Introduction to the Second Law (Section 6-1)

• Satisfying the first law of thermodynamics is required for any process, but is not enough to ensure that it will actually happen.
• The second law asserts that processes proceed in a certain direction and not in the reverse direction.
• The second law also asserts that energy has quality as well as quantity.
• Energy has high quality if it has high energy because it can produce more work.
• The second law is used to determine the theoretical limits of commonly used systems such as heat engines and refrigerators.

Thermal Energy Reservoirs (Section 6-2)

A thermal energy reservoir is a body that has a large thermal energy capacity such that its temperature does not change as a result of absorbing or supplying heat.

Examples: Lakes, oceans, rivers, atmosphere

Source
A reservoir that supplies energy in the form of heat

Sink
A reservoir that absorbs energy in the form of heat

Heat Engines (Section 6-3)

It is easy to convert work into heat, but converting heat into work requires special devices called heat engines

Characteristics of Heat Engines
1. They receive heat from a high-temperature source (solar energy, oil furnace, etc.)
2. They convert part of this heat to work
3. They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.)
4. They operate in a cycle

Working Fluid
A fluid to and from which heat is transferred while undergoing a cycle

Example of a Heat Engine: Steam Power Plant

$Q_{\text{in}} =$ 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 (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

• $W_{\text{net,out}} = W_{\text{out}} - W_{\text{in}}$
• Energy Balance: $(Q_{\text{in}} - Q_{\text{out}}) + (W_{\text{in}} - W_{\text{out}}) = \Delta E_{\text{system}}$
• For a cycle: $\Delta E_{\text{system}} = 0 \iff W_{\text{net,out}} = Q_{\text{in}} - Q_{\text{out}}$
Thermal Efficiency
The fraction of the heat input that is converted to net work output.

\[
\text{Performance} = \frac{\text{Desired output}}{\text{Required input}}
\]

\[\Rightarrow \text{Thermal Efficiency} = \frac{\text{Net work output}}{\text{Total heat input}}\]

or: \[\eta_{\text{th}} = \frac{W_{\text{net, out}}}{Q_{\text{in}}}\]

\[\Rightarrow \eta_{\text{in}} = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}}\]

or: \[\Rightarrow \eta_{\text{th}} = 1 - \frac{Q_{L}}{Q_{H}}\]

where:
- \(Q_L\) is the magnitude of heat rejected to the heat sink
- \(Q_H\) is the magnitude of heat received from the heat source

Using \(Q_{\text{out}}\)
- \(Q_{\text{out}}\) is usually called waste heat
- This energy cannot be reused in its entirety to produce additional useful work
- Only a small part of this heat can be used to produce useful work, while the remaining portion is completely wasted
- This energy also cannot be given back to the heat source because the heat source is at a higher temperature

**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

What does this statement mean?
It means that no heat engine can have a thermal efficiency of 100%

**Refrigerators and Heat Pumps (Section 6-4)**

**Refrigerators**
- A device that transfers heat from a low-temperature medium to a high-temperature one
- The objective of a refrigerator is to remove \(Q_L\) from the cooled space

**Refrigerant**
The working fluid used in the refrigeration cycle

**Example:** Vapor-compression refrigeration cycle
Coefficient of Performance of Refrigerators (COP$_R$)

The efficiency of a refrigerator is expressed in terms of the coefficient of performance (COP), denoted by COP$_R$ which can be expressed as:

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

where: $W_{\text{net,in}} = Q_H - Q_L$

The COP can also be expressed as:

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

**Important Note**

The COP can be greater than 1, while thermal efficiency of heat engines can never be greater than or equal to 1.

Heat Pumps

- A device that transfers heat from a low-temperature medium to a high-temperature one
- The objective of a heat pump is to maintain a heated space at a high temperature

Coefficient of Performance of Heat Pumps (COP$_{HP}$)

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

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

Comparison of COP$_R$ and COP$_{HP}$

COP$_{HP}$ = COP$_R$ + 1

---

**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.

Equivalence of the two statements

- The Kelvin-Planck statement and the Clausius statement of the second law are equivalent
- Violation of one of them leads to the violation of the other

Perpetual Motion Machines (Section 6-5)

A perpetual motion machine is any device that violates either the first law or the second law of thermodynamics.

Perpetual Motion Machine of the First Kind (PMM1)

A device that violates the first law of thermodynamics (by creating energy)
Perpetual Motion Machine of the Second Kind (PMM2)
A device that violates the second law of thermodynamics

Reversible and Irreversible Processes (Section 6-6)

Reversible Process
- A process that can be reversed without leaving any trace on the surroundings
- Both the system and the surroundings are returned to their initial states at the end of the reverse process
- Reversible processes are idealized and they do not actually occur in nature
- Work-producing devices deliver the most work if they use reversible processes
- Work-consuming devices consume the least work if they use reversible processes
  *Example*: Frictionless pendulum

Irreversible Process
- Any process that is not reversible
- All natural processes are irreversible

Irreversibilities
Factors that cause a process to be irreversible

**Friction**
- When two bodies in contact are forced to move relative to each other, friction develops
- Work is needed to overcome friction
- Work is converted to heat during the process
- This heat cannot be used to produce the same amount of work again

**Unrestrained Expansion of Gas**
- Unrestrained expansion of gas is an irreversible process
- It is possible to return the system to its original state, but it is not possible to return the surroundings to its original state because heat will be rejected to the surroundings during the compression of the gas

**Heat Transfer Through a Finite Temperature Difference**
- Once heat is transferred from a high temperature to a low temperature system, it is possible to return the system to its original state by applying refrigeration, but then the surroundings cannot be restored to the original state because the refrigerator will reject heat to the surroundings
- Heat transfer through a differential temperature difference, $dT$, is considered reversible

**Internally Reversible Processes**
- No irreversibilities occur within the boundaries of the system
- During such a process, a system proceeds through a series of equilibrium states
- When the process is reversed, the system passes through exactly the same equilibrium states
Externally Reversible Processes
- No irreversibilities occur outside the system boundaries
- Heat transfer between a reservoir and a system is externally reversible if the outer surface of the system is at the temperature of the reservoir

The Carnot Cycle (Section 6-7)
- The Carnot cycle is a cycle that consists completely of reversible processes
- It was proposed by French engineer Sadi Carnot in 1824
- Since it consists of reversible processes, it produces the highest possible net work output

Carnot Cycle Processes

Process 1-2: Reversible Isothermal Expansion
- The system exchanges heat with a heat source while keeping the temperature, $T_H$, constant
- The gas expands slowly and produces work

Process 2-3: Reversible Adiabatic Expansion
- The system is now insulated and the gas continues to expand slowly and produce work
- At the end of the process, the temperature decreases to $T_L$

Process 3-4: Reversible Isothermal Compression
- The insulation is removed and the system exchanges heat with a heat sink while keeping the temperature, $T_L$, constant
- The gas is compressed and consumes work to do so

Process 4-1: Reversible Adiabatic Compression
- The system is insulated again and the gas continues to be compressed slowly and consume more work
- At the end of the process, the temperature goes back to $T_H$, and the system returns to its original state

The Reversed Carnot Cycle
- The direction of all the processes described in the Carnot heat engine above can be reversed
- The result is called Carnot refrigeration cycle
- This cycle consumes the least possible work input because it consists completely of reversible processes

The Carnot Principles (Section 6-8)
1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs
2. The efficiencies of all reversible heat engines operating between the same two reservoirs are the same
The Thermodynamic Temperature Scale (Section 6-9)
- A thermodynamic temperature scale is a scale that is independent of the properties of the substances that are used to measure temperature
- The thermal efficiency of a reversible heat engine is a function of reservoir temperatures only
- For a reversible heat engine, it can be proven that:
  \[
  \left( \frac{Q_H}{Q_L} \right)_{\text{rev}} = \frac{T_H}{T_L}
  \]
- This is called the Kelvin scale because it was introduced by Lord Kelvin
- It shows that temperature ratios depend on ratios of heat transfer between a reversible heat engine and the reservoirs
- Therefore, temperature is independent of the physical properties of any substance

Efficiency of Carnot Heat Engine (Section 6-10)
In general: \( \eta_{\text{th}} = 1 - \frac{Q_L}{Q_{HI}} \)

Special Case: Carnot Heat Engine or any Reversible Heat Engine
\[
\eta_{\text{th}} = 1 - \frac{T_L}{T_H}
\]
\[
\begin{align*}
< \eta_{\text{th,rev}} & \quad \text{irreversible heat engine} \\
= \eta_{\text{th,rev}} & \quad \text{reversible heat engine} \\
> \eta_{\text{th,rev}} & \quad \text{impossible heat engine}
\end{align*}
\]

COP of Carnot Refrigerator and Heat Pump (Section 6-12)
In general: \( \text{COP}_R = \frac{1}{Q_{HI}/Q_L - 1} \) and \( \text{COP}_{HP} = \frac{1}{1 - Q_L/Q_{HI}} \)
For a Carnot Refrigerator and Heat Pump (or any reversible refrigerator and heat pump):
\[
\text{COP}_{R,\text{rev}} = \frac{1}{T_H/T_L - 1} \quad \text{and} \quad \text{COP}_{HP,\text{rev}} = \frac{1}{1 - T_L/T_H}
\]
\[
\begin{align*}
< \text{COP}_{R,\text{rev}} & \quad \text{irreversible refrigerator} \\
= \text{COP}_{R,\text{rev}} & \quad \text{reversible refrigerator} \\
> \text{COP}_{R,\text{rev}} & \quad \text{impossible refrigerator}
\end{align*}
\]

The Quality of Energy
- The above discussion shows that the efficiency of a heat engine increases when the temperature of the heat source is higher
- This means that the quality of energy is higher when the temperature of the heat source is higher because more energy can be converted to work