Second Law of Thermodynamics

First Law (energy conservation)

$$Q = \Delta U + W$$

But some processes that satisfy 1st law never occur.

e.g.

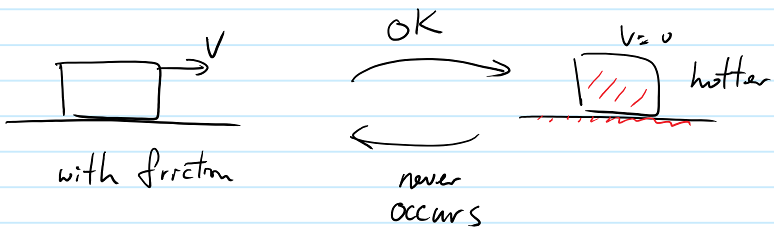
① 

$\Delta U = -Q$ $\qquad$ $\Delta U = Q$

OK ✓

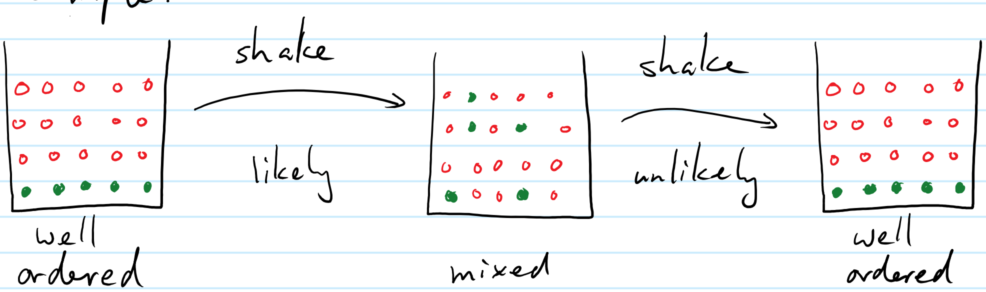
$\Delta U = Q$ $\qquad$ $\Delta U = -Q$ $\qquad$ 1st law ok ✓

But it never occurs.

② 

Direction of heat flow may not be reversible.

Another Example:



In the large N limit, it becomes impossible to order beans by shaking them.

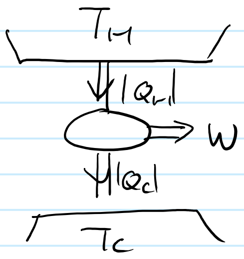
First Law denies creating and destroying energy.

Second Law limits the conversion of energy.

(some heat cannot be used)

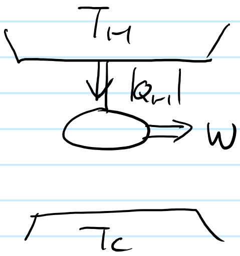
Statements of 2nd Law

① Engine Statement (Kelvin-Plank)



OK ✓

But



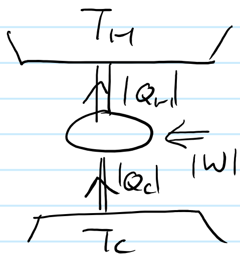
Not OK!

$|Q_C|$ cannot be zero for engine which does positive work.

$\Rightarrow$ $\boxed{\text{No engines could have 100\% efficiency.}}$

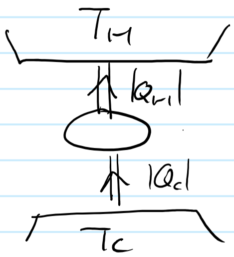
No ideal / perfect engines.

② Refrigerator Statement. (Clausius)



OK ✓

But



Not OK!

Heat cannot flow from cold reservoir to hot reservoir without the refrigerator receiving work. $(W < 0)$

$\Rightarrow$ No perfect refrigerator with $K = \frac{|Q_C|}{W} \to \infty$

Both statements are referred to as the 2nd Law.

They are logically equivalent.: ① $\Longleftrightarrow$ ②

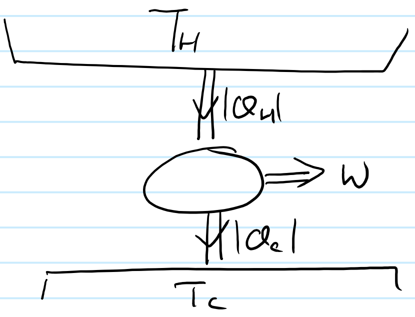
Let's prove ① $\Longleftrightarrow$ ② by showing $\sim$① $\Longleftrightarrow$ $\sim$②.

i.e. not ① $\Longleftrightarrow$ not ②

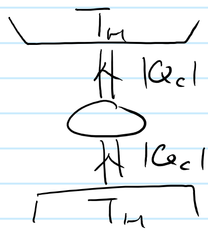
Proof: $\sim ② \Rightarrow \sim ①$

Suppose $\sim ②$ is true, i.e. there exists a perfect refrigerator.

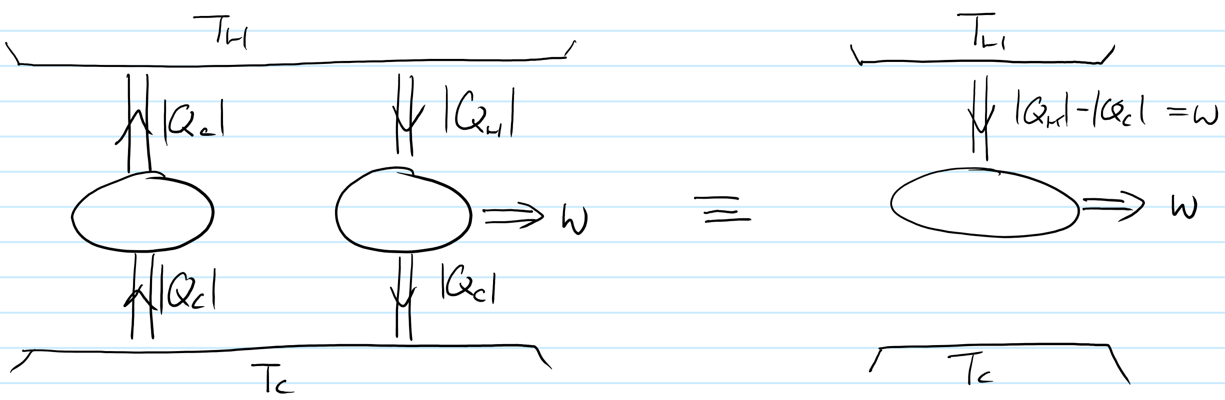
Consider an engine obeying ①



We insert a perfect refrigerator to form a new engine.



We have:



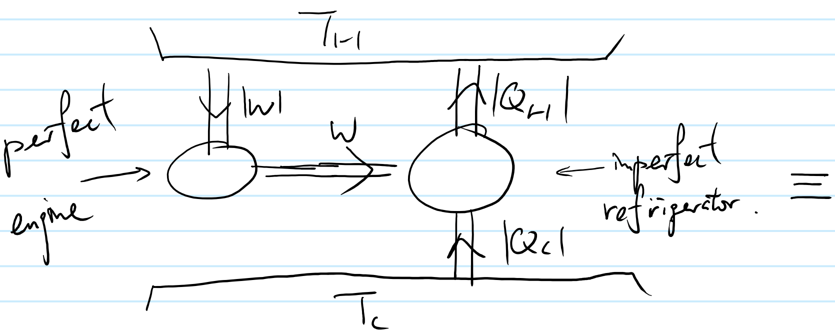
Perfect engine obtained!

$\boxed{\sim ② \Rightarrow \sim ①}$ ✓

Proof: $\sim ① \Rightarrow \sim ②$

Suppose $\sim ①$ is true, i.e. perfect engine exist.

we combine a perfect engine with a imperfect refrigerator.



no net W

$\boxed{\sim ① \Rightarrow \sim ②}$ perfect refrigerator obtained!

Properties of Carnot cycle

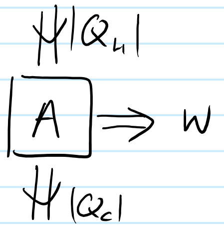
- Given only 2 reserviors, Carnot cycle is the only reversible cycle working between two fixed temperature reserviors.

  ∵ Heat transfer from cold to the hotter system is impossible. Therefore, reversible process must have the heat transfer occurs when the system is thermal equilibrium with the reserviors.

  ⇒ Only isothermal process. & adiabatic process are reversible.

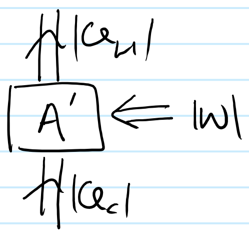
- Carnot engine is the most efficient engine operating between two reserviors.

Proof: Consider a reversible Carnot engine $\boxed{A}$



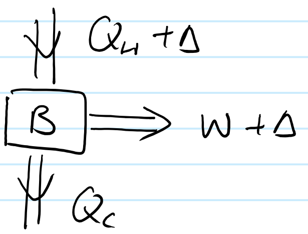
$$e_A = 1 - \frac{|Q_c|}{|Q_H|}$$

we can run $\boxed{A}$ backward and refer it as $\boxed{A'}$



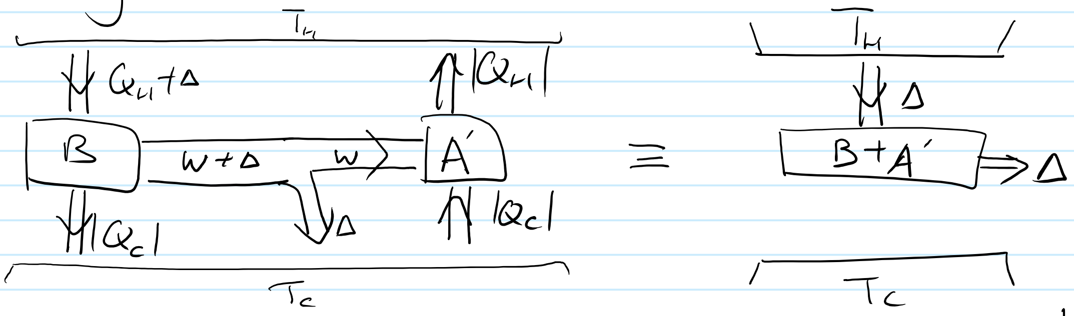
Refrigerator $\boxed{A'}$

Suppose there is an engine $\boxed{B}$ which has a higher efficiency than $\boxed{A}$ does.



$$e_B = 1 - \frac{|Q_c|}{|Q_H| + \Delta} > e_A$$

Combining $\boxed{A'}$ and $\boxed{B}$, we have



perfect engine!
violate 2nd Law!

$\Rightarrow$ It is impossible to have such an engine B.

$\Rightarrow$ Carnot engine is the most efficient engine.

- Carnot cycle is unique. It is used to define temperature scale. Since it is sustance independent, it is more objective than any scale defined by state of a particular matter, such as freezing pt & boiling pt. of water.

Recall: $e_{Carnot} = 1 - \frac{T_C}{T_H}$

Suppose we know T_C already and want to measure the temperature of T_H.
One can run a Carnot cycle between the two reserviors, then measure the efficiency e_{Carnot}.

T_H is then $T_H = \frac{T_C}{1 - e_{Carnot}}$.

Carnot engine serves as a thermometer.

Entropy and reversibility.

on Carnot cycle we have

$$e_{carnot} = 1 - \frac{T_c}{T_H} \quad , \quad e = 1 - \frac{|Q_c|}{|Q_H|} = 1 + \frac{Q_c}{Q_H}$$

$\because$ $Q_c < 0$
release heat.

$$\Rightarrow \quad -\frac{T_c}{T_H} = \frac{Q_c}{Q_H}$$

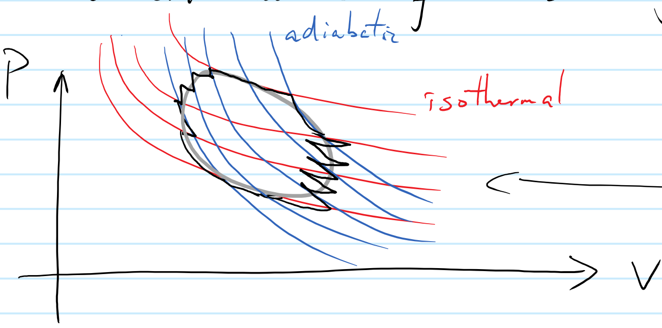
$$\Rightarrow \quad \frac{Q_c}{T_c} + \frac{Q_H}{T_H} = 0 \quad \text{over Carnot cycle.}$$

We write $\displaystyle\sum_{\text{Carnot}} \frac{Q_i}{T_i} = 0$

$$\left(\text{Sum } \frac{Q}{T} \text{ over processes along Carnot cycle.} \right) = 0$$

In general, if many reservoirs are given instead of 2, we can have as many isothermal processes as we want.

$\Rightarrow$ Every cycle on p-V diagram can be considered as a combination of a set of Carnot cycle.

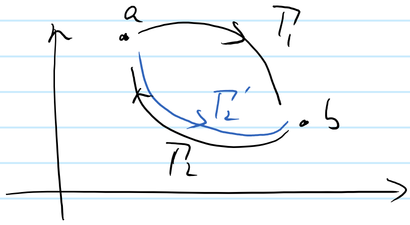


The cycle is approximated by a set of isothermal and adiabatic processes.

To the limit that we have infinitely many reservoirs, the isotherms will be infinitely dense and the approximation will become exact.

$$\Rightarrow \quad \sum \frac{Q}{T} \rightarrow \oint_{\text{any cycle}} \frac{dQ}{T} = \oint_{\text{Carnot}} \frac{dQ}{T} = 0$$

Since $\oint_{\text{any cycle}} \frac{dQ}{T} = 0$



$$\int_{T_1} \frac{dQ}{T} + \int_{T_2} \frac{dQ}{T} = 0$$

$$\Rightarrow \int_{T_1} \frac{dQ}{T} - \int_{T_2'} \frac{dQ}{T} = 0 \Rightarrow \underset{a\to b}{\int_{T_1}} \frac{dQ}{T} = \underset{a\to b}{\int_{T_2'}} \frac{dQ}{T}$$

$\int_a^b \frac{dQ}{T}$ is independent of path!

Definition: $\int_a^b \frac{dQ}{T} \equiv \Delta S$ = change of entropy from a to b.

S = entropy (state function, similar to potential energy).

Relation to Reversibility.

Second Law of Thermodynamics can be stated in terms of entropy as

$\boxed{\text{The entropy of an isolated system never decreases.}}$

If $\Delta S_{tot} = 0$, process is reversible

If $\Delta S_{tot} > 0$, process is irreversible.

If $\Delta S_{tot} < 0$, process is impossible. e.g. perfect engine, perfect refrigerator.

Example: Consider heat transfer between two objects.

$$\boxed{T_A} \xrightarrow{Q} \boxed{T_B}$$

Suppose net heat Q is transfered from A to B.

$$\text{Entropy change} = \Delta S_{tot} = \Delta S_A + \Delta S_B$$

$$= \frac{-Q}{T_A} + \frac{Q}{T_B}$$

$$= Q\left(\frac{T_A - T_B}{T_A T_B}\right)$$

Calculation of ΔS_{tot}		Reality check	Agree with 2nd Law
If $T_A > T_B$,	$\Delta S_{tot} > 0$	It happen but irreversible.	✓
If $T_A = T_B$,	$\Delta S_{tot} = 0$	Isothermal heat transfer is reversible.	✓
If $T_A < T_B$,	$\Delta S_{tot} < 0$	Heat never transfer from hot object to cold object.	✓