Chapter 10
The First Law of Thermodynamics

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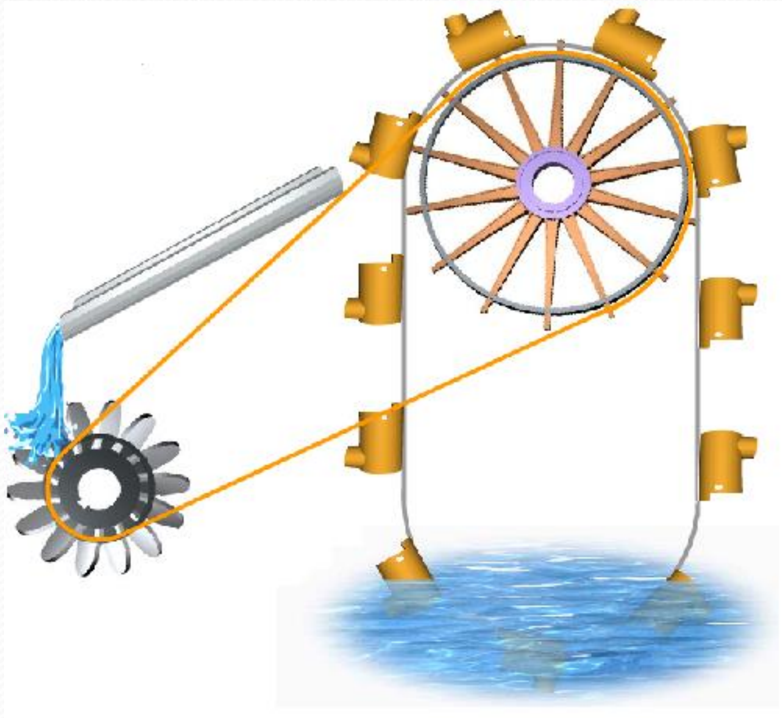
The First Law of Thermodynamics

- Perpetual mobile of the first kind



Three great persons

Julius Robert von Mayer (1814 –1878) a German physician and physicist and one of the founders of thermodynamics

Hermann Ludwig Ferdinand von Helmholtz (1821 – 1894) a German physicist

James Prescott Joule (1818 – 1889) an English physicist and brewer

- **The First Law of Thermodynamics**

- **The applications of the first law of thermodynamics in different kind of thermodynamic processes.**

◆The First Law of Thermodynamics

The balloon is made of a special material. Heating the balloon and it will ……

Temperature will rise?

Volume will expand?

……

The First Law of Thermodynamics:

Energy is always conserved. It can change forms: kinetic, potential, internal etc., but the total energy is a constant. Another way to say it is that the change in internal energy of a system is equal to the sum of the work done on it and the amount of heat energy transferred to it.

$$Q = E_2 - E_1 + W$$

Work

heat energy

the change in internal energy

Infinitesimal changes of state

$$dQ = dE + dW$$

dQ: a small amount of heat added to the system

dW: the system does a small amount of work

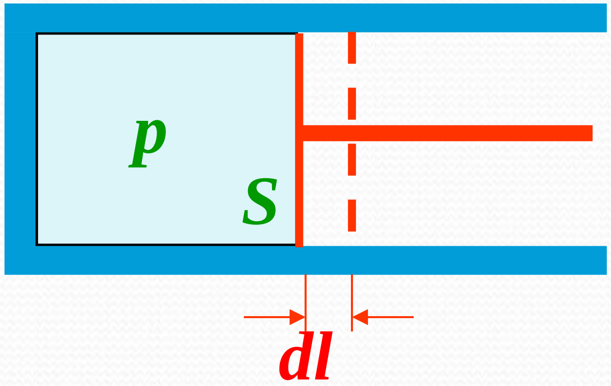
dE: internal energy changes by a small amount

Signs for Heat and Work in Thermodynamics

- **A positive value of Q represents heat flow into the system; negative Q represents heat flow out of the system.**
- **A positive value of W represents work done by the system against its surroundings, such as work done by an expanding gas, and hence corresponds to energy leaving the system. Negative W, such as work done during compression of a gas in which work is done on the gas by its surroundings, represents energy entering the system.**

◆Work done during volume changes

In a quasistatic process, $V \to V+dV$:



$$dW = pSdl = pdV$$

$V_1 \to V_2$:

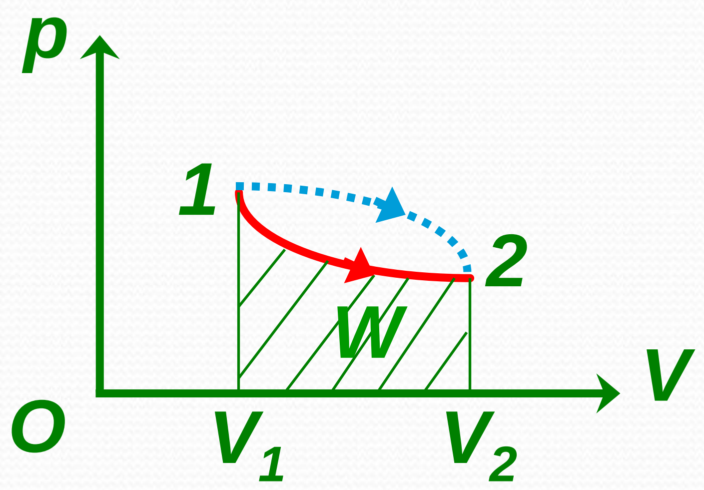
$$W = \int_{V_1}^{V_2} pdV$$

valid for any quasistatic process

Notes:

◆The area under the curve is the work done in this process.

◆The work done by the system depends not only on the initial and final state, but also on the intermediate states——that is, on the path.



◆Heat added in a thermodynamic process

In a quasistatic process, $T \rightarrow T+dT$:

$$dQ = \frac{M}{M_{mol}} C dT$$

molar heat capacity of this process

Adiabatic compressing Process

$dQ=0,\ dT>0 \rightarrow\ C=0$

Isothermal expanding Process

$dQ>0,\ dT=0 \rightarrow\ C \rightarrow \infty$

◆Internal energy

Ideal gas：

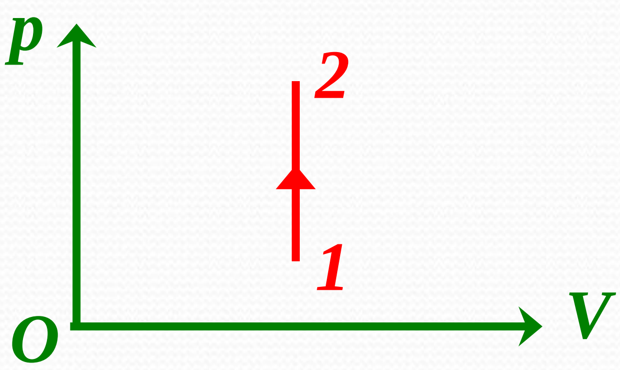
$$E = \frac{M}{M_{mol}} \cdot \frac{i}{2} RT$$

Notes:

Internal energy depends on initial and final states, and has noting to do with the process. Internal energy is a state quantity.

◆ The applications of the first law of thermodynamics in different kind of thermodynamic processes.

1. Isochoric Process



Constant volume

→ $dW=0$

$dQ=dE$

Because $$dQ = \frac{M}{M_{mol}} C_V dT$$

molar heat capacity at constant volume

$$dE = \frac{M}{M_{mol}} \cdot \frac{i}{2} R dT$$

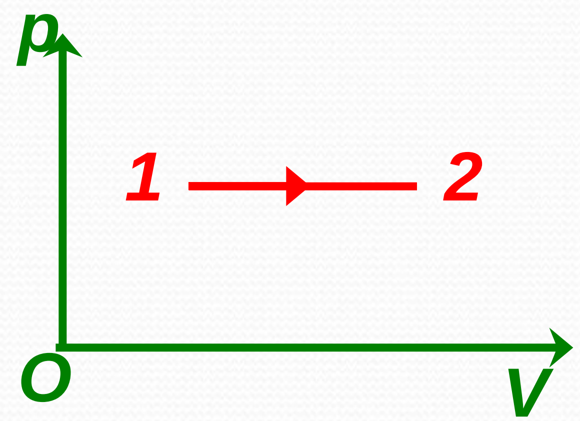
So $$\boxed{C_v = \frac{i}{2} R}$$ constant

In an isochoric process

$$E_2 - E_1 = \frac{M}{M_{mol}} \cdot \frac{i}{2} R(T_2 - T_1) = \frac{M}{M_{mol}} C_V (T_2 - T_1)$$

It is valid for an ideal gas for every kind of process.

2. Isobaric Process



Because

$$dQ = \frac{M}{M_{mol}} C_p dT$$

molar heat capacity at constant pressure

p=constant

dQ=dE+dA

$$dE = \frac{M}{M_{mol}} C_V dT$$

$$dW = \frac{M}{M_{mol}} R dT$$

$$\left(\begin{aligned} & pV = \frac{M}{M_{mol}} RT \quad , \quad p = \text{constant} \\ & \rightarrow pdV = \frac{M}{M_{mol}} RdT \end{aligned} \right)$$

Because $dQ=dE+dW$

We get

$$\boxed{C_p = C_V + R}$$

——**Mayer formula**

or

$$\boxed{C_p = \frac{i+2}{2} R}$$

——**constant**

In an isobaric process：

$$Q=\frac{M}{M_{mol}}C_p(T_2-T_1)$$

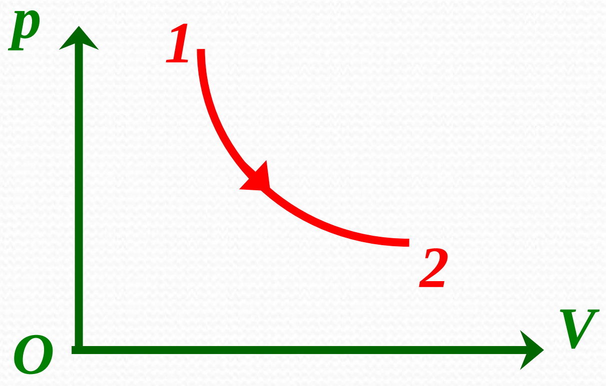
And $$E_2-E_1=\frac{M}{M_{mol}}C_V(T_2-T_1)$$

$$W=p(V_2-V_1)=\frac{M}{M_{mol}}R(T_2-T_1)$$

So $$\boxed{Q:(E_2-E_1):W=C_p:C_V:R=\frac{i+2}{2}:\frac{i}{2}:1}$$

Valid only in isobaric process

3. Isothermal Process



T=constant

$\rightarrow$ $dE=0$

$dQ=dW$

Then:

$$Q = W$$

$$= \int_{V_1}^{V_2} p dV$$

$$= \int_{V_1}^{V_2} \frac{M}{M_{mol}} RT \frac{dV}{V}$$

$$= \frac{M}{M_{mol}} RT \ln \frac{V_2}{V_1}$$

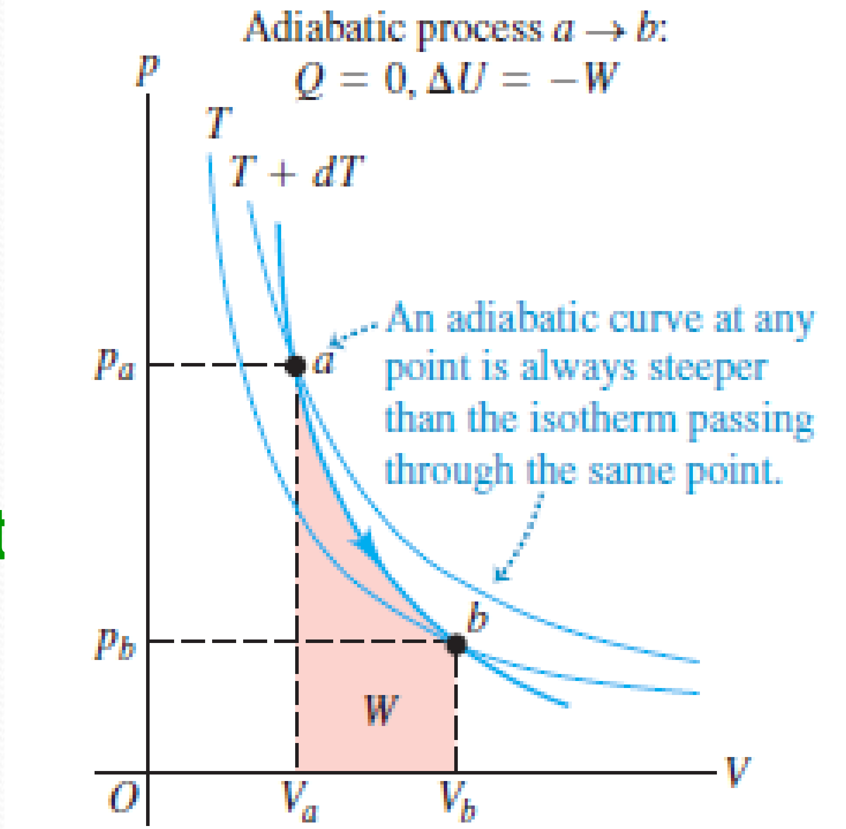
$$= \frac{M}{M_{mol}} RT \ln \frac{P_1}{P_2}$$

4. Adiabatic Process

$dQ=0$

$\rightarrow dE+dW=0$

(1) **using the ideal-gas equation + constraint condition ⇒adiabatic process equation**



$$pV=\frac{M}{M_{mol}}RT \rightarrow pdV+Vdp=\frac{M}{M_{mol}}RdT \qquad ①$$

$$dE+dW=0 \rightarrow \frac{M}{M_{mol}}C_V dT+pdV=0 \qquad ②$$

①②→ $$\frac{dp}{p} = -\gamma \frac{dV}{V}$$ ③

Where $$\boxed{\gamma = \frac{C_p}{C_V}}$$ **——ratio of heat capacities**

Take integral of ③, we get

$$pV^{\gamma} = C_1$$ ④

——Poisson formula

Using the ideal-gas equation we get

$$TV^{\gamma-1}=C_2 \qquad ⑤$$

$$p^{\gamma-1}T^{-\gamma}=C_3 \qquad ⑥$$

(C_1 , C_2 , C_3 are all constants)

④⑤⑥——adiabatic process equation

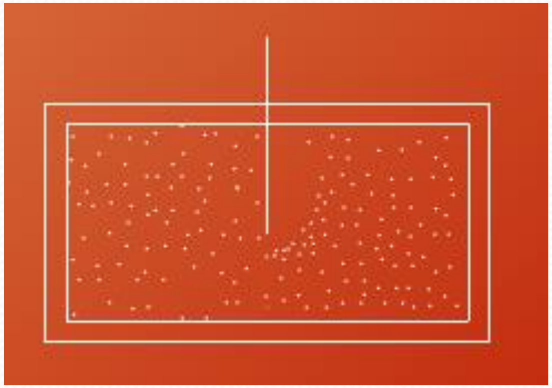
(2) We can also calculate the work done by an ideal gas during an adiabatic process

$$W=\int_{V_1}^{V_2} pdV=\int_{V_1}^{V_2}\frac{p_1V_1^{\gamma}}{V^{\gamma}}dV=\frac{p_1V_1}{\gamma-1}[1-(\frac{V_1}{V_2})^{\gamma-1}]$$

And $A=-(E_2-E_1)$

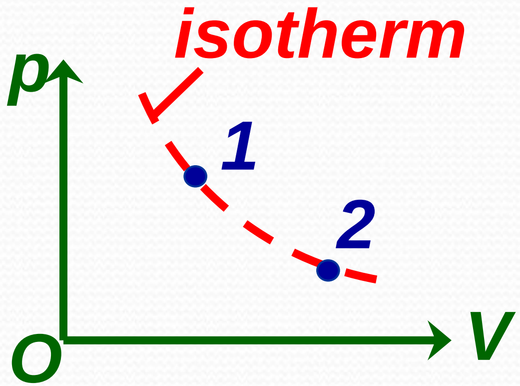
5. Adiabatic free expansion

Adiabatic free expansion is not a quasistatic process, but it obey the First Law of Thermodynamics.



Adiabatic $\rightarrow$ $Q=0$
Free expansion $\rightarrow W=0$

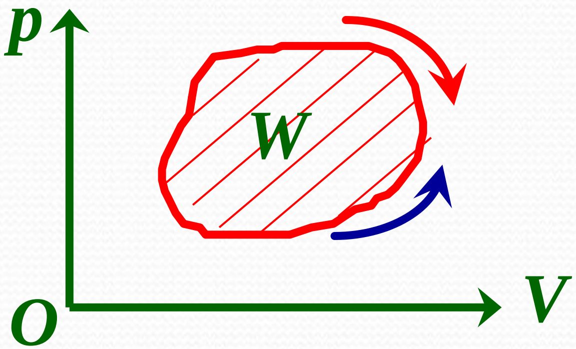
$\Rightarrow$ $E_2 - E_1 = 0 \quad T_2 = T_1$



Why the curve is dotted line in the P-V diagram?

◆ Cyclic process

——After a series of changing, the system returns to its initial state.



——positive cycle(W>0)

——thermomotor

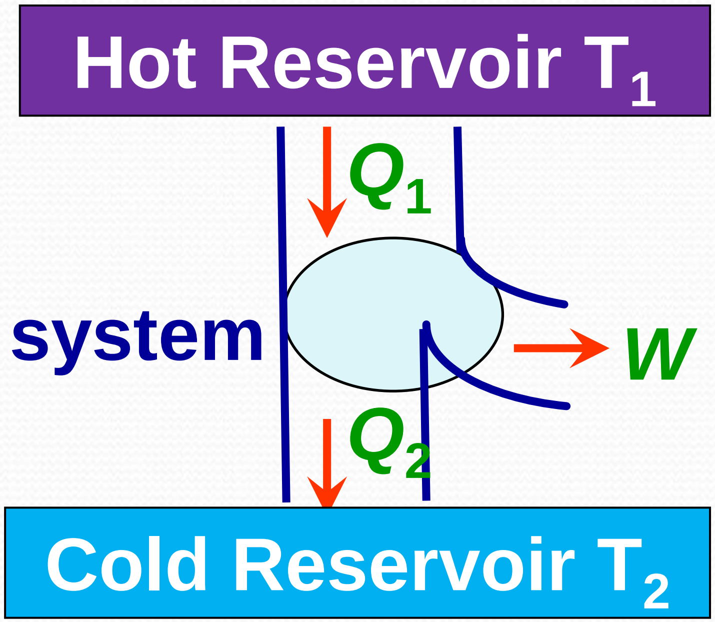
——reverse cycle(W<0)

——refrigerating machine

Characteristic of a cycle process：

$$\Delta E=0 \quad Q=W$$

1. Efficiency of heat engine



During a cyclic process：

System absorbs heat from T_1 ——Q_1

System discards heat to T_2 ——Q_2

Work *done by the system* ——W

Efficiency of a heat engine： $\eta \equiv \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$

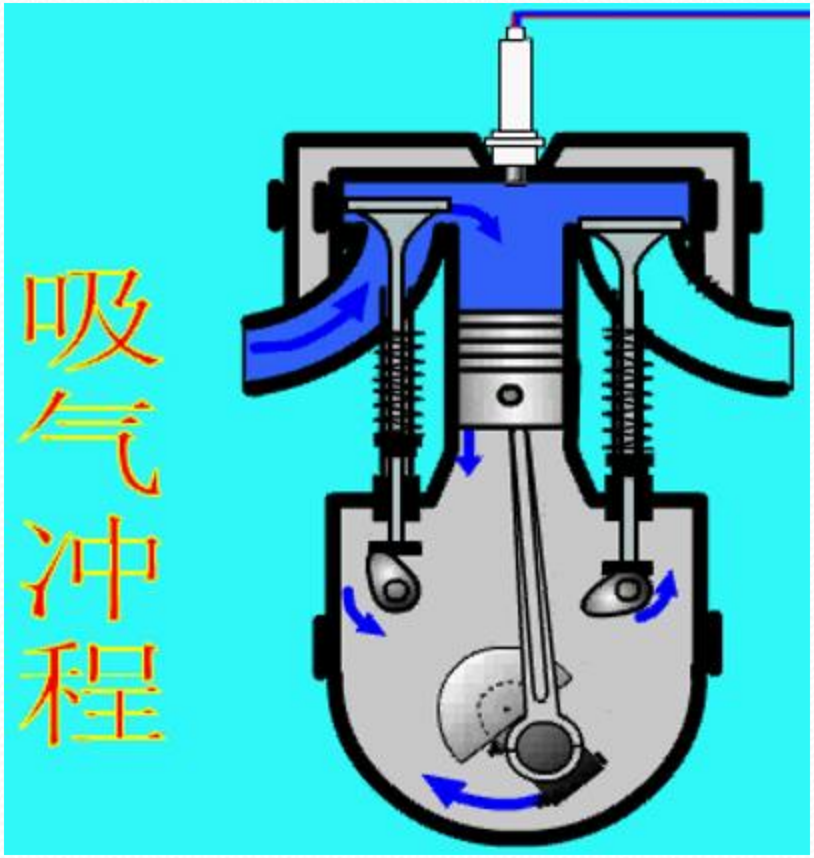
Otto internal combustion 奥托内燃机

Intake吸气冲程

Compression压缩冲程

Power 做功冲程

Exhaust排气冲程

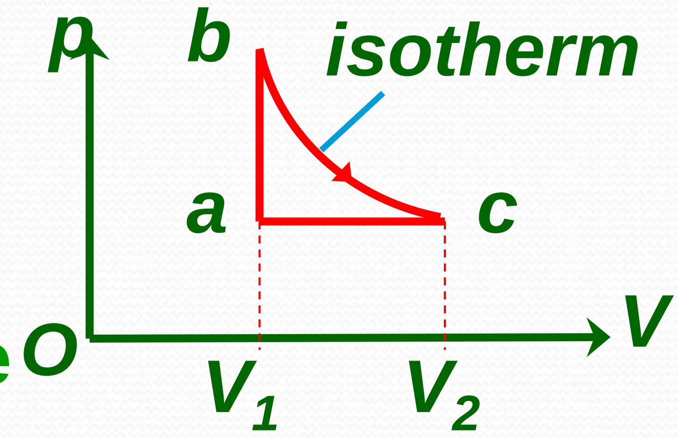


Steam locomotive(蒸气机)	η=8%
Gasoline engine (汽油机)	25%
Diesel engine (柴油机)	37%
Steam turbine (蒸气轮机)	46%

Notes:

Usually, $Q_1=\Sigma Q_{1i}$, $Q_2=\Sigma Q_{2i}$.

Some ideal gas of diatomic molecule undergoes a cyclic process as shown in the diagram, $V_2/V_1=2$. Find the efficiency η.



ab——absorbs heat

bc——absorbs heat

ca——discards heat

$Q_1=Q_{ab}+Q_{bc}$, $Q_2=-Q_{ca}$

Where

$$Q_{ab} = \frac{M}{M_{mol}} C_V (T_b - T_a) = \frac{5}{2} \cdot \frac{M}{M_{mol}} R(T_b - T_a)$$

$$Q_{bc} = W_{bc} = \frac{M}{M_{mol}} RT_b \ln \frac{V_2}{V_1} = \frac{M}{M_{mol}} RT_b \ln 2$$

$$Q_{ca} = \frac{M}{M_{mol}} C_p (T_a - T_c) = \frac{7}{2} \cdot \frac{M}{M_{mol}} R(T_a - T_b)$$

Then $$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{-Q_{ca}}{Q_{ab} + Q_{bc}}$$

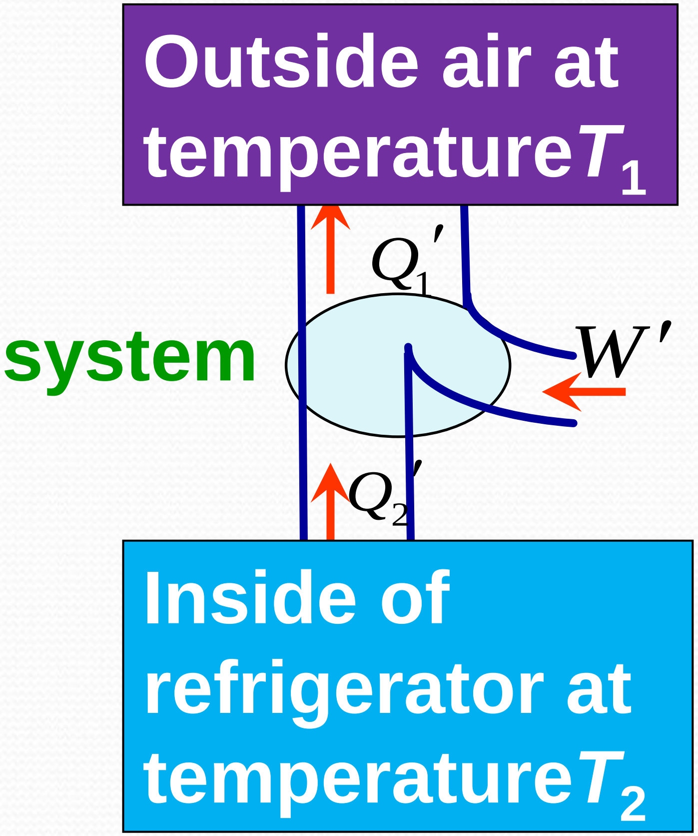
$$= 1 - \frac{7(T_b - T_a)}{(5 + 2\ln 2)T_b - 5T_a}$$

$$= 1 - \frac{7(1 - T_a / T_b)}{(5 + 2\ln 2) - 5T_a / T_b}$$

Where $$\frac{T_a}{T_b} = \frac{T_a}{T_c} = \frac{V_1}{V_2} = \frac{1}{2}$$

So $$\eta = 1 - \frac{7}{5 + 4\ln 2} \approx 10\%$$

2.Coefficient of performance of a refrigerator



For a cyclic process：

System absorbs heat fromT_2 —— Q_2'

System discards heat to T_1 —— Q_1'

Work done to the system —— W'

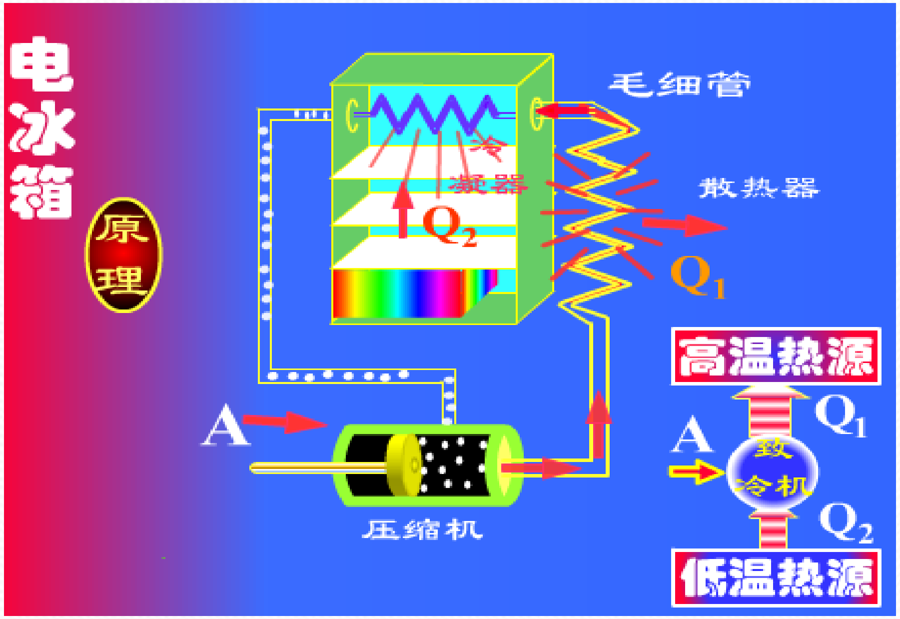
According to the first law of thermodynamics→

$$Q_1' - Q_2' = W'$$

Coefficient of performance of a refrigerator

$$\boxed{w \equiv \frac{Q_2'}{W'} = \frac{Q_2'}{Q_1' - Q_2'}}$$

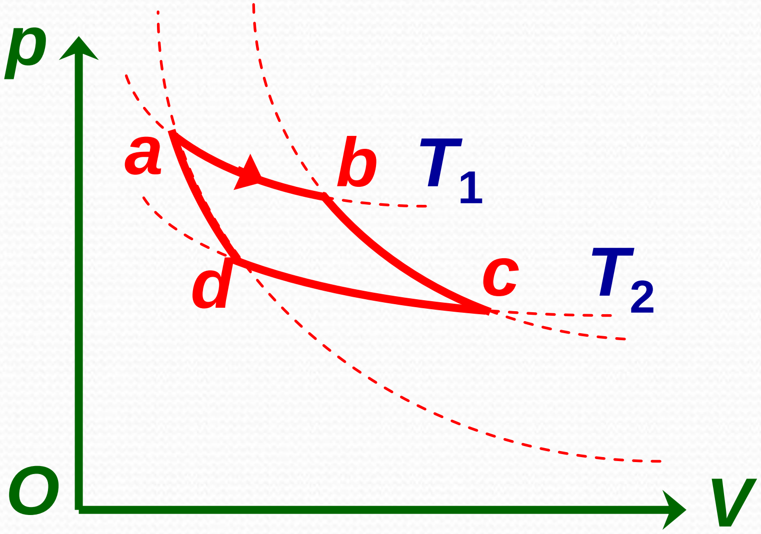
usually *w*>1



3. The Carnot Cycle

S. Carnot (1796~1832), French engineer,

in 1824, he developed Carnot cycle.



It consists of two isothermal processes and two adiabatical processes.

The Carnot heat engine

The Carnot Refrigerator

Efficiency of Carnot heat engine

【Derivation】

$$Q_1 = Q_{ab} = W_{ab} = \frac{M}{M_{mol}} RT_1 \ln\frac{V_b}{V_a}$$

$$Q_2 = -Q_{cd} = -W_{cd} = \frac{M}{M_{mol}} RT_2 \ln\frac{V_c}{V_d}$$

And

$$\left.\begin{aligned} T_1 V_b^{\gamma-1} &= T_2 V_c^{\gamma-1} \\ T_1 V_a^{\gamma-1} &= T_2 V_d^{\gamma-1} \end{aligned}\right\} \Longrightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d}$$

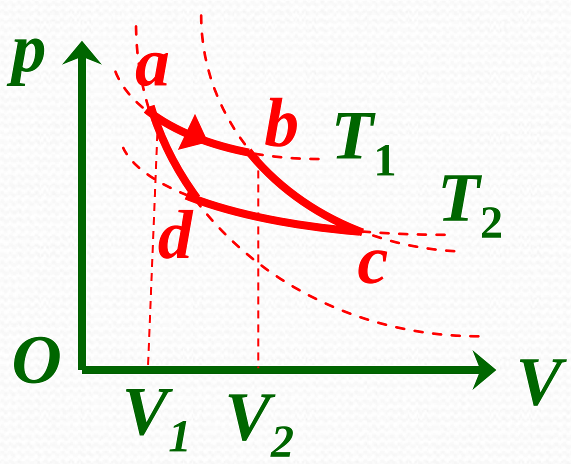
Then

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

Notes:

- The efficiency of a Carnot engine depends only on the temperatures of the two heat reservoirs.
- The efficiency is large when the temperature difference is large, and it is very small when the temperatures are nearly equal.

Suppose 1mol of an ideal diatomic gas undergoes a Carnot cycle between T_1=400K and T_2=300K, starting at V_1=0.001m^3 at point a. The volume at point b is V_2=0.005m^3. Find the heat absorbed from the hot reservoir Q_1, the heat discarded to the cold reservoir Q_2 and the work *W* done of the ideal gas for the entire cycle.



① $$Q_1 = Q_{ab} = W_{ab} = \frac{M}{M_{mol}} RT_1 \ln\frac{V_2}{V_1}$$

$$= 1 \times 8.31 \times 400 \times \ln\frac{0.005}{0.001}$$

$$= 5.35 \times 10^3\ (J)$$

②

$$\because \eta = \frac{W}{Q_1}$$

$$\therefore W = Q_1\eta = Q_1(1 - \frac{T_2}{T_1})$$

$$= 1.34 \times 10^3\ J$$

③

$$\because Q_1 - Q_2 = W$$

$$\therefore Q_2 = Q_1 - W$$

$$= 4.01 \times 10^3\ J$$

See you next time!