V. The Second Law of Thermodynamics

E. The Carnot Cycle

1. The reversible heat engine (a piston cylinder device) that operates on a cycle between heat reservoirs at \( T_H \) and \( T_L \), as shown below on a P-v diagram, is the Carnot cycle.

2. Because the cycle is reversible, the Carnot cycle, operating between \( T_H \) and \( T_L \), is the most efficient cycle possible. We want to know how much heat, \( Q_L \), must be rejected by the engine.

3. If the Carnot heat engine is operated in reverse, we call it a Carnot refrigeration cycle.

\[ \eta_{th} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{Q_L}{Q_H} \]

\[ W_{net,out} = \text{shaded area} \]

\[ Q_{12} = 0, Q_{23} = 0 \]

\[ \text{1-2 rev., isothermal expansion} \]
\[ \text{2-3 rev., adiabatic expansion} \]
\[ \text{3-4 rev., isothermal compression} \]
\[ \text{4-1 rev., adiabatic compression} \]

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F. 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.” (p. 302)

2. “The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.” (p. 302)

Both principles are based on the Kelvin-Plank and Clausius statements of the second law. From the second principle we conclude that the thermal efficiency is a function only of the temperatures of the reservoirs.

\[ \eta_{th} = 1 - \frac{Q_L}{Q_H} = 1 - f(T_H, T_L) \]  

(6-13)
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3. Proof of the Second Carnot Principle
Suppose we have a “super engine” that is more efficient than a reversible engine. Let both engines receive the same amount of thermal energy, $Q_H$, from a high temperature reservoir. Then

$$W_{\text{rev}} < W_{\text{srev}} \text{ and } Q_{LS} < Q_L.$$

If we run the “normal” engine in reverse, and power it with $W_{\text{srev}}$, then the combined engine takes heat from a single reservoir and produces a net amount of work. This violates the Kelvin-Plank statement of the 2nd law. We conclude that both reversible engines have the same efficiency.

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G. The Thermodynamic Temperature Scale
1. Define such that the T scale is independent of the properties of the substance being used to measure the temperature.

2. Derivation
Consider three reversible engines. By the 2nd Carnot principle,

$$\eta_{\text{th}} = 1 - \frac{Q_L}{Q_H} = 1 - f(T_H, T_L) \tag{6-13}$$

Apply (6-13) to each engine:

$$\frac{Q_2}{Q_1} = f(T_1, T_2), \quad \frac{Q_3}{Q_2} = f(T_2, T_3), \quad \frac{Q_3}{Q_1} = f(T_1, T_3)$$

$$\frac{Q_3}{Q_1} = \frac{Q_2}{Q_1} \cdot \frac{Q_3}{Q_2} = f(T_1, T_3) = f(T_1, T_2)f(T_2, T_3)$$

$$Q_3 = \phi(T_3) \text{ or } Q_L = \phi(T_L)$$

$$Q_H = \phi(T_H)$$

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G. The Thermodynamic Temperature Scale

2. Derivation

Because it is the simplest possible choice, Kelvin proposed taking $\phi(T) = T$ to give the Kelvin scale:

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad (6-16)$$

The magnitude of a kelvin is $1/273.16$ of the temperature interval between absolute zero and the triple-point of water ($0.01^\circ C$).

The magnitude of the Kelvin and Celsius scales are the same ($1 \text{ K} = 1^\circ C$) and $T(\circ C) = T(K) - 273.15$.

The smallest possible value of $Q_L$ is

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

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H. The Carnot Heat Engine

For any heat engine,

$$\eta_{th} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{\dot{Q}_L}{\dot{Q}_H}$$

For any reversible heat engine, Carnot or otherwise,

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad (6-16)$$

and

$$\eta_{th,rev} = 1 - \frac{T_L}{T_H} \quad (6-18)$$
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I. The Carnot Refrigerator and Heat Pump

\[
\text{COP}_{R,\text{rev}} = \frac{1}{Q_H / Q_L - 1} = \frac{1}{T_H / T_L - 1}
\] (6-20)

\[
\text{COP}_{\text{HP,rev}} = \frac{1}{1 - Q_L / Q_H} = \frac{1}{1 - T_L / T_H}
\] (6-21)

Example - An inventor claims to have a heat engine that will use the temperature difference between the top and bottom layers of a lake to produce \(W_{\text{net,out}} = 1 \text{ MW}\) of work for centuries. Is this person telling the truth? The lake and conditions are shown below.

- Average solar flux = 240 W/m²
- Area of lake = \(10^4 \text{ m}^2\)
- \(25 \text{ C}\)
- \(15 \text{ C}\)
V. The Second Law of Thermodynamics

7. Example
   a. First law analysis: not violated since $2.4 \text{ MW} > 1 \text{ MW}$

   $$Q_H = 240 \frac{W}{m^2} \cdot 10^4 m^2 = 2.4 \text{ MW}$$

   b. Second law analysis (what is the best we can hope for?)

   $$\eta_{\text{max}} = \frac{W_{\text{out}}}{Q_H} = 1 - \frac{T_L}{T_H} = 1 - \frac{15 + 273}{25 + 273} = 0.0336$$

   $$W_{\text{out, max}} = \eta Q_H = 0.0336(2.4 \text{ MW}) = 0.0805 \text{ MW}$$

   c. Conclusion: inventor is not telling the truth because claimed work output is too high.