

Chapter 6

The Second Law of Thermodynamics

Advanced Thermodynamics

Min Soo Kim

6.1 Introduction to the Second Law of Thermodynamics



Figure 6.1 Coffee

6.1 Introduction to the Second Law of Thermodynamics

- Is there any way in which we can write the first law in terms of state variables only? → **The Second Law of thermodynamics**
- Is there some state variable by which we can distinguish between a reversible and an irreversible process?
→ **The Second Law of thermodynamics**

Most general form (for closed system) is,

$$dU = \delta Q - \delta W \quad (\text{eq. 6.1})$$

(Neither δQ or δW is an exact differential)

6.2 The Mathematical Concept of Entropy

$$\delta W_r = PdV$$

(V is a state variable and dV is an exact

differential)

$$\frac{\delta W_r}{P} = dV$$

(eq. 6.2)

($\frac{1}{P}$ is integrating factor)

$$\frac{\delta Q_r}{T} \equiv dS$$

(eq 6.3)

(Clausius definition of the entropy S)

Substituting eq(6.2) & eq(6.3) in eq(6.1) ,

$$dU = TdS - PdV$$

6.3 Irreversible Processes (Clausius statement)

- **Clausius statement** : It is impossible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a cooler body to a hotter body

→ If $T_2 > T_1$ then $Q_2 = Q_1$,
with $W = 0$. is impossible

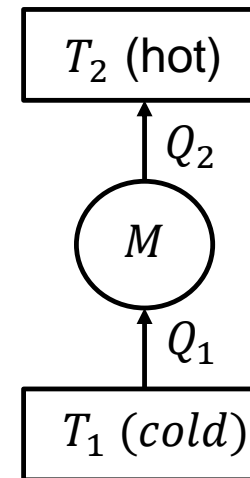


Figure 6.2 Schematic diagram of a device forbidden by the Clausius statement of the second law.

6.3 Irreversible Processes (Kelvin-Planck statement)

- **Kelvin-Planck statement** : It is impossible to construct a device that operates in a cycle and produces no other effect than the performance of work and the exchange of heat with a single reservoir.

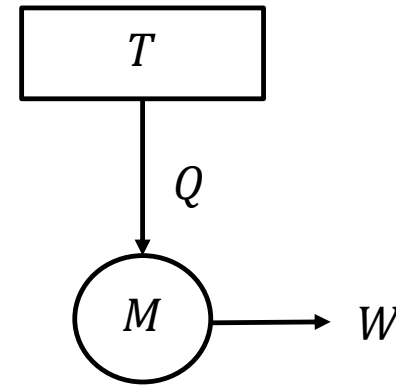


Figure 6.3 Schematic diagram of a device forbidden by the Kelvin-Planck statement of the second law.

→ *It is impossible to have $W = Q_2$*

6.4 Carnot's Theorem

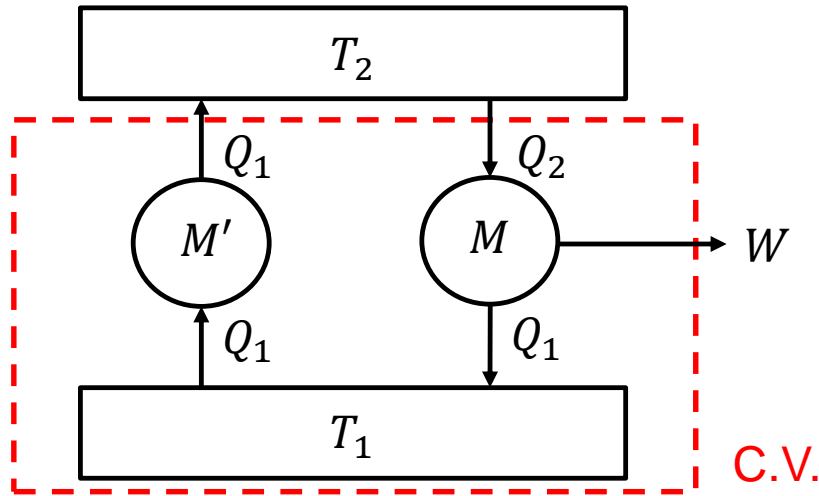


Figure 6.4 A composition engine in violation of the Clausius statement

Work generation from?

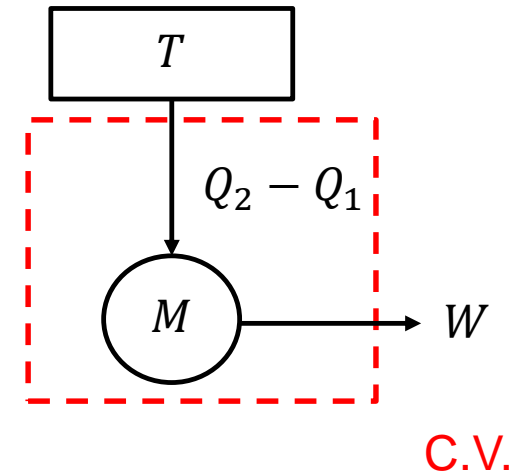


Figure 6.5 The equivalent engine in violation of the Kelvin-Planck statement

Heat is transported from T to where?

Applying Carnot's theorem to both statement, it is impossible to make engine which goes against the statements.

6.5 The Clausius Inequality and The Second Law

For Carnot cycle,

$$\frac{Q_2}{T_2} + \frac{Q_1}{T_1} = 0$$

$$\frac{\delta Q_2}{T_2} + \frac{\delta Q_1}{T_1} = 0$$

$$\sum \frac{\delta Q_t}{T_t} \rightarrow \oint \frac{\delta Q_r}{T} = 0$$

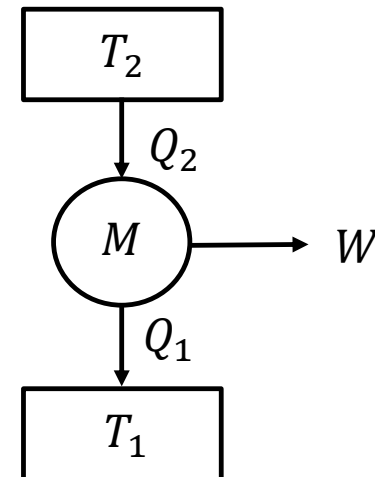


Figure 6.6 Schematic diagram of Carnot's cycle

6.5 The Clausius Inequality and The Second Law

For irreversible cycle,

$$\frac{Q_1'}{Q_2'} < \frac{Q_1}{Q_2} = -\frac{T_1}{T_2} \quad \rightarrow \quad \frac{Q_2'}{T_2} + \frac{Q_1'}{T_1} < 0$$

$$\oint \frac{\delta Q_r}{T} < 0 \rightarrow \frac{\delta Q_2'}{T_2} + \frac{\delta Q_1'}{T_1} < 0 \rightarrow \oint \frac{\delta Q}{T} \leq 0 \rightarrow \oint \frac{\delta Q}{T} = \int_1^2 \frac{\delta Q}{T} + \int_2^1 \frac{\delta Q_r}{T} \leq 0$$

$$\int_1^2 \frac{\delta Q}{T} \leq \int_2^1 \frac{\delta Q_r}{T} \equiv S_2 - S_1 \quad \rightarrow \quad dS \geq \frac{\delta Q}{T}$$

$$\Delta S \equiv S_2 - S_1 \geq 0 \quad (\text{isolated system})$$

6.5 The Clausius Inequality and The Second Law

$$\Delta S \equiv S_2 - S_1 \geq 0 \quad (\textit{isolated system})$$

The entropy of an isolated system increases in any irreversible process and is unaltered in any reversible process. This is the principle of increasing entropy.