Chapter 6

The Second Law of Thermodynamics

Advanced Thermodynamics

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Not possible !

Irreversible Process

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,

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

(Neither $\boldsymbol{\delta} Q$ or $\boldsymbol{\delta} W$ is an exact differential)

$\boldsymbol{\delta W_r = PdV}$ (V is a state variable and $\mathrm{d}V$ is an exact differential)

$\boldsymbol{\frac{\delta W_r}{P} = dV}$ $(\boldsymbol{eq. 6. 2})$ ($\frac{1}{P}$ is integrating factor)

$\boldsymbol{\frac{\delta Q_r}{T} \equiv dS}$ $(\boldsymbol{eq\ 6. 3})$ (Clasius definition of the entropy S)

Subtituting *eq(6.2)* & *eq(6.3)* in *eq(6.1)* ,

$$\boldsymbol{dU = TdS - PdV}$$

- **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

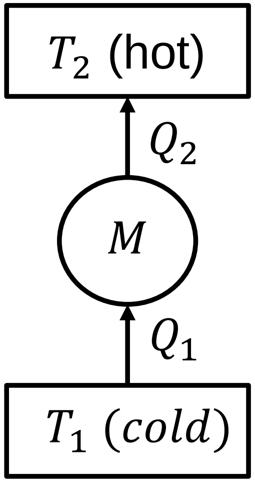

Figure 6.2 Schematic diagram of a device forbidden by the Clausius statement of the second law.

$$\rightarrow If \quad T_2 > T_1 \text{ then } Q_2 = Q_1 ,$$
$$with\ W = 0. is\ impossible$$

- **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.

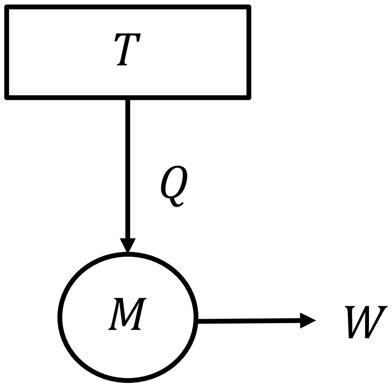

Figure 6.3 Schematic diagram of a device forbidden by the Kelvin-Planck statement of the second law.

$\rightarrow It\ is\ impossible\ to\ have\ W = Q_2$

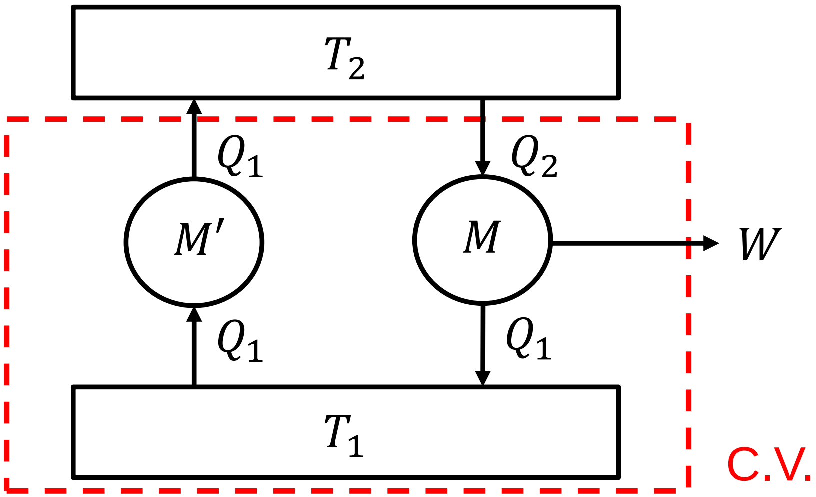

Figure 6.4 A composition engine in violation of the Clausius statement

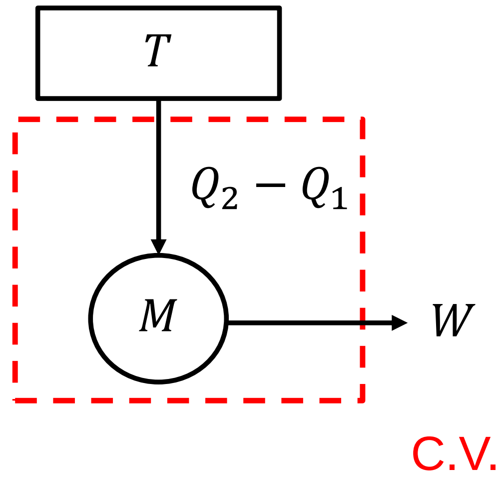

Figure 6.5 The equivalent engine in violation of the Kelvin-Planck statement

Work generation from?

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.

For Carnot cycle,

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

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

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

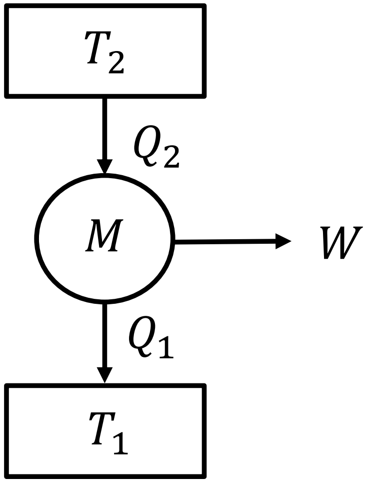

Figure 6.6 Schematic diagram of Carnot's cycle

For irreversible cycle,

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

$$\oint \frac{\boldsymbol{\delta} Q_r}{T} < 0 \rightarrow \frac{\boldsymbol{\delta} Q_2{}'}{T_2} + \frac{\boldsymbol{\delta} Q_1{}'}{T_1} < 0 \quad \rightarrow \oint \frac{\boldsymbol{\delta} Q}{T} \leq 0 \rightarrow \oint \boldsymbol{\frac{\delta Q}{T}} = \oint_1^2 \boldsymbol{\frac{\delta Q}{T}} + \oint_2^1 \boldsymbol{\frac{\delta Q_r}{T}} \leq \mathbf{0}$$

$$\oint_1^2 \frac{\boldsymbol{\delta} Q}{T} \leq \oint_2^1 \frac{\boldsymbol{\delta} Q_r}{T} \equiv S_2 - S_1 \qquad \rightarrow \qquad \boldsymbol{dS \geq \frac{\delta Q}{T}}$$

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

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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.