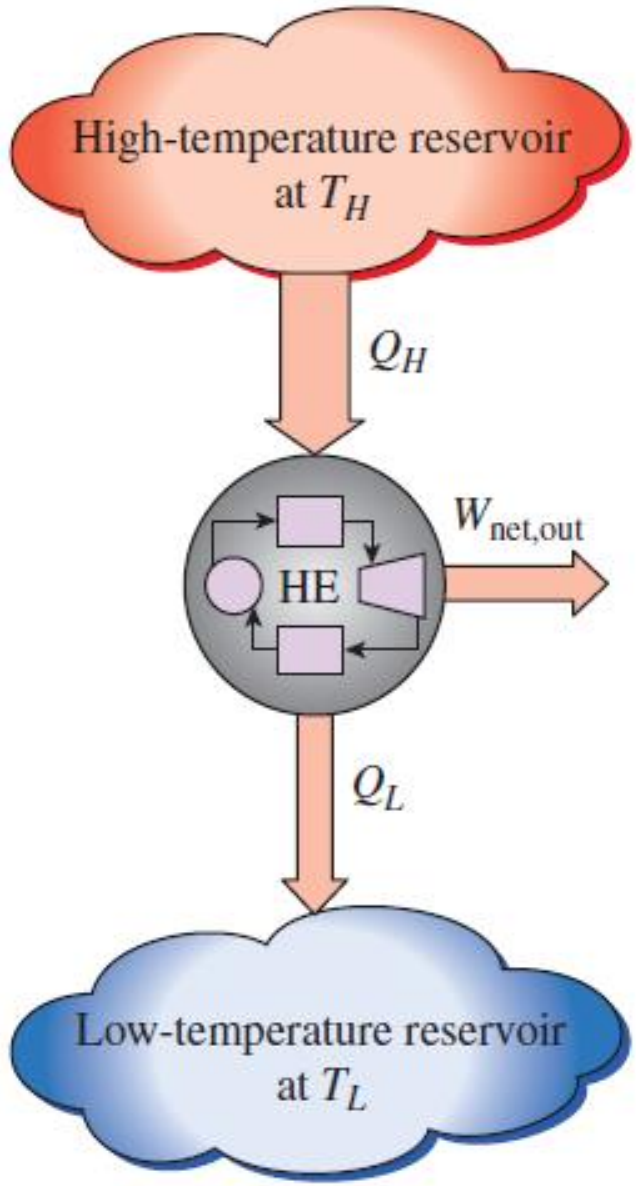


FIGURE 6–13
Schematic of a heat engine.

THE THERMODYNAMIC TEMPERATURE SCALE

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

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

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

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

$$f(T_1, T_3) = \underbrace{f(T_1, T_2)\cdot f(T_2, T_3)}_{\text{Must be a function of } T_1 \text{ and } T_3 \text{ and not } T_2}$$

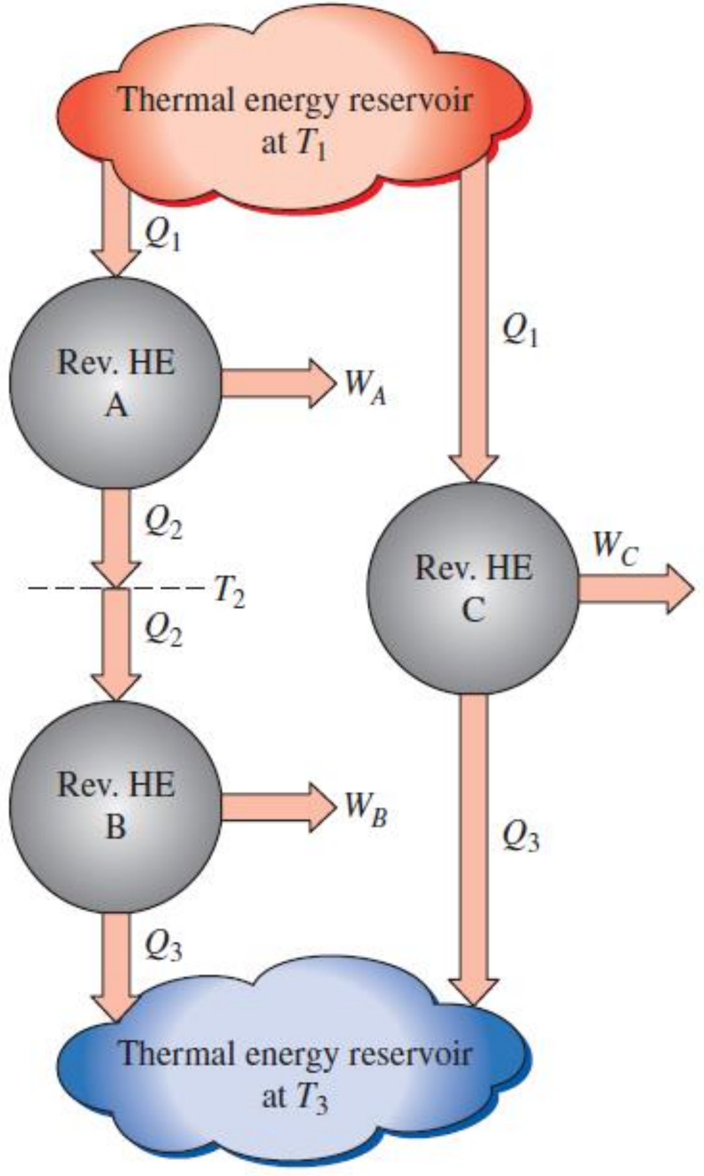


FIGURE 6–42
The arrangement of heat engines used to develop the thermodynamic temperature scale.

THE THERMODYNAMIC TEMPERATURE SCALE

The condition is satisfied only if ***f* has the following form**

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

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

$$\frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)}$$

This is the only requirement that the second law places on the ratio of heat transfers to and from the reversible heat engines

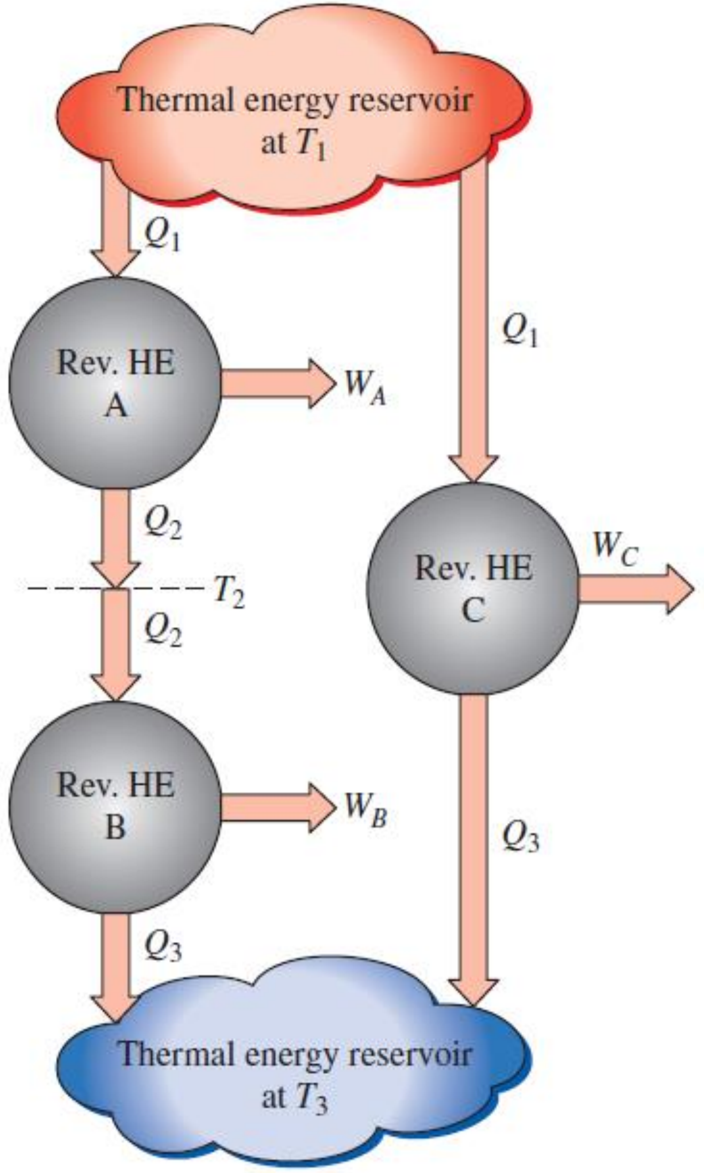


FIGURE 6–42
The arrangement of heat engines used to develop the thermodynamic temperature scale.

Kelvin scale

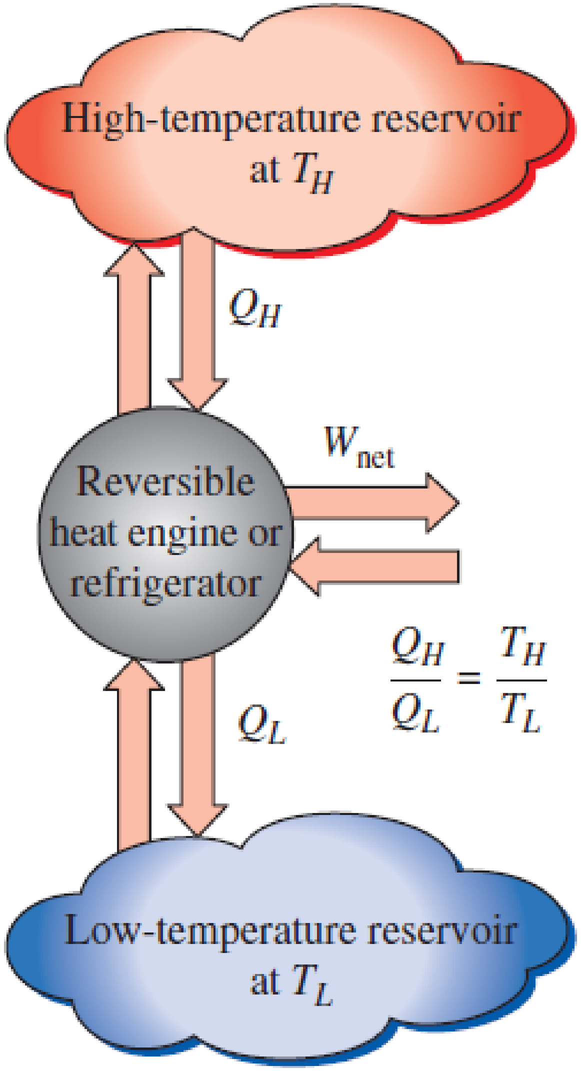


FIGURE 6–43

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

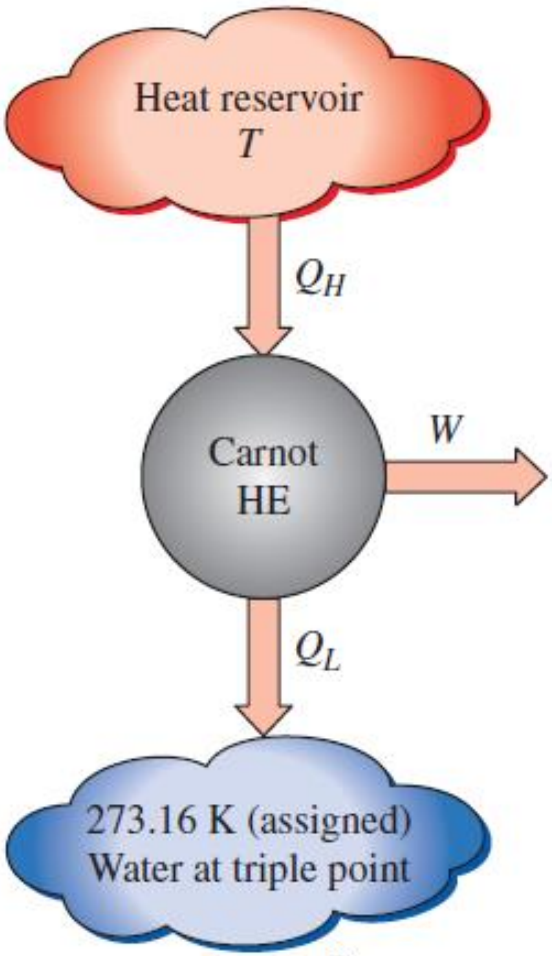
$$\frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)}$$

Several functions $\phi(T)$ satisfies this equation. *Lord Kelvin first proposed taking $\phi(T) = T$ to define thermodynamic temperature scale as*

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

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

On this scale, temperatures vary between zero and infinity



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

FIGURE 6–44
A conceptual experimental setup to determine thermodynamic temperatures on the Kelvin scale by measuring heat transfers Q_H and Q_L.

The magnitude of a kelvin is defined as 1/273.16 of the temperature interval between absolute zero and the triple point of water (0.01 °C)

$$T(^\circ\mathrm{C}) = T(\mathrm{K}) - 273.15$$

THE CARNOT HEAT ENGINE

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

Any heat engine

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

Carnot heat engine (since $Q_L/Q_H = T_L/T_H$ for Carnot engine)

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

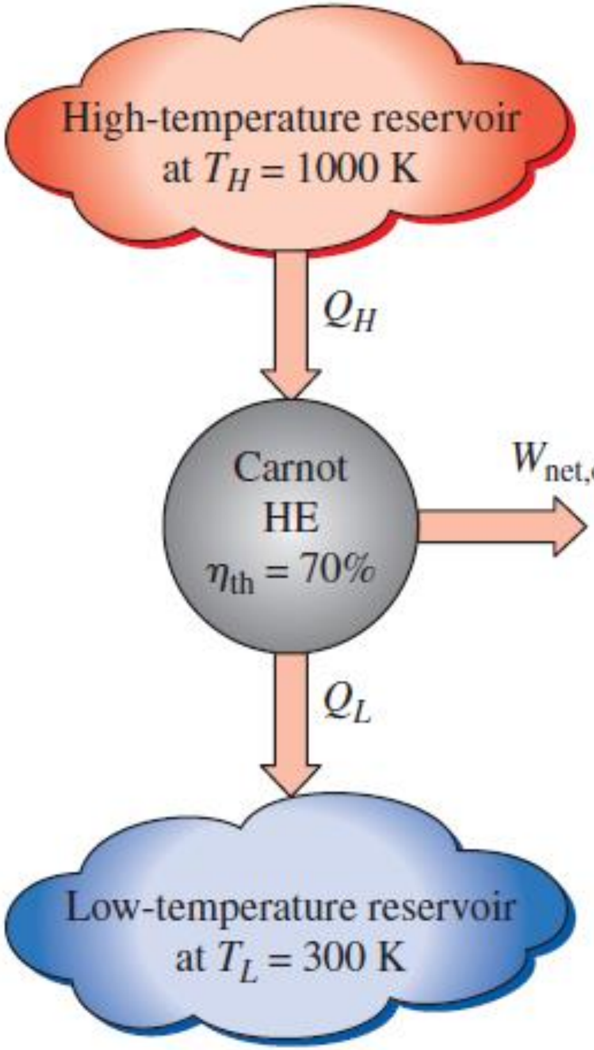


FIGURE 6–45
The Carnot heat engine is the most efficient of all heat engines operating between the same high- and low-temperature reservoirs.

THE CARNOT EFFICIENCY

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

- This is the *highest efficiency a heat engine operating between two thermal energy reservoirs at temperatures T_L and T_H can have*
- ***Note that T_L and T_H are absolute temperatures***
- An actual heat engine cannot reach this maximum theoretical efficiency because it is impossible to completely eliminate all the irreversibilities associated with the actual cycle

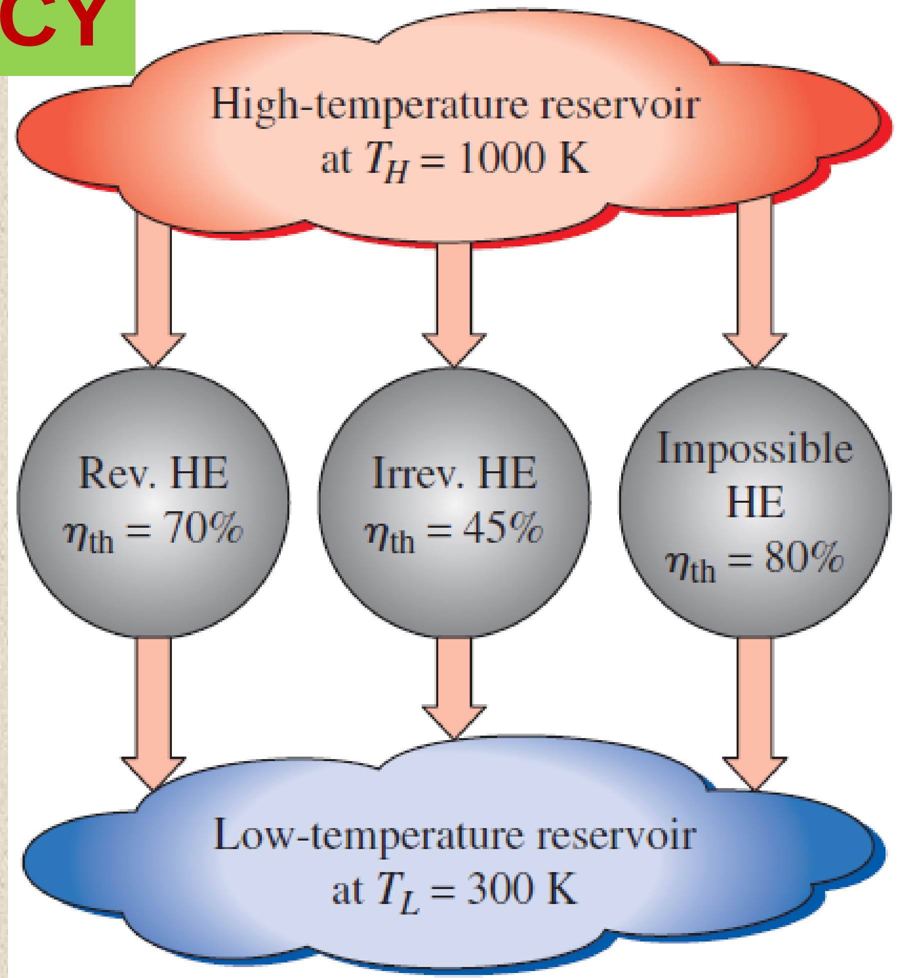
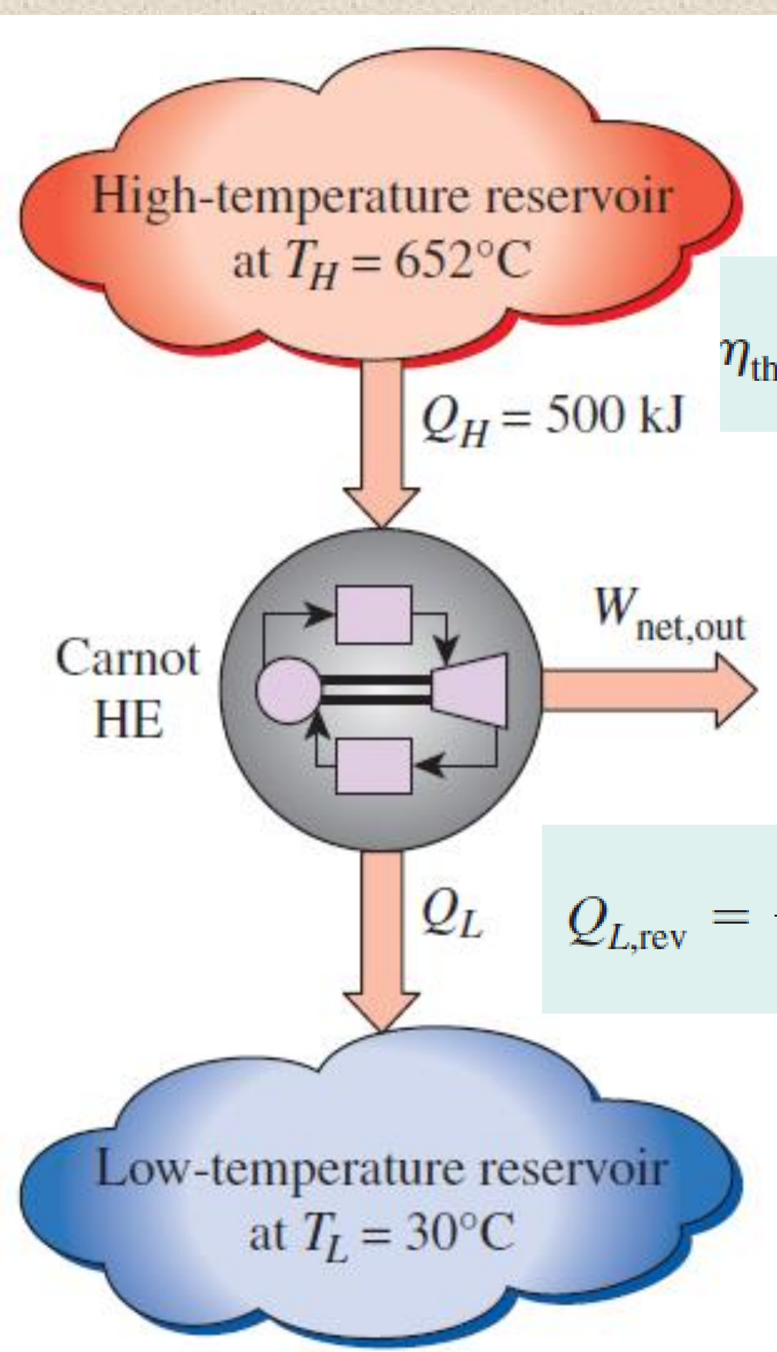


FIGURE 6–46

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

Example: Analysis of a Carnot Heat Engine



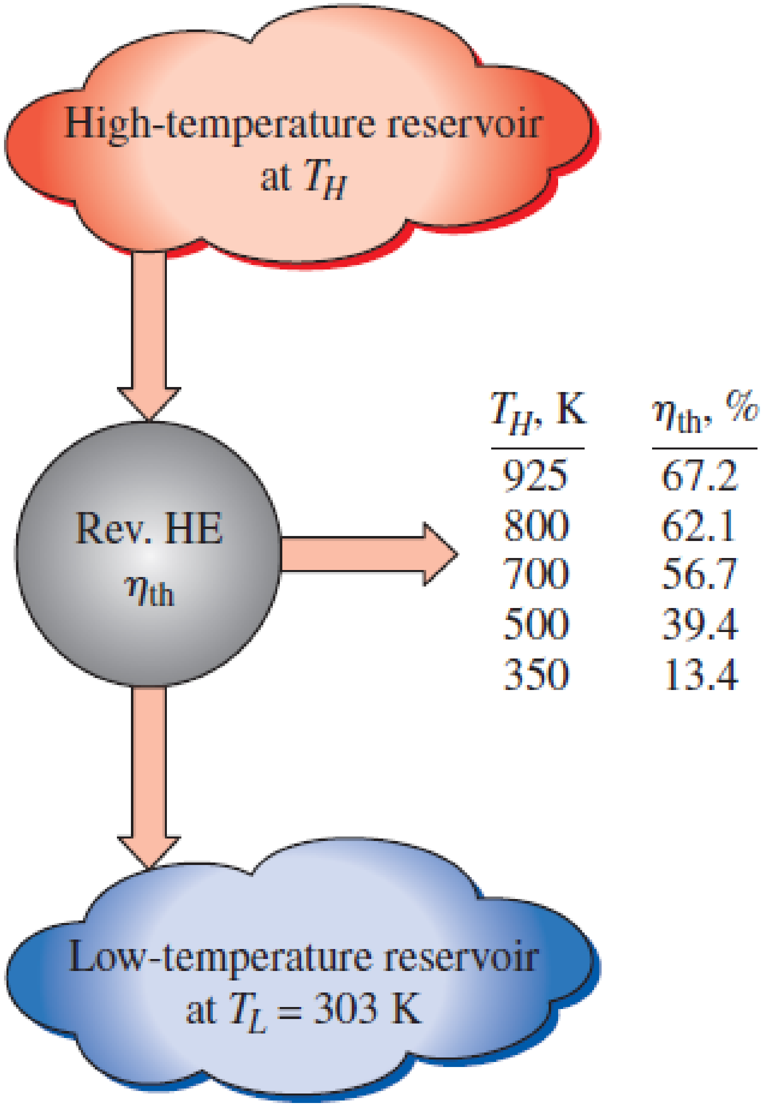
$$\eta_{th,rev} = 1 - \frac{T_L}{T_H} = 1 - \frac{(30 + 273)\text{ K}}{(652 + 273)\text{ K}} = \mathbf{0.672}$$

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

The Quality of Energy

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

- *Carnot efficiency increases as the source temperature increases*, this shows that energy has **quality** as well as quantity
- More of the high-temperature thermal energy can be converted to work, Therefore, ***the higher the temperature, the higher the quality of the energy***



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

FIGURE 6–48
The fraction of heat that can be converted to work as a function of source temperature (for $T_L = 303$ K).

The Quality of Energy

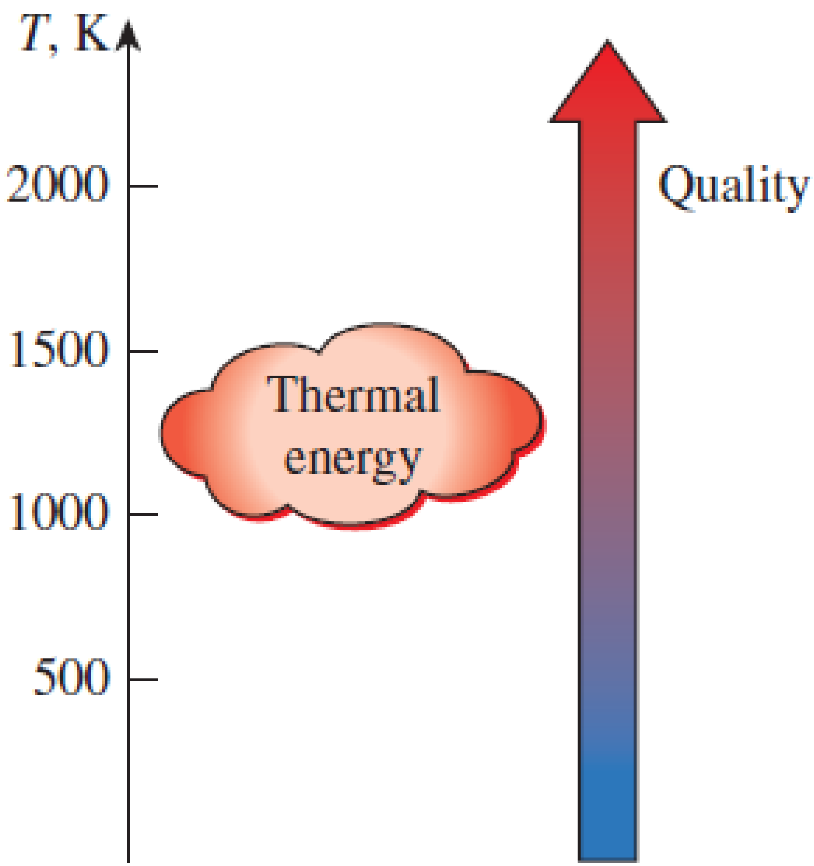
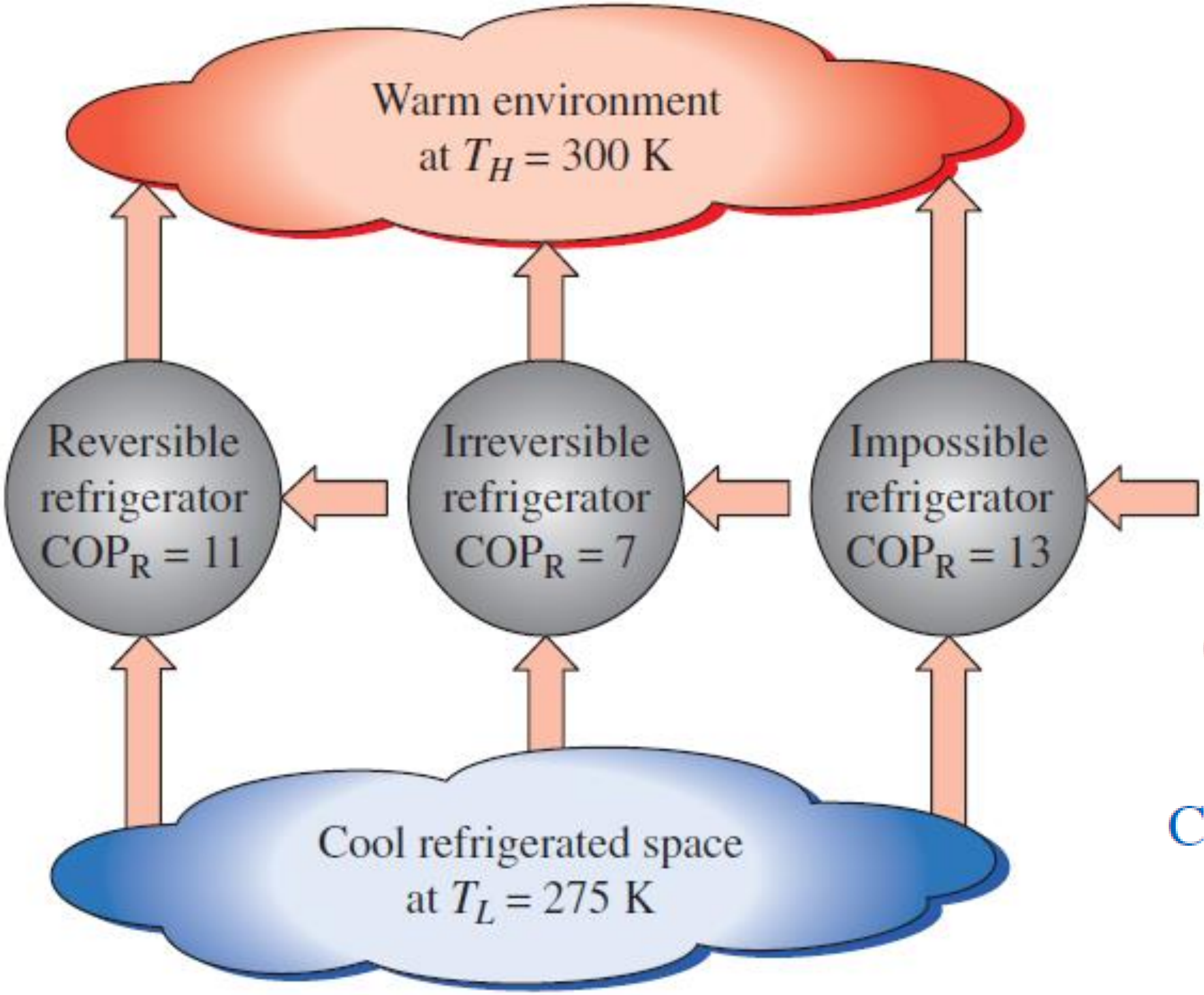


FIGURE 6–49

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

- *Work is a more valuable form of energy than heat since 100% of work can be converted to heat, **but only a fraction of heat can be converted to work!***
- In a process, quantity of energy is conserved, but not quality
- Assessment of a process **should not** be done on the basis of quantity (first law) only

THE CARNOT REFRIGERATOR AND HEAT PUMP



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

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

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

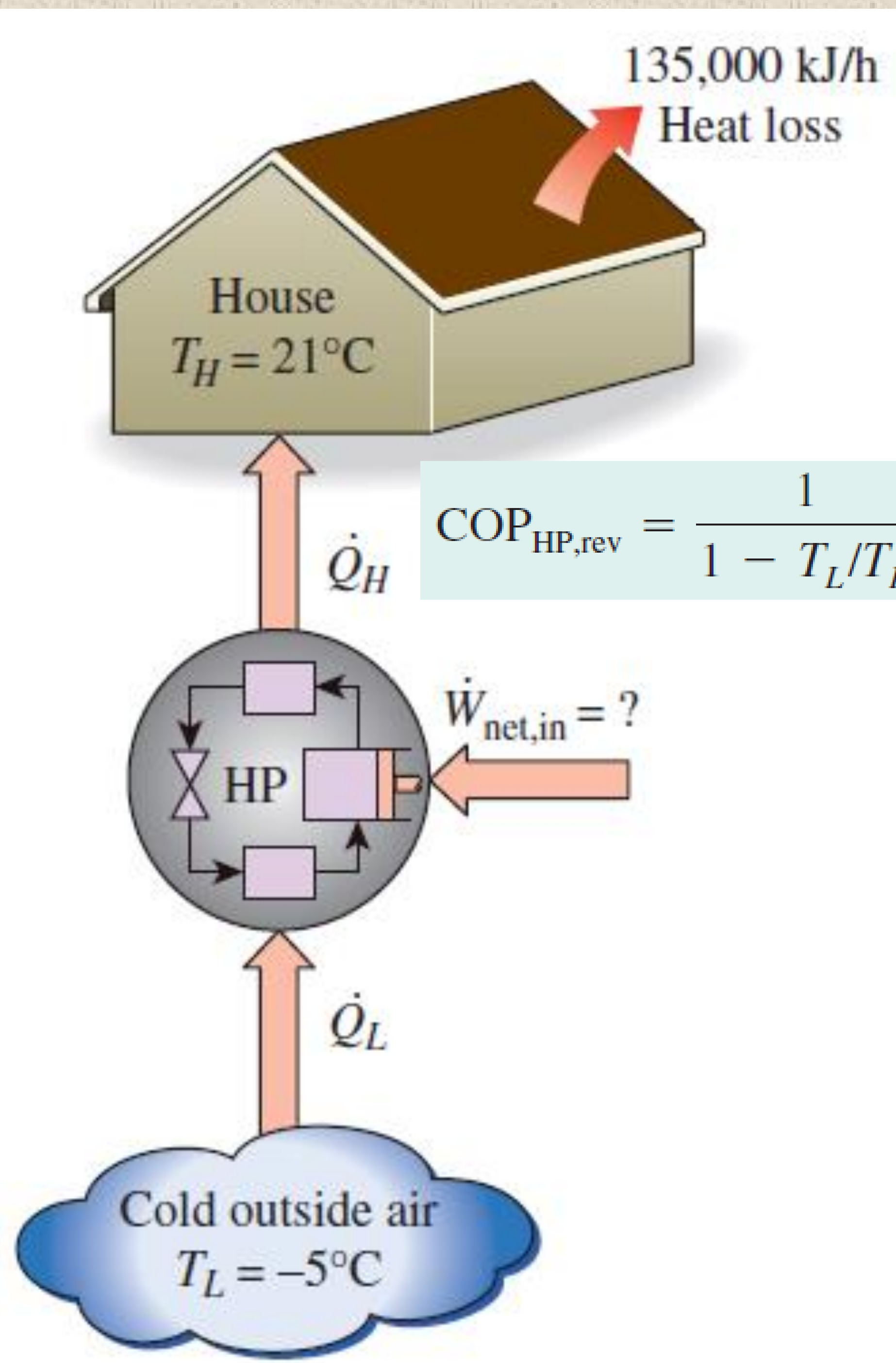
FIGURE 6–50

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

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

- The COP of a reversible refrigerator or heat pump is the maximum theoretical value for the specified temperature limits
- Actual refrigerators or heat pumps may approach these values as their designs are improved, but they can never reach them
- The COPs of both the refrigerators and the heat pumps decrease as T_L decreases
- That is, it requires more work to absorb heat from lower-temperature media

Example: Heating a House by a Carnot Heat Pump



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

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

Summary

- Introduction to the second law
- Thermal energy reservoirs
- Heat engines
  - ✓ Thermal efficiency
  - ✓ The 2nd law: Kelvin-Planck statement
- Refrigerators and heat pumps
  - ✓ Coefficient of performance (COP)
  - ✓ The 2nd law: Clasius statement
- Perpetual motion machines
- Reversible and irreversible processes
  - ✓ Irreversibilities, Internally and externally reversible processes
- The Carnot cycle
  - ✓ The reversed Carnot cycle
- The Carnot principles
- The thermodynamic temperature scale
- The Carnot heat engine
  - ✓ The quality of energy
- The Carnot refrigerator and heat pump