Chapter 6

The Second Law of Thermodynamics
The 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.
INTRODUCTION
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THERMAL ENERGY RESERVOIRS

Thermal energy
SOURCE

HEAT

HEAT

Thermal energy
SINK
Heat Engines

![Diagram showing heat engines with and without work]

WATER

Heat

Work

No work
Heat Engines
Heat Engines

Energy source (such as a furnace)

System boundary

Boiler

Pump

Turbine

Condenser

Energy sink (such as the atmosphere)

$Q_{in}$

$W_{in}$

$Q_{out}$

$W_{out}$
Heat Engines

Heat Engine

$W_{in}$

$W_{out}$

$W_{net,out}$
Thermal Efficiency

Heat input: 100 kJ
Net work output: 20 kJ
Net work output: 30 kJ

Waste heat: 80 kJ
SINK

\[ \eta_{th,1} = 20\% \]

Waste heat: 70 kJ

\[ \eta_{th,2} = 30\% \]
Thermal Efficiency

High-temperature reservoir
at $T_H$

$Q_H$

$W_{\text{net, out}}$

Low-temperature reservoir
at $T_L$

$Q_L$
Thermal Efficiency

$Q_H = 100 \text{ MJ}$

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

$Q_L = 45 \text{ MJ}$

The atmosphere
Can We Save $Q_{out}$?

Reservoir at 100°C

Heat in (100 kJ)

GAS 30°C

LOAD

GAS 90°C

(15 kJ)

GAS 30°C

Heat out (85 kJ)

Reservoir at 20°C
Kelvin–Planck Statement

Thermal energy reservoir

\[ \dot{Q}_H = 100 \text{ kW} \]

\[ \dot{W}_{\text{net, out}} = 100 \text{ kW} \]

\[ \dot{Q}_L = 0 \]
REFRIGERATORS AND HEAT PUMPS

Surrounding medium such as the kitchen air

CONDENSER

800 kPa
30°C

EXPANSION VALVE

120 kPa
−25°C

COMPRESSOR

800 kPa
60°C

EVAPORATOR

120 kPa
−20°C

Refrigerated space

Q_H

W_{net,in}

Q_L
Coefficient of Performance

Warm environment at $T_H > T_L$

Cold refrigerated space at $T_L$

$Q_H$

$Q_L$

Required input $W_{\text{net,in}}$

Desired output
Coefficient of Performance

Refrigerator

Warm environment at $T_H > T_L$

- Required input
- Desired output

Cold refrigerated space at $T_L$

Heat Pump

Warm heated space at $T_H > T_L$

- Desired output
- Required input

Cold environment at $T_L$
Heat Pumps

COP = 3.5

Warm indoors at 20°C

\[ Q_H = 7 \text{ kJ} \]

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

\[ Q_L = 5 \text{ kJ} \]

Cold outdoors at 4°C
Clausius Statement

Food compartment
4°C

\begin{align*}
\dot{Q}_H &= \text{heat input}\n\dot{Q}_L &= 360 \text{ kJ/min}\n\dot{W}_{\text{net, in}} &= 2 \text{ kW}
\end{align*}
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 MACHINES
REVERSIBLE AND IRREVERSIBLE PROCESSES

(a) Frictionless pendulum

(b) Quasi-equilibrium expansion and compression of a gas
REVERSIBLE AND IRREVERSIBLE PROCESSES

(a) Slow (reversible) process

(b) Fast (irreversible) process
Irreversibilities
Irreversibilities

(a) Fast compression

(b) Fast expansion

(c) Unrestrained expansion
Irreversibilities

(a) An irreversible heat transfer process

(b) An impossible heat transfer process
Internally and Externally Reversible Processes

(a) Totally reversible

Thermal energy reservoir at 20.000...1°C

(b) Internally reversible

Thermal energy reservoir at 30°C

Boundary at 20°C
CARNOT CYCLE
CARNOT CYCLE

Carnot Heat Engine Cycle

Carnot Refrigerator Cycle
THE CARNOT PRINCIPLES

1 Irrev. HE
2 Rev. HE
3 Rev. HE

$\eta_{th,1} < \eta_{th,2}$
$\eta_{th,2} = \eta_{th,3}$

High-temperature reservoir at $T_H$

Low-temperature reservoir at $T_L$
THE CARNOT PRINCIPLES

(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
THERMODYNAMIC TEMPERATURE SCALE

High-temperature reservoir at $T_H = 1000$ K

A reversible HE $\eta_{th,A}$

Another reversible HE $\eta_{th,B}$

$\eta_{th,A} = \eta_{th,B} = 70\%$

Low-temperature reservoir at $T_L = 300$ K
THERMODYNAMIC TEMPERATURE SCALE
THERMODYNAMIC TEMPERATURE SCALE

High-temperature reservoir at $T_H$

$Q_H$

Reversible heat engine or refrigerator

$W_{net}$

$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$

Low-temperature reservoir at $T_L$

$Q_L$
THERMODYNAMIC TEMPERATURE SCALE

Heat reservoir $T$

Carnot HE

$Q_H$

$Q_L$

273.16 K (assigned)
Water at triple point

$T = 273.16 \frac{Q_H}{Q_L}$
CARNOT HEAT ENGINE

High-temperature reservoir at $T_H = 1000$ K

Carnot HE

$\eta_{th} = 70\%$

Low-temperature reservoir at $T_L = 300$ K

$Q_H$

$W_{net, out}$

$Q_L$
CARNOT HEAT ENGINE

High-temperature reservoir at $T_H = 1000$ K

Rev. HE $\eta_{th} = 70\%$

Irrev. HE $\eta_{th} = 45\%$

Impossible HE $\eta_{th} = 80\%$

Low-temperature reservoir at $T_L = 300$ K
The Quality of Energy

High-temperature reservoir at $T_H$

Rev. HE $\eta_{th}$

<table>
<thead>
<tr>
<th>$T_H$, K</th>
<th>$\eta_{th}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>925</td>
<td>67.2</td>
</tr>
<tr>
<td>800</td>
<td>62.1</td>
</tr>
<tr>
<td>700</td>
<td>56.7</td>
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<tr>
<td>500</td>
<td>39.4</td>
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<tr>
<td>350</td>
<td>13.4</td>
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</tbody>
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Low-temperature reservoir at $T_L = 303$ K
CARNOT REFRIGERATOR AND HEAT PUMP

Warm environment at $T_H = 300 \, \text{K}$

- Reversible refrigerator $COP_R = 11$
- Irreversible refrigerator $COP_R = 7$
- Impossible refrigerator $COP_R = 13$

Cool refrigerated space at $T_L = 275 \, \text{K}$