Chapter 5

Consequences of the First Law

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A.1 Partial Derivatives

Consider a function of three variables, $f(x, y, z) = 0$

Since only two variables are independent, we can write

$$x = x(y, z), \; y = y(x, z)$$

Then $dx = (\frac{\partial x}{\partial y})_z dy + (\frac{\partial x}{\partial z})_y dz$, and

$$dy = (\frac{\partial y}{\partial x})_z dx + (\frac{\partial y}{\partial z})_x dz$$

We obtain,

$$dx = (\frac{\partial x}{\partial y})_z \left\{ (\frac{\partial y}{\partial x})_z dx + (\frac{\partial y}{\partial z})_x dz \right\} + (\frac{\partial x}{\partial z})_y dz$$

$$\mathrm{d}x = \left(\frac{\partial x}{\partial y}\right)_z \left\{ \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \right\} + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y \right] dz$$

If $\mathrm{d}z = 0$ and $\mathrm{d}x \neq 0$,

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$. This expression is known as the ***reciprocal relation***.

If $\mathrm{d}x = 0$ and $\mathrm{d}z \neq 0$,

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y \quad \text{(previous slide)}$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y} \quad \text{(using reciprocal relation)}$$

Substituting these equations yield,

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \qquad \text{The } \textbf{\textit{cyclical rule}}, \text{ or } \textbf{\textit{cyclical relation.}}$$

A.1 Partial Derivatives

Consider a function u of three variables x, y, z can be written as a function of only two variables and those two variables are independent.

$$u = u(x, y)$$

Alternatively,

$$x = x(u, y)$$

Then

$$\mathrm{d}x = \left(\frac{\partial x}{\partial u}\right)_y du + \left(\frac{\partial x}{\partial y}\right)_u dy.$$

If we divide the equation by $\mathrm{d}z$ while holding u constant,

$\left(\frac{\partial x}{\partial z}\right)_u = \left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial z}\right)_u$. The ***chain rule of differentiation***.

In general, $u = u\,(\,T, v\,)$

Using the cyclical and reciprocal relations,

$$\left(\frac{\partial T}{\partial v}\right)_u = -\,\frac{\left(\frac{\partial u}{\partial v}\right)_T}{\left(\frac{\partial u}{\partial T}\right)_v}$$

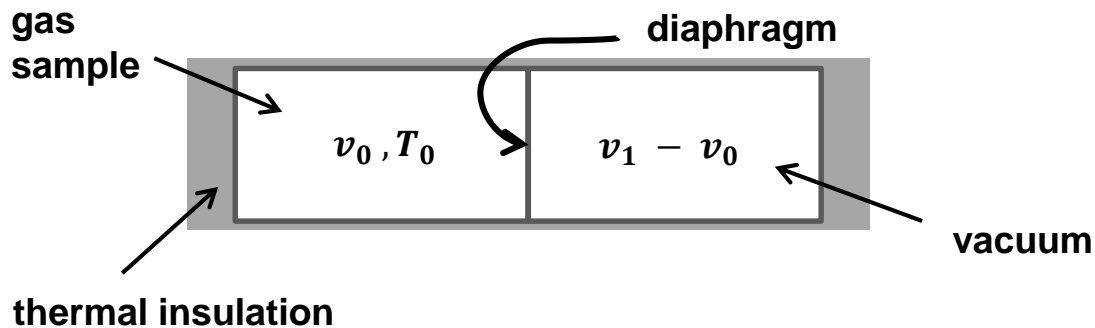For a reversible process, $c_v = \left(\frac{\partial u}{\partial T}\right)_v$

$$\therefore\ \left(\frac{\partial u}{\partial v}\right)_T = -c_v \left(\frac{\partial T}{\partial v}\right)_u$$

Then how can we keep u constant during the expansion?

5.1 The Gay-Lussac-Joule Experiment

$du = \underline{\delta q} - \underline{\delta w} \Rightarrow$ free expansion

$\quad\;$ **= 0** $\quad\;\;$ **= 0**

$\;$ **(adiabatic)** $\;$ **(no work)**

$T_1 = T_0 + \int_{v_0}^{v_1} (\frac{\partial T}{\partial v})_u \, dv, \quad \eta \equiv (\frac{\partial T}{\partial v})_u$: Joule's coefficient

From Joule's experimental result,

$|\eta| = \left|\left(\frac{\partial T}{\partial v}\right)_u\right| < 0.001 \text{ K kilomole m}^{-3}$

For a Van der Waals gas, (Problem 5-3)

$$\eta = -\frac{a}{v^2 c_v}$$

For an ideal gas,

by using the equation $du = Tds - Pdv,$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_v - P = T\left[\frac{\partial}{\partial T}\left(\frac{RT}{v}\right)\right]_v - P$$

$$= \frac{RT}{v} - P = 0$$

Then $u = u(T)$

For a real gas,

by using the equation $dq = \left(\dfrac{\partial u}{\partial T}\right)_v dT + \left[\left(\dfrac{\partial u}{\partial v}\right)_T + P\right] dv$ divide by the

temperature T,

$$\frac{dq}{T} = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v dT + \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv$$
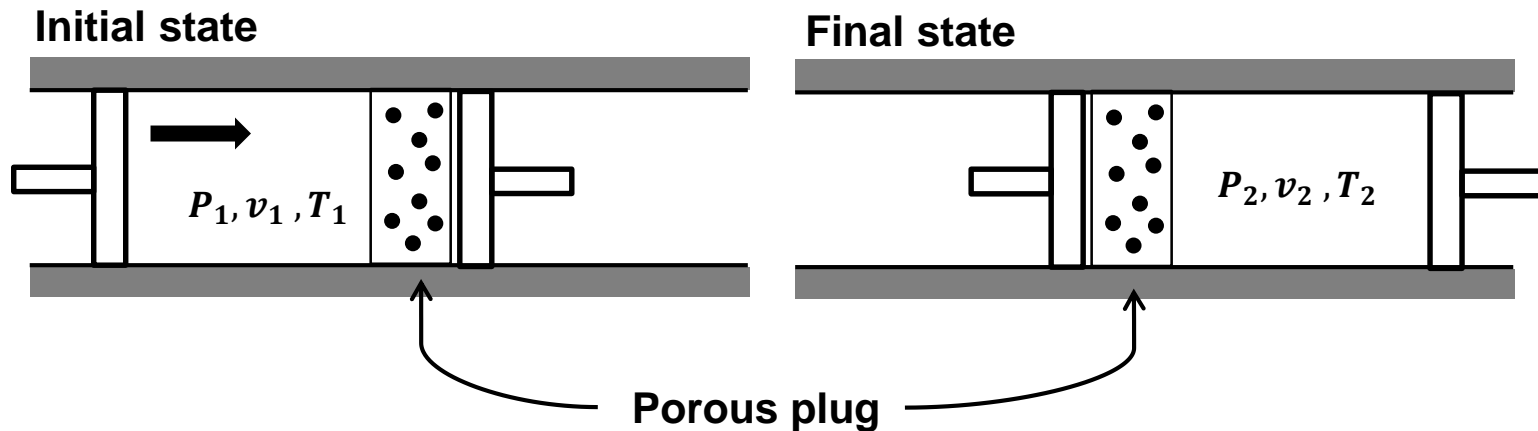
$$\frac{\partial}{\partial v}\left(\frac{1}{T}\frac{\partial u}{\partial T}\right) = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial u}{\partial v} + P\right)\right]$$

$$\frac{1}{T}\frac{\partial^2 u}{\partial v \partial T} = -\frac{1}{T^2}\left(\frac{\partial u}{\partial v} + P\right) + \frac{1}{T}\frac{\partial^2 u}{\partial v \partial T} + \frac{1}{T}\frac{\partial P}{\partial T}$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$$

Since the process takes place in an insulated cylinder,

Initial state

Final state

P_1, v_1, T_1

P_2, v_2, T_2

Porous plug

$\delta q = 0$

Specific work done in forcing the gas through the plug, $w_1 = \int_{v_1}^{0} P_1\, dv = -P_1 v_1$

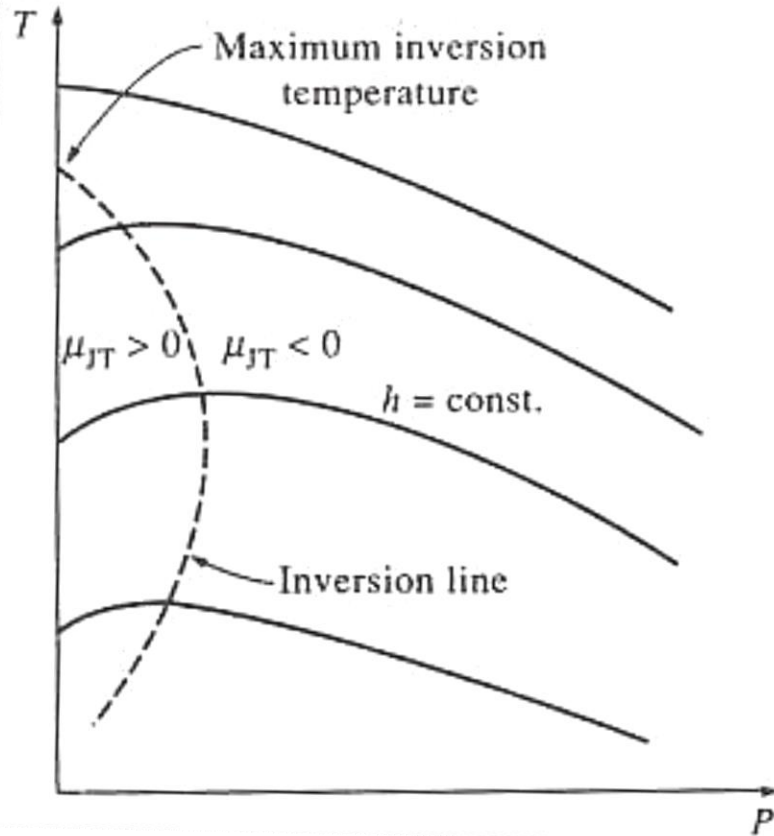Specific work done by the gas in the expansion, $w_2 = \int_{0}^{v_2} P_2\, dv = P_2 v_2$

The total work, $w = w_1 + w_2 = P_2\, v_2 - P_1\, v_1 = u_1 - u_2$

$$u_1 + P_1\, v_1 = u_2 + P_2\, v_2 \qquad \Leftrightarrow \qquad h_1 = h_2$$

constant

Thus, a throttling process occurs at constant enthalpy.

Joule-Thomson coefficient

$$\mu_{JT} \equiv (\frac{\partial T}{\partial P})_h$$

the point where $\mu_{JT} = 0$ is called inversion point.

from $h = h(T, P)$,

$$dh = (\frac{\partial h}{\partial T})_P \, dT + (\frac{\partial h}{\partial P})_T \, dP$$

$$\mu_{JT} \equiv (\frac{\partial T}{\partial P})_h = \left[\frac{T_2 - T_1}{P_2 - P_1}\right]_h$$

$$T_2 = T_1 - \mu(P_2 - P_1)$$

The gas is cooling when the μ is positive

and heating when the μ is negative

Joule-Thomson coefficient

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = -\left(\frac{\partial T}{\partial h}\right)_P \left(\frac{\partial h}{\partial P}\right)_T = \frac{1}{C_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right]$$

For a real gas,

$$Tds = dh - vdP$$

$$T\left(\frac{\partial s}{\partial P}\right)_T = \left(\frac{\partial h}{\partial P}\right)_T - v$$

$$\left(\frac{\partial s}{\partial P}\right)_T = \frac{\partial(s,T)}{\partial(P,T)} = \frac{\partial(v,P)}{\partial(P,T)} = -\left(\frac{\partial v}{\partial T}\right)_P$$

$$\left(\frac{\partial h}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P + v$$

Joule-Thomson coefficient

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = -\left(\frac{\partial T}{\partial h}\right)_P \left(\frac{\partial h}{\partial P}\right)_T = \frac{1}{C_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right]$$

For an ideal gas, $\mu_{JT} = 0$,

$$\left(\frac{\partial h}{\partial P}\right)_T = 0 \text{ and } h = h(T)$$

For a Van der Waals gas, $P = \frac{RT}{v-b} - \frac{a}{v^2}$

$$\mu_{JT} = \frac{1}{c_P}\left[\frac{\frac{2a}{RT}\left(1-\frac{b}{v}\right)^2 - b}{1 - \frac{2a}{vRT}\left(1-\frac{b}{v}\right)^2}\right]$$

If $\mu_{JT} = 0$, $T_i = \frac{2a}{bR}\left(1-\frac{b}{v}\right)^2$
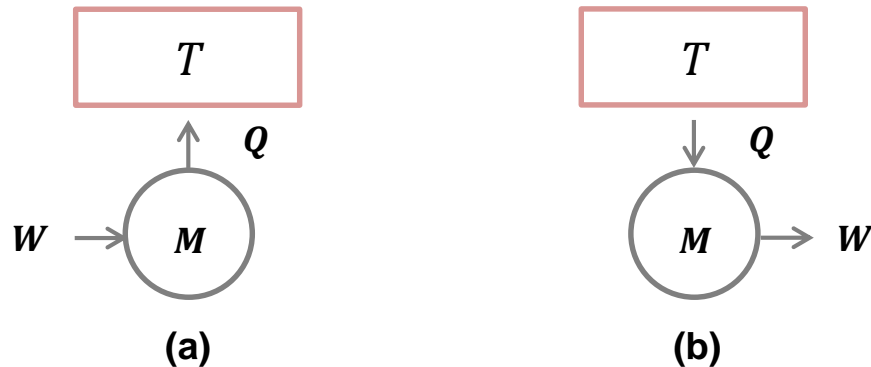
Carnot cycle

Fig. The concept of a heat engine.

In (a), work is done on the system and is converted to heat.

In (b), heat is extracted from a reservoir and is converted to mechanical work.

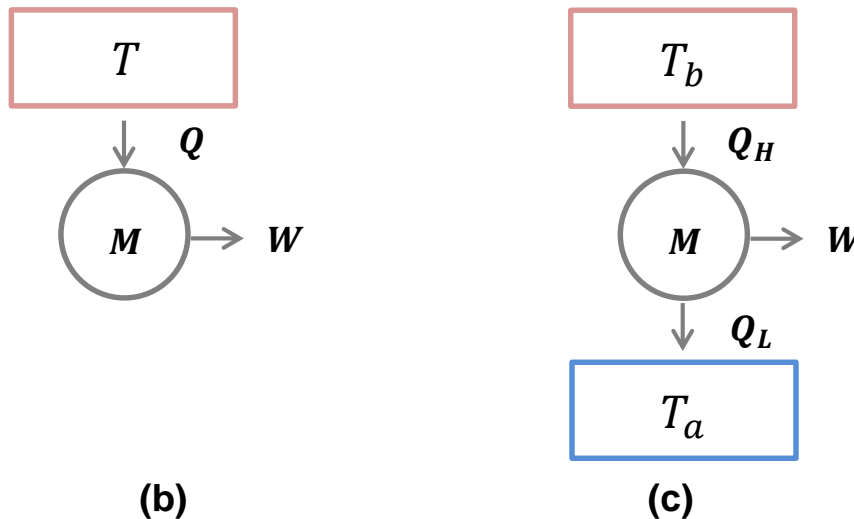   This configuration is not possible.

Carnot cycle

Fig. The concept of a heat engine.

Can the work done by the system be equal to the heat in?

The second law of thermodynamics states *unequivocally* that it is impossible to construct a perfect heat engine.

Thus case (b) must be modified as case (c)

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.

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.
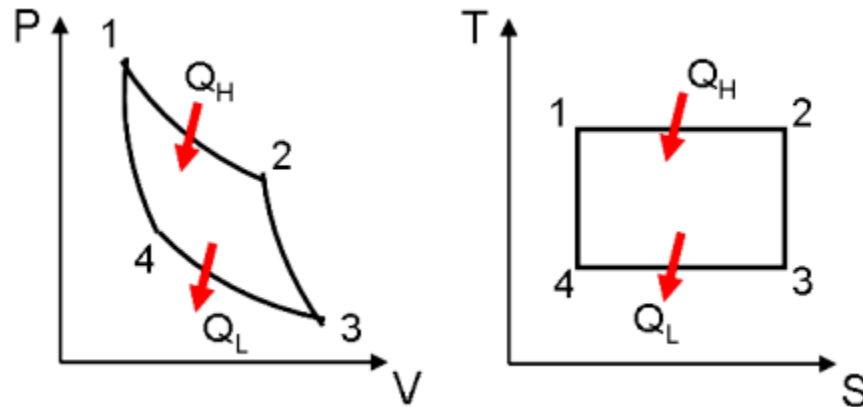
Carnot cycle

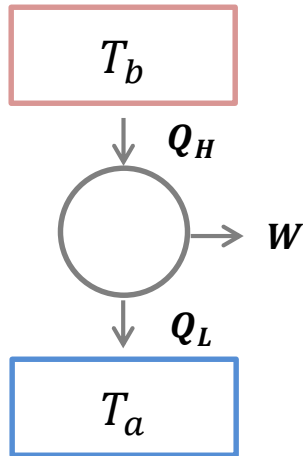**Fig. P-V and T-S diagrams of Carnot cycle.**

1 – 2 : isothermal expansion

2 – 3 : adiabatic expansion

3 – 4 : isothermal compression

4 – 1 : adiabatic compression

The efficiency of the engine,

$$\eta = \frac{W}{Q_H} = \frac{|W|}{|Q_H|} = \frac{\text{output}}{\text{input}}$$

Applying the first law to the system,

$$\Delta U = Q_H + Q_L - W = |Q_H| - |Q_L| - |W| \qquad\qquad Q_L < 0$$

Since the system is in a cyclical process, $\Delta U = 0$. Then,

$$W = Q_H + Q_L \text{ or } W = |Q_H| - |Q_L|$$

Substituting the equations,

$$\eta = \frac{Q_L + Q_H}{Q_H} = 1 + \frac{Q_L}{Q_H} = 1 - \frac{|Q_L|}{|Q_H|}$$

For an ideal gas, $Pv = RT$, $u = u(T)$,

For isothermal process, $Q_H = W_{12} = n\bar{R}\, T_b\, \ln\dfrac{V_2}{V_1} > 0$

$$-Q_L = W_{34} = n\bar{R}\, T_a\, \ln\dfrac{V_4}{V_3} < 0$$

For adiabatic process, $PV^\gamma = constant$,

$$T_b\, V_2{}^{\gamma-1} = T_a\, V_3{}^{\gamma-1}$$

$$T_b\, V_1{}^{\gamma-1} = T_a\, V_4{}^{\gamma-1}$$

$$\Rightarrow \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\Rightarrow \quad \frac{Q_H}{Q_L} = \frac{T_b}{T_a}$$

$$\left(\begin{array}{c} s_2 - s_1 = c_v \ln\dfrac{T_2}{T_1} + R\ln\dfrac{v_2}{v_1} \\[2mm] = c_p \ln\dfrac{T_2}{T_1} - R\ln\dfrac{P_2}{P_1} = 0 \\[2mm] c_v = \dfrac{1}{\kappa - 1}R, \qquad c_p = \dfrac{\kappa}{\kappa - 1}R \\[2mm] \dfrac{P_2}{P_1} = \left(\dfrac{v_1}{v_2}\right)^\kappa \end{array} \right)$$

The efficiency of the Carnot cycle, $\eta = 1 - \dfrac{Q_L}{Q_H} = 1 - \dfrac{T_a}{T_b}$
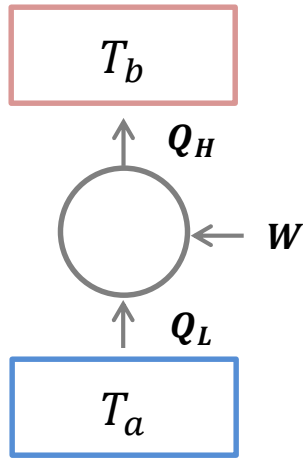
5.3 Heat engines and the Carnot cycle

Carnot engine has the maximum efficiency for any engine that one might design.

1. Carnot engine operates between two reservoirs and that it is reversible.

2. If a working substance other than an ideal gas is used, the shape of curves in the P-V diagram will be different.

3. The efficiency would be 100 percent if we were able to obtain a low temperature reservoir at absolute zero. → However this is forbidden by the third law.

Carnot refrigerator

T_b

Q_H

W

Q_L

T_a

Reverse process of Carnot engine

Coefficient of performance(COP)

$$\text{COP} \equiv -\frac{Q_L}{W} = \frac{|Q_L|}{|W|} = \frac{|Q_L|}{|Q_2| - |Q_L|} = \frac{T_1}{T_2 - T_1}$$

We introduce a minus sign in order to make the COP a positive quantity.

The heat Q_L is extracted from the low temperature reservoir and W is the work done on the system. Q_L is positive (heat flow **into** the system) and W is negative (work done **on** the system)
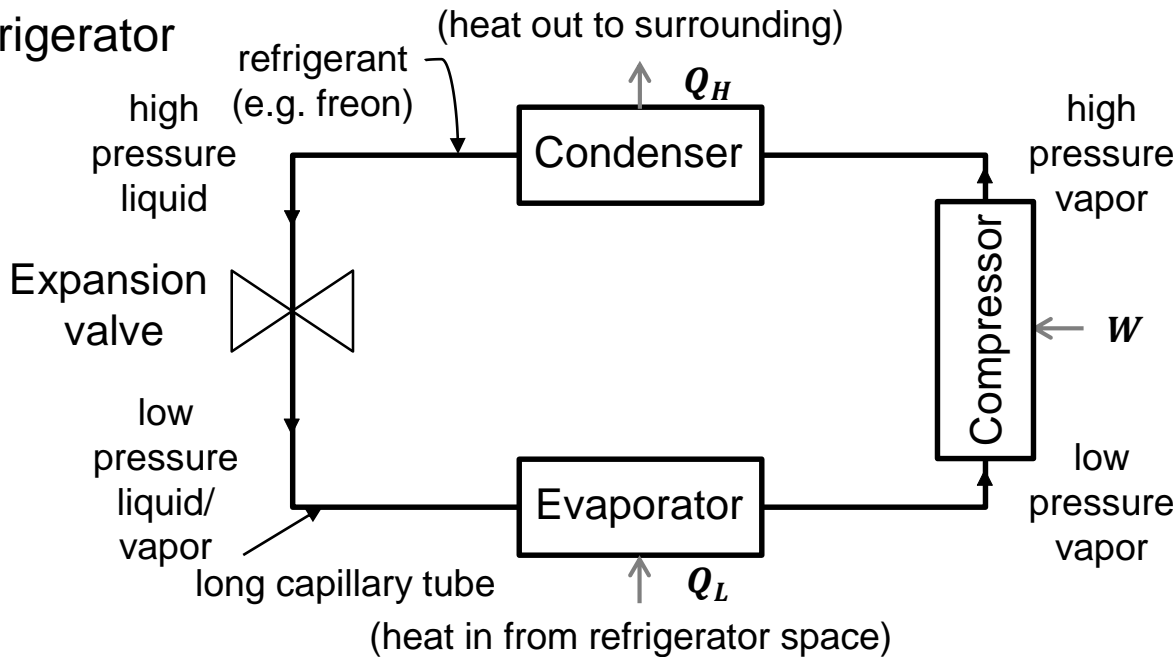
Typical refrigerator

Fig. Schematic diagram of a typical refrigerator

1. The refrigerant is a substance chosen to be a saturated liquid at the pressure and temperature of condenser.

2. The liquid undergoes a throttling process in which it is cooled and is partially vaporized.
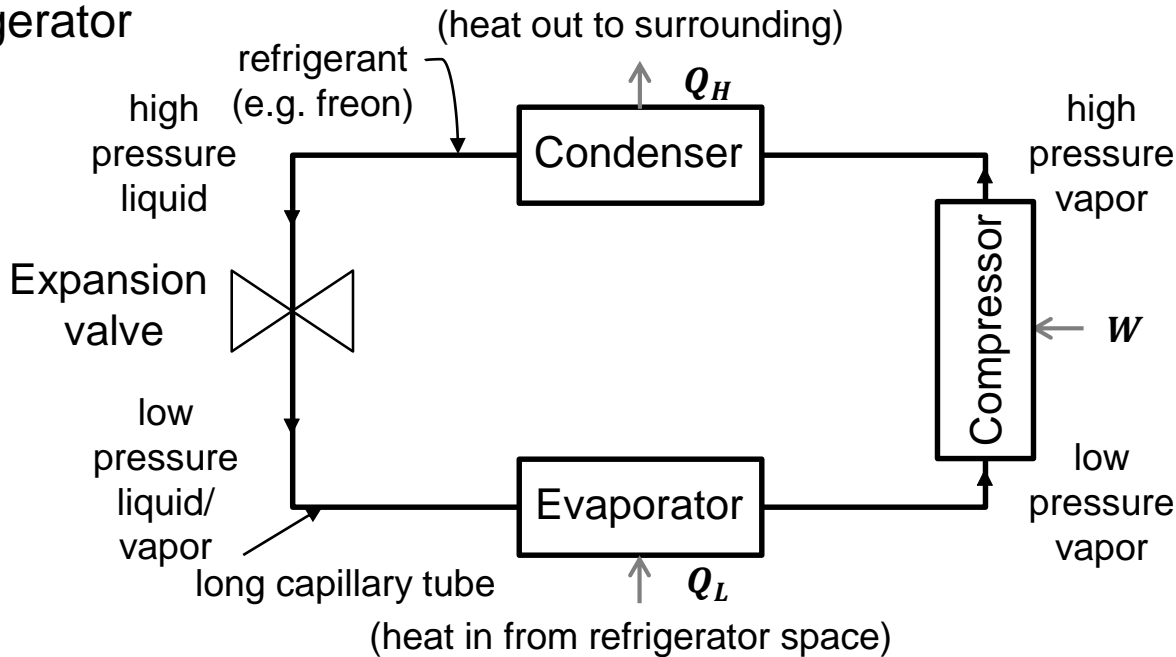
Typical refrigerator

Fig. Schematic diagram of a typical refrigerator

3. The vaporization is completed in the evaporator: the heat is absorbed by the refrigerant from the low temperature reservoir (the interior refrigerator space).

4. The low pressure vapor is then adiabatically compressed and isobarically cooled until it becomes a liquid again.

Chapter 6

The Second Law of Thermodynamics

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Not possible !

Irreversible Process

Figure 6.1 Coffee

- 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 any 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,

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

(Neither δQ or δW is an exact differential)

$$\delta W_r = PdV \qquad \text{(V is a state variable and dV is an exact differential)}$$

$$\frac{\delta W_r}{P} = dV \qquad (eq.\ 6.2) \qquad \text{($\frac{1}{P}$ is integrating factor)}$$

$$\frac{\delta Q_r}{T} \equiv dS \qquad (eq.\ 6.3) \qquad \text{(Clausius definition of the entropy S)}$$

Substituting *eq. 6.2* & *eq. 6.3* in *eq. 6.1* ,

_____

- **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

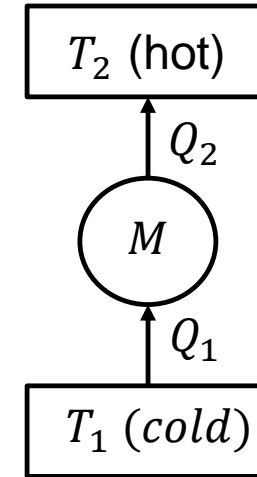$$\rightarrow If \quad T_2 > T_1 \text{ then } Q_2 = Q_1 \,,$$
$$with\ W = 0 \quad is\ impossible$$

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

- **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.

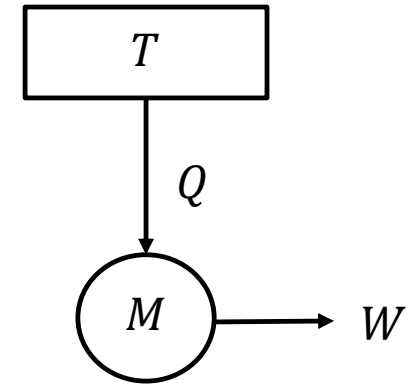$\rightarrow It\ is\ impossible\ to\ have\ W = Q$

Figure 6.3 Schematic diagram of a device forbidden by the Kelvin-Planck statement of the second law.
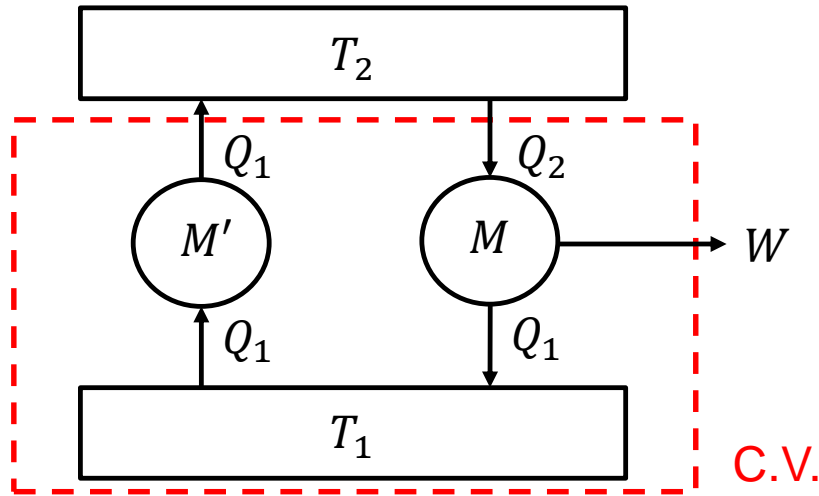
6.4 Carnot's Theorem

Figure 6.4 A composition engine in violation of the Clausius statement

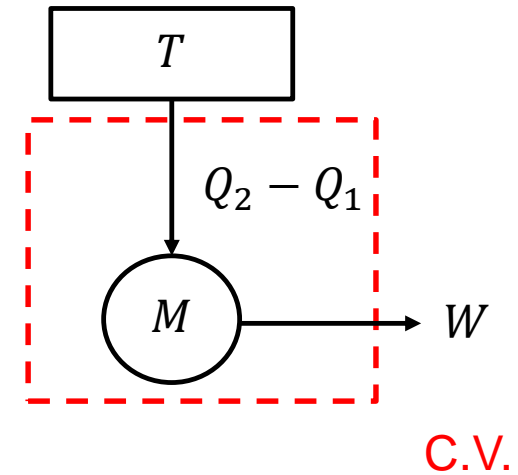**Figure 6.5** The equivalent engine in violation of the Kelvin-Planck statement

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,

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

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

$$\sum \frac{\boldsymbol{\delta}Q_t}{T_t} \rightarrow \underline{\hspace{4cm}}$$
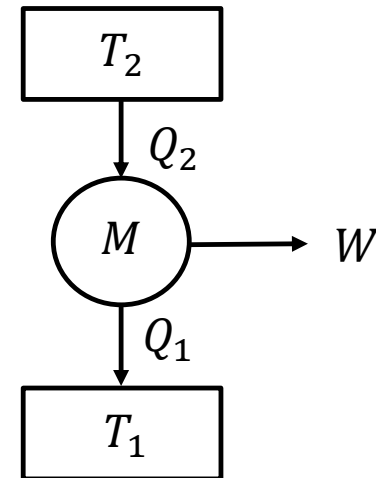
Figure 6.6 Schematic diagram of Carnot's cycle

For irreversible cycle,

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

$$\oint \frac{\delta Q_r}{T} < 0 \rightarrow \underline{\hspace{4cm}} \rightarrow \oint \frac{\delta Q}{T} \leq 0 \rightarrow \oint \frac{\delta Q}{T} = \oint_1^2 \frac{\delta Q}{T} + \oint_2^1 \frac{\delta Q_r}{T} \leq 0$$

$$\oint_1^2 \frac{\delta Q}{T} \leq \oint_2^1 \frac{\delta Q_r}{T} \equiv \underline{\hspace{2cm}} \rightarrow dS \geq \frac{\delta Q}{T}$$

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

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

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

This is the _____