

## 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 and cyclic devices.
- 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.

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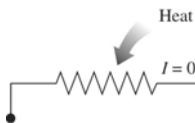
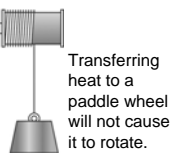
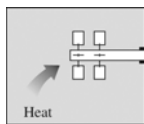
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### INTRODUCTION TO THE SECOND LAW

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



Transferring heat to a wire will not generate electricity.

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

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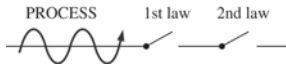
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Processes occur in a certain direction, and not in the reverse direction.



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. 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.

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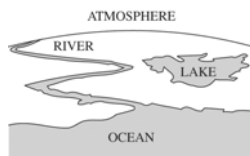
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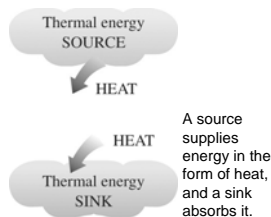
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### THERMAL ENERGY RESERVOIRS



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.

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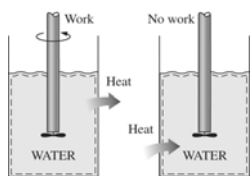
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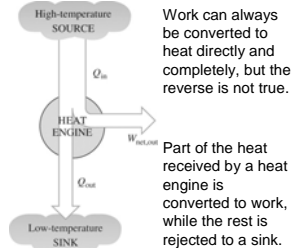
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Work can always be converted to heat directly and completely, but the reverse is not true.



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

### 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.

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**.

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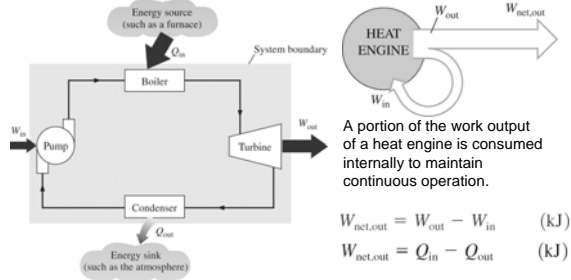
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## A steam power plant



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

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

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

$Q_{\text{in}}$  = amount of heat supplied to steam in boiler from a high-temperature source (furnace)

$Q_{\text{out}}$  = amount of heat rejected from steam in condenser to a low-temperature sink (the atmosphere, a river, etc.)

$W_{\text{out}}$  = amount of work delivered by steam as it expands in turbine

$W_{\text{in}}$  = amount of work required to compress water to boiler pressure

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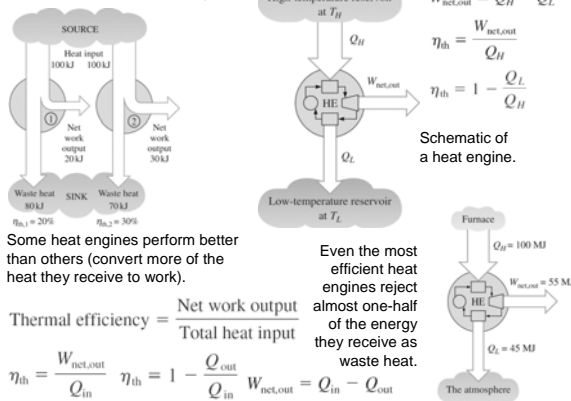
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## Thermal efficiency



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

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

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

Schematic of a heat engine.

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

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

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

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

$Q_H = 100 \text{ MJ}$

$W_{\text{net,out}} = 55 \text{ MJ}$

$Q_L = 45 \text{ MJ}$

The atmosphere

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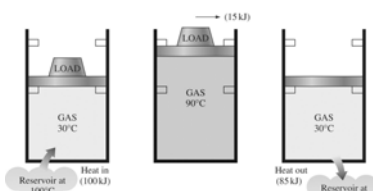
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## Can we save $Q_{\text{out}}$ ?



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.

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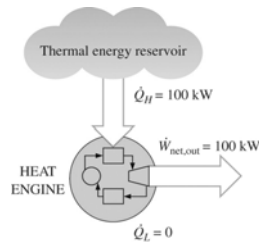
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### The Second Law of Thermodynamics: Kelvin–Planck Statement

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.

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.



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

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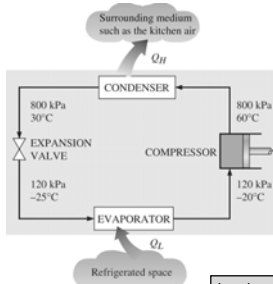
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### REFRIGERATORS AND HEAT PUMPS



Basic components of a refrigeration system and typical operating conditions.

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.

- 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*.

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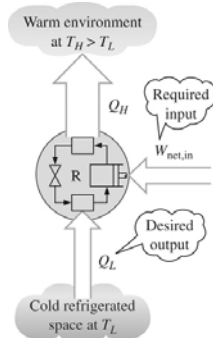
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### Coefficient of Performance



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.

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

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

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

Can the value of  $\text{COP}_R$  be greater than unity?

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### 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.

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

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

$$\text{COP}_{\text{HP}} = \text{COP}_R + 1 \text{ for fixed values of } Q_L \text{ and } Q_H$$

Can the value of  $\text{COP}_{\text{HP}}$  be lower than unity?  
 What does  $\text{COP}_{\text{HP}}=1$  represent?

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- 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.
- **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.

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

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

**Energy efficiency rating (EER):** The amount of heat removed from the cooled space in Btu's for 1 Wh (watt-hour) of electricity consumed.

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### 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.

*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.

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

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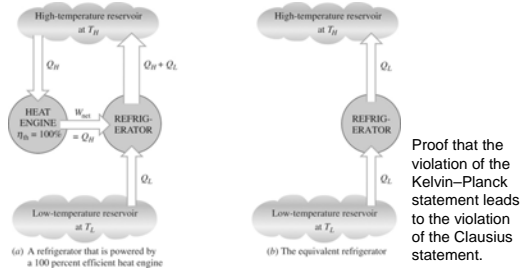
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### Equivalence of the Two Statements



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.

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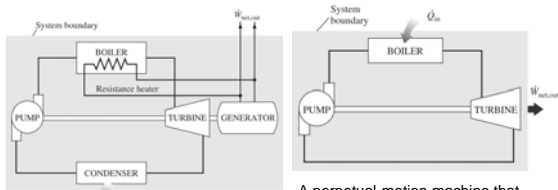
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### PERPETUAL-MOTION MACHINES



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

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

**Perpetual-motion machine:** 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.**

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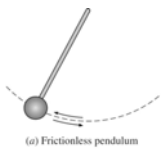
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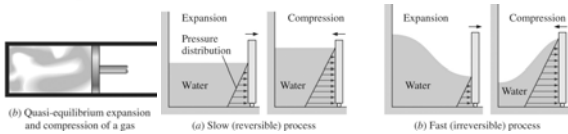
### REVERSIBLE AND IRREVERSIBLE PROCESSES

**Reversible process:** A process that can be reversed without leaving any trace on the surroundings.

**Irreversible process:** A process that is not reversible.



- 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.
- We try to approximate reversible processes. **Why?**



Two familiar reversible processes.

Reversible processes deliver the most and consume the least work.

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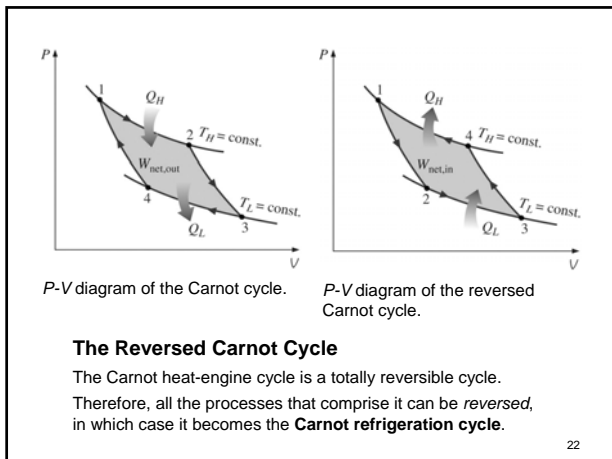
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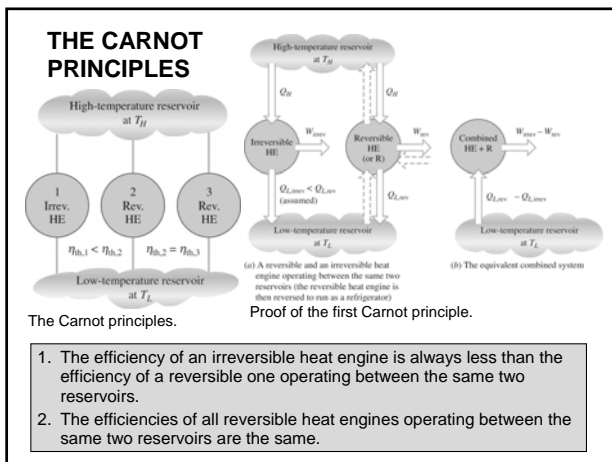
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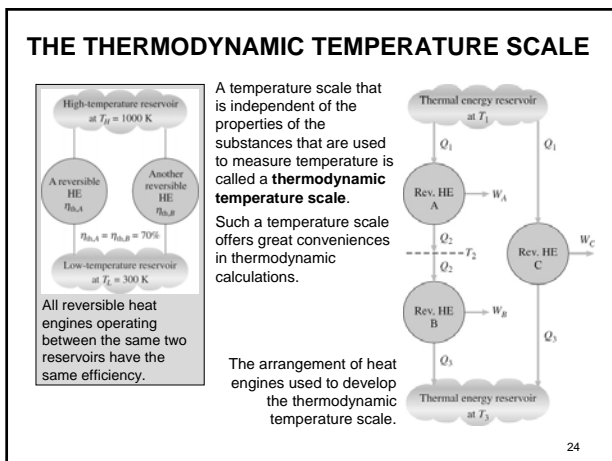
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$\left(\frac{Q_H}{Q_L}\right)_{\text{rev}} = \frac{T_H}{T_L}$

This temperature scale is called the **Kelvin scale**, and the temperatures on this scale are called **absolute temperatures**.  
 $T(^{\circ}\text{C}) = T(\text{K}) - 273.15$

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  $Q_L$ .

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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.

Any heat engine	Carnot heat engine	$\eta_{\text{th}} \begin{cases} < \eta_{\text{th,rev}} & \text{irreversible heat engine} \\ = \eta_{\text{th,rev}} & \text{reversible heat engine} \\ > \eta_{\text{th,rev}} & \text{impossible heat engine} \end{cases}$
$\eta_{\text{th}} = 1 - \frac{Q_L}{Q_H}$	$\eta_{\text{th,rev}} = 1 - \frac{T_L}{T_H}$	

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### The Quality of Energy

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

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

Can we use  $^{\circ}\text{C}$  unit for temperature here?

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

How do you increase the thermal efficiency of a Carnot heat engine? How about for actual heat engines?

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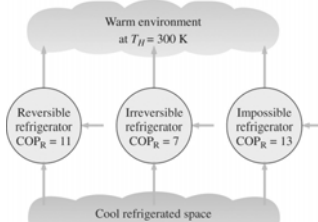
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## THE CARNOT REFRIGERATOR AND HEAT PUMP



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

Any refrigerator or heat pump

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

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

Carnot refrigerator or heat pump

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

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

How do you increase the COP of a Carnot refrigerator or heat pump? How about for actual ones?

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## Summary

- Introduction to the second law
- Thermal energy reservoirs
- Heat engines
  - ✓ Thermal efficiency
  - ✓ The 2<sup>nd</sup> law: Kelvin-Planck statement
- Refrigerators and heat pumps
  - ✓ Coefficient of performance (COP)
  - ✓ The 2<sup>nd</sup> law: Clausius 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

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