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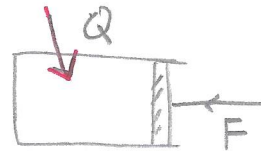0

Lect 3   The laws of Thermodynamics

1. First law

2. Carnot cycle

3. 2nd law

   Thermodynamic ~~temperature~~

§1 The first law of thermal dynamics   (1842-1847)

Mayer, Joule, Helmholtz — energy conservation and transfer

$$\Delta U = W + Q$$

the sign of W, and Q: $W > 0$, the environment does work to the system, and $W < 0$ means the system does work to the enviroment

$Q > 0$ means heat transfers to the system, and < 0 mean heat transfers outside.
~~from the system to the~~

For an infinitesmal process we write $dU = dW + dQ$, dQ means heat transfer is process-dependent.

Nevertheless, later we will show that $dQ = TdS$ for revesible processes, and S is entropy. In this case, $dU = dW + TdS$, For the system with a box and piston $\boxed{dU = -pdV + TdS.}$

But more generally, we have $dS > \dfrac{dQ}{T}$ for irreversible processes.

Carnot Cycle

§2. 2nd law of thermodynamics
1824. Carnot

How to increase the efficiency of a thermal engine? Does the alcohol work better than water steam? Carnot gave the universal answer which does not depend on the concrete working substances.
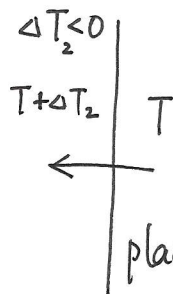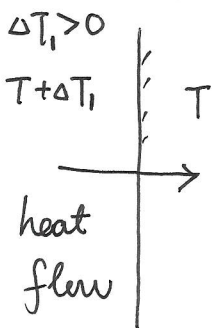
图 1.3 卡诺（1796～1832）

Carnot thought about the ideal limit, — "gedanken experiment". In mechanics. we often think about frictionless motion. Can we think about the counterpart of frictionless motion? Certainly, we can require the motion of piston is frictionless. We could also design "frictionless heat transfer". We set the temperature defenerce between the system and the reservoir ΔT to be infinitesmall. such that transfer heat takes

$\Delta T_1 > 0$

$T + \Delta T_1$ | T

heat flow

$\Delta T_2 < 0$

$T + \Delta T_2$ | T

places between two essentially at the same objects

temperature. This heat transfer process is reversible by change the sign of ΔT. But if the ΔT is finite, the system needs to change temperature in a finite way to reverse the direction of heat flow, and the system cannot come back to its original state.

✻ Carnot cycle — the simplest cycle � reversible

① Consider a box with a piston expanses very slowly by keeping contact with the reservoir at temperature T_1.
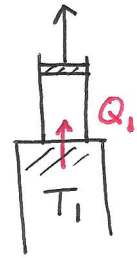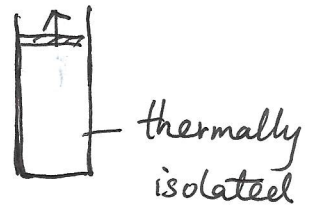
If the piston moves very slowly, the gas temperature is just lower than T_1 by a very small amount, such that the heat transfer is essentially reversible. This is the isothermal expansion follwing $PV = Nk_BT$.

② Then move the box away from the reservoir at temperature T_1, and make it heat-isolation from the envionment. Then the piston continues to move upward — adiabatic exanpsion. Since no heat transfer, the temperature drops following $PV^\gamma = const$.

— thermally isolated

③ When the temperature drops to T_2, move the box to the reservoir with T_2. low temperature

Then push the piston to compress the system isothermally.
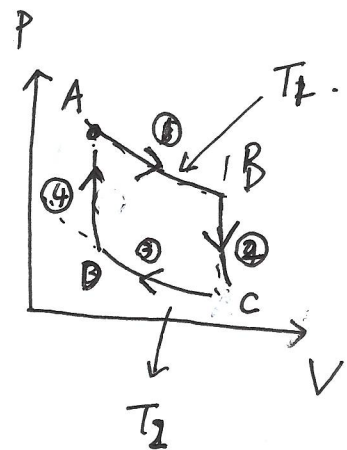
④ Then remove the reservoir, and further compress the box adiabatically such that the temperature increases to T_1. The cycle is completed.

The simplicity lies in the fact that only two heat reservoirs are needed!

- Efficiencity of the Carnot cycle — ideal gas as working substance

① For A to B, isothermal expansion

$$PV = N k_B T_1 \quad \Rightarrow \quad P = \frac{N k_B T_1}{V}$$

$$du = 0 = -pdv + dQ \quad \Rightarrow \quad dQ = pdv = \frac{N k_B T_1}{V} dV$$

$$Q_1 = N k_B T_1 \int_{V_A}^{V_B} \frac{dV}{V} = N k_B T_1 \ln \frac{V_B}{V_A}$$

② Similarly, for the isothermal compression from C to D.

The system damps a heat to the low temperature reservoir.

$$Q_2 = N k_B T_2 \ln \frac{V_C}{V_D}$$

③ Check the adiabatic expansion from B → C

$$PV^\gamma = \text{constant} \qquad \frac{PV}{T} = \text{const} \quad \Rightarrow \quad T V^{\gamma-1} = \text{const}$$

$$T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1}$$

Similarly $\quad T_1 V_A^{\gamma-1} = T_2 V_D^{\gamma-1} \qquad \Rightarrow \qquad \frac{V_B}{V_A} = \frac{V_C}{V_D}$

$$\Rightarrow \quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad \Rightarrow \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

We used the equation of states for ideal gas. Does this result rely on the working substances?

§ 2nd law of thermodynamics

Some processes satisfying energy conservation never occur. This is regulated by the 2nd law of thermodynamics. There are equivalent ways to state it.

Kelvin: No such a process exists whose sole effect is to extract heat from a given reservoir and convert into work entirely

Clausius: No such a process exists whose sole effect to extract a quantity of heat from a cold reservoir to a hot one.

These two statements are equivalent it to each other:
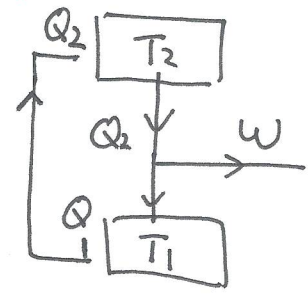
Proof: ① If K is false, then C is false.

Consider two reservoirs with $T_2 > T_1$. If K is false, we can take heat Q from T_1, and convert it completely to $W = Q$, then W can transfer to Q and add to $T_2 \Rightarrow$ C is false.
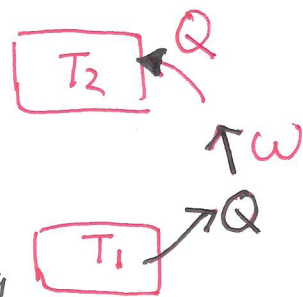
② If C is false, then K is false.

Consider such a thermal engine process:

Take heat Q_2 from high temp reservoir T_2, damp heat Q_1 to the low temp reservoir T_1 and do work W.

If C is false, we extract heat Q_2 from T_1 to T_2, then T_2 come back to itself. The net effect is to extract heat $Q_1 - Q_2$ from reservoir T_1, which is completely → work!

Ⓧ Carnot engine:

Consider two reservoirs 1 and 2 with temperatures $T_1 > T_2$.

① Thermo engines 1 and 2 work between them. Engine 1 is reversible, which is called Carnot engine. Engine 2 is irreversible. Then the efficiency of $\widehat{\eta_1}$ engine 1 is higher the η_2 of engine 2. i.e $\eta_1 > \eta_2$.

Proof: The thermal engine 2 is irreversible. Let us run it to extract heat Q_1' from R_1, and damp heat Q_2' to R_2. Then $W' = Q_1' - Q_2' \Rightarrow \eta_2 = 1 - \dfrac{Q_2'}{Q_1'}$.
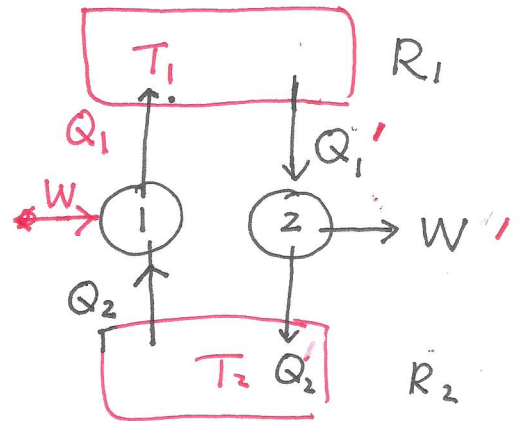
Consider a similar process for the engine 1. in parallel, such that $\eta_1 = 1 - \dfrac{Q_2}{Q_1}$ and $W = Q_2 - Q_1$.

Now set $Q_2 = Q_2'$, and reverse engine 2.

If $\eta_1 < \eta_2$, then $\dfrac{Q_2}{Q_1} > \dfrac{Q_2'}{Q_1'} = \dfrac{Q_2}{Q_1'}$ $\Rightarrow$ $Q_1 < Q_1'$ and $W' > W$

Then the net effect is to extract heat $Q_1' - Q_1$ from R_1

and $\underset{\text{completely} / \text{transfer to work}}{\underline{W' - W \geq 0}}$. This is impossible.

$\Rightarrow \eta_1 > \eta_2$.

② For two reversible engines 1 and 2, their efficiencies $\eta_1 = \eta_2$.

If we reverse engine 1, repeat the reasoning in ① $\Rightarrow \eta_1 \geq \eta_2$.

. . . . . . 2, ... $\Rightarrow \eta_2 \leq \eta_1$ $\left.\begin{array}{c}\\ \end{array}\right\} \Rightarrow \eta_1 = \eta_2$.

Hence, reversible engines' sufficiencies are independent on concrete working substances. It only depends on the temperatures T_1 and T_2.

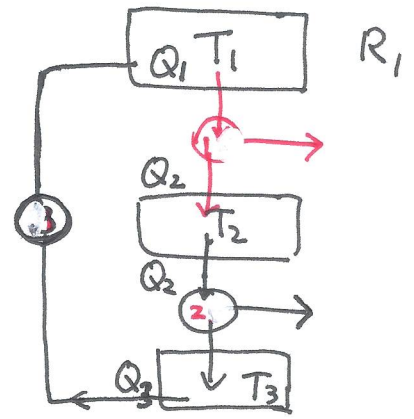$\Rightarrow$ universality. of reversible engines!

We define $Q_1 / Q_2 = f(T_1, T_2)$, then $Q_2 / Q_1 = f(T_2, T_1)$

$\Rightarrow$ $f(T_1, T_2) = \left[f(T_2, T_1) \right]^{-1}$.

③ Now consider three heat reservoirs $T_1 > T_2 > T_3$. We have

$$f(T_1, T_3) = f(T_1, T_2)\, f(T_2, T_3).$$

Assume engine 1 working between R_1 and R_2, engine 2 working between R_2, R_3 engine 3 working between R_3, R_1.

engine 1 : extract Q_1 from R_1, damp Q_2 to R_2

engine 2 : extract Q_2 from R_2, damp Q_3 to R_3

$\Rightarrow$ combine engines 1 and 2 : $\Rightarrow$ extract Q_1 from R_1 and damp Q_3 to R_3,

This can be view as one engine whose efficiency $= \dfrac{Q_3}{Q_1} = \dfrac{Q_3}{Q_2} \cdot \dfrac{Q_2}{Q_1}$

This has to be the same as engine 3 directly working between R_1, and R_3,

$$\Rightarrow \boxed{f(T_1, T_3) = f(T_1, T_2)\, f(T_2, T_3)}$$

This relation hints that $f(T_1, T_2) = \phi(T_1)/\phi(T_2)$.

Since $f(T_1, T_2) = Q_1/Q_2 \iff T_1 > T_2 \Rightarrow Q_1 > Q_2 \Rightarrow \phi(T_1) > \phi(T_2)$.

Hence $\phi(T)$ is an asending function of T. Let us define $T = \phi(T)$, and we will see, it agrees with previous convention that $\dfrac{1}{T} = \left(\dfrac{\partial S}{\partial E}\right)_V$.

$\cdots \cdots \hat{}$

Clausius' theorem : For any cyclic process, the following inequality holds

$$\oint dQ/T \leq 0.$$

The equality holds if the process is reversible.

Proof: Denote the cyclic process as ⓞ, and imagine it's done by contacting many reserviers $R_1, \cdots R_n$ with temperatures $T_1, \cdots T_N$. At each step, the system absorbs heat ΔQ_i. ($\Delta Q > 0$ means absorption, $\Delta Q < 0$ means releasing heat).
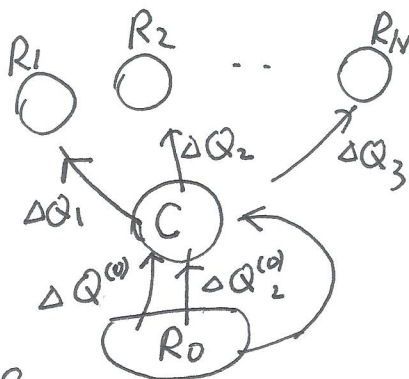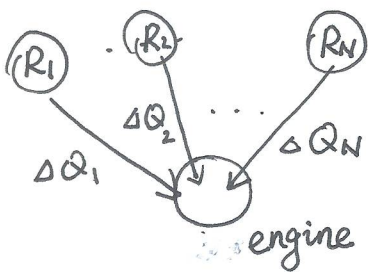
Then we use a carnot engine C, extrac heat $\Delta Q_1^{(0)}$ from heat reservior R_0 with temperature T_0 and damp heat ΔQ_1 back to R_1, Similarly, we do all the processes for $R_2, \cdots R_N$. Since "C" is carnot, we have

$$\Delta Q_1^{(0)} / \Delta Q_1 = \frac{T_0}{T_1}, \quad \frac{\Delta Q_2^{(0)}}{\Delta Q_2} = \frac{T_0}{T_2}, \quad \cdots \cdots$$

$$\Rightarrow \quad \Delta Q_1^{(0)} + \Delta Q_2^{(0)} + \cdots \Delta Q_N^{(0)} = T_0 \sum_{i=1}^{N} \frac{\Delta Q_i}{T_i}$$

After, we run the cyclic ⓞ, and combine with the processess with the carnot, the net effect is to extrat $\Delta Q = T_0 \sum_{i=1}^{N} \frac{\Delta Q_i}{T_i}$ from the reservor, and convert them into work. This is only possible if

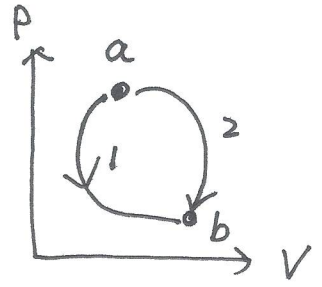$\Delta Q < 0$, i.e. work is anverted into heat. $\Rightarrow$

$$\sum_{i=1}^{N} \frac{\Delta Q_i}{T_i} \leq 0 \rightarrow \oint \frac{dQ}{T} \leq 0.$$

If the $\mathbb{C}$ is reversible, then $\oint \frac{-dQ}{T} \leq 0$.

reverse the process.

$\Rightarrow \oint \frac{dQ}{T} = 0$.

※ Hence: consider two states "a" and "b".

Suppose the system evolves along two paths 1 and 2. it's easy to show $\int_{1,a}^{b} \frac{dQ}{T} = \int_{a}^{b} \frac{dQ}{T}$, i.e. path independence.
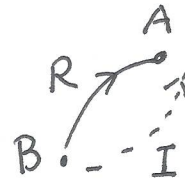
we can define a state function: S

$$dS = \frac{dQ}{T} \qquad \text{and} \qquad S(A) - S(0) = \int_{0}^{A} \frac{dQ}{T}, \text{ where}$$

"0" is a reference point.

and $S(A) - S(B) = \int_{B}^{A} \frac{dQ}{T}$ for any reversible paths.

⊗ if the process is inversible, we have $S(A) - S(B) > \int_{A}^{B} \frac{dQ}{T}$

Consider a reversible path connecting B to A, and an irreversible path.

Then reverse the process R, we have

$$\int_{B}^{A} \frac{dQ}{T} \Big|_{I} + \int_{A}^{B} \frac{dQ}{T} \Big|_{-R} < 0 \Rightarrow S(A) - S(B) = \int_{A}^{B} \frac{dQ}{T} \Big|_{R}$$

$$> \int_{A}^{B} \frac{dQ}{T}$$

(I)

※ A thermally isolated system, $dQ = 0$

$\Rightarrow$ Any process, entropy never decrease!

$$\boxed{S_A - S_B \geq 0.}$$

• Example of entropy increase.

  • friction convert work to heat $\quad \Delta S = \dfrac{Q}{T} = \dfrac{W}{T} > 0$

  • heat transfer between two systems with temperature difference.

$$\Delta S = \left. \dfrac{Q}{T_2} - \dfrac{Q}{T_1} \right\} \Rightarrow \Delta S > 0$$

$$T_2 < T_1$$

  • Why do we need to eat? life is needs negative entropy.
Our body has a tendency to generate entropy. In order to
$\overbrace{\qquad}^{\Delta S \text{ perday}}$
keep us alive, this amount of entropy ΔS need to be
removed. This means that we need to transfer heat
$$\boxed{Q = T \Delta S} \text{ to the enviroment.}$$
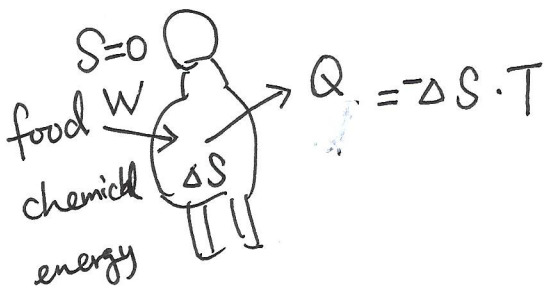
$Q = \bar{}\Delta S \cdot T$ This amount of heat Q can be
converted from work W, which
is the chemical energy in the food.

Hence, $\quad \left\{ \begin{array}{l} \Delta U = W + Q = 0 \\[20pt] \Delta S - \dfrac{Q}{T} = 0 \end{array} \right.$