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.

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.

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

Thermal Energy Reservoirs

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.

Heat Engines

Heat engines are 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 absorb heat and from which heat is transferred while undergoing a cycle. This fluid is called the working fluid.
A steam power plant

Thermal efficiency

Schematic of a heat engine.

Thermal efficiency = Net work output / Total heat input

\[ \eta = \frac{W_{\text{net, out}}}{Q_H} \]

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

Can we save \( Q_{\text{out}} \)?

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.

Can we save \( Q_{\text{out}} \)?

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

Can we save \( Q_{\text{out}} \)?

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

Kelvin-Planck Statement

 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.
Refrigerators and Heat Pumps

- 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.

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.

Coefficient of Performance for Refrigerators

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

\[
\text{COP}_{R} = \frac{Q_H}{W_{\text{net,in}}} = \frac{Q_H}{Q_L} \text{(kJ)}
\]

\[
\text{COP}_{R} = \frac{Q_L}{Q_H - Q_L} = 1 \quad \frac{Q_H}{Q_L - 1}
\]

\[
\text{COP}_{R} \text{ can be greater than unity. That is, the amount of heat removed from the refrigerated space can be greater than the amount of work input.}
\]

Coefficient of Performance for Heat Pumps

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

\[
\text{COP}_{HP} = \frac{Q_H}{W_{\text{net,in}}} \quad \text{for fixed values of } Q_H \text{ and } Q_L
\]

\[
\text{COP}_{HP} = \text{COP}_{R} + 1
\]

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

Coefficient of Performance for Refrigerator

Example 6-3

The food compartment of a refrigerator, shown in Fig. 6-24, 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.

\[
\text{Food compartment } 4°C
\]

\[
Q_H = 360 \text{ kJ/min}
\]

\[
W_{\text{net,in}} = 2 \text{ kW}
\]

(a) The coefficient of performance of the refrigerator:

\[
\text{COP}_{R} = \frac{Q_H}{W_{\text{net,in}}} = \frac{360 \text{ kJ/min}}{2 \text{ kW}} = 180 \text{ kJ/kW} = 3
\]

(b) The rate of heat ejected to room:

\[
\dot{Q_L} = \dot{Q}_H + W_{\text{net,in}} = 360 \text{ kJ/min} + 2 \text{ kW} = 360 \text{ kJ/(60s)} + 2 \text{ kJ/s} = 8 \text{ kJ/s}
\]

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

\[ EER = 3.412 \text{ COP}_{R} \]

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

Most heat pumps in operation today have a seasonally averaged COP of 2 to 3.
- Most existing heat pumps use the cold outside air as the heat source in winter (air-source HP).
- 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.

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

A 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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**Irreversible Processes**

- The factors that cause a process to be irreversible are called irreversibilities.
- They include friction, unrestrained expansion, mixing of two fluids, heat transfer across a finite temperature difference, electric resistance, inelastic deformation of solids, and chemical reactions.
- The presence of any of these effects renders a process irreversible.
Irreversible Processes

Irreversible compression and expansion processes.

(a) Fast compression

(b) Fast expansion

(c) Unrestrained expansion

Internally & 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 and internally reversible heat transfer processes.

Internally & Externally Reversible Processes

A reversible process involves no internal and external irreversibilities.

The Carnot Cycle

Execution of the Carnot cycle in a closed system.

(a) Process 1-2
(b) Process 2-3

Reversible Isothermal Expansion (process 1-2): $T_H = \text{constant}$, $P_v = mRT = C$; heat input $Q_H$

Reversible Adiabatic Expansion (process 2-3): temperature drops from $T_H$ to $T_L$; $Pvn = C$

P-V diagram of the 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

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

The Carnot Principles

The Carnot refrigeration cycle.

The Thermodynamic Temperature Scale

Since the energy of reservoirs is characterized by the temperature, the thermal efficiency if reversible heat engines is a function of the reservoir temperature only:

\[ \eta_{rev} = \frac{W_{net}}{Q_{in}} = \frac{Q_{H} - Q_{L}}{Q_{H}} = 1 - \frac{Q_{L}}{Q_{H}} = g(T_2, T_1) \]

For all the engines in the figure:

\[ Q_{H} = f(T_H, T_L) \]
\[ Q_{L} = f(T_L) \]
\[ Q_{H} = f(T_H, T_L) \]
\[ Q_{L} = f(T_L) \]

Now consider the identity:

\[ \frac{Q_{H}}{Q_{L}} = \frac{Q_{H}}{Q_{L}} \]

which corresponds to

\[ f(T_2, T_1) = f(T_2, T_1) \]

Left side is not a function of \( T_2 \) the condition will be met if the right side will be:

\[ f(T_2, T_1) = f(T_2, T_1) \]

The Thermodynamic Temperature Scale

The temperature scale is called the Kelvin scale. The temperature on this scale is called absolute temperature.

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.
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 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.

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

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?
The Carnot Refrigerator and Heat Pump

Any refrigerator or heat pump

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

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

Carnot refrigerator or heat pump

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

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

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

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

The Carnot Refrigerator and Heat Pump

Example 6-7

A heat pump is used to heat a house during the winter as shown in Fig. 6-53. The house is maintained at 21 °C at all times. The house is estimated to be losing heat at a rate of 135 MJ/h when the outside temperature drops to -5 °C. Determine the minimum power required to drive this heat pump.

FIGURE 6-53

\[ Q_H = 135,000 \text{ kJ/h} \]

\[ T_H = 21^\circ \text{C} \]

\[ T_L = -5^\circ \text{C} \]

Summary

• Introduction to the second law
• Heat engines
  ✓ Thermal efficiency
  ✓ The 2nd law: Kelvin-Planck statement
• Refrigerators and heat pumps
  ✓ Coefficient of performance (COP)
  ✓ The 2nd 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

Example 6-7

Analysis

The heat pump must supply heat to the house at a rate of \( Q_H = 135,000 \text{ kJ/h} = 37.5 \text{ kW} \). 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

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

Then the required power input to this reversible heat pump becomes

\[ W_{\text{in, min}} = \frac{Q_H}{\text{COP}_{HP}} = \frac{37.5 \text{ kW}}{11.3} = 3.32 \text{ kW} \]

Discussion

This reversible heat pump can meet the heating requirements of this house by consuming electric power at a rate of 3.32 kW only. If this house were to be heated by electric resistance heaters instead, the power consumption would jump up 11.3 times to 37.5 kW. This is because in resistance heaters the electric energy is converted to heat at a one-to-one ratio.