

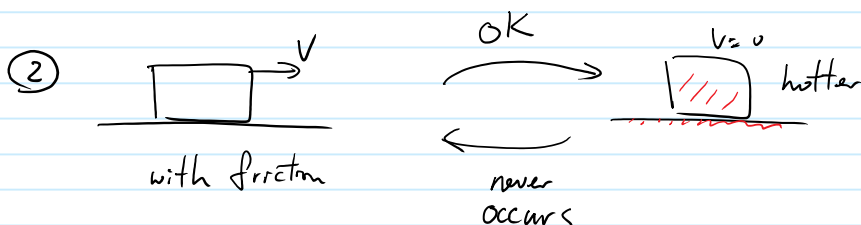
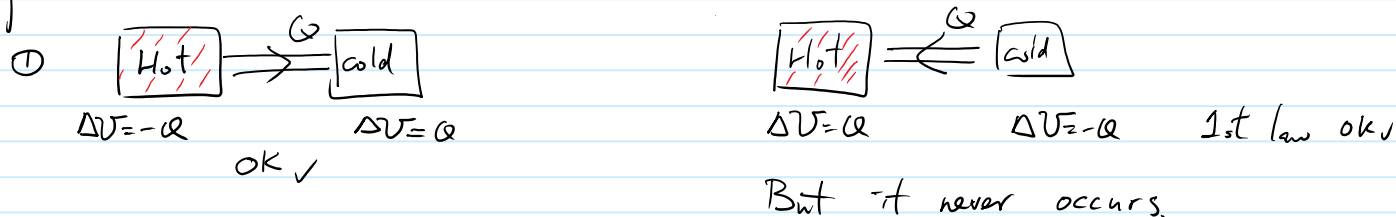
Second Law of Thermodynamics

First Law (energy conservation)

$$Q = \Delta U + W$$

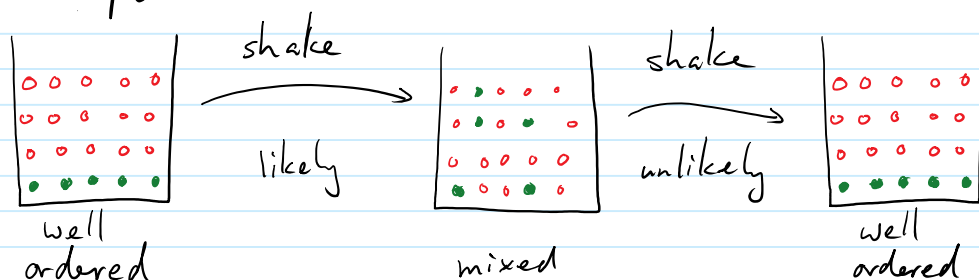
But some processes that satisfy 1st law never occur.

e.g.



Direction of heat flow may not be reversible.

Another Example:



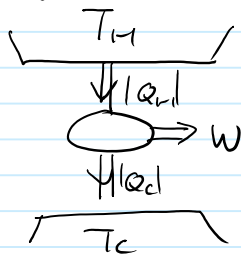
In the large N limit, it becomes impossible to order beans by shaking them.

First Law denies creating and destroying energy.

Second Law limits the conversion of energy.
(some heat cannot be used)

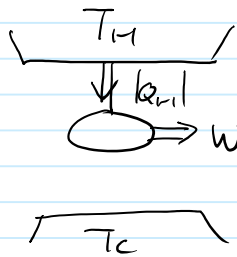
Statements of 2nd Law

① Engine statement (Kelvin-Planck)



OK ✓

But



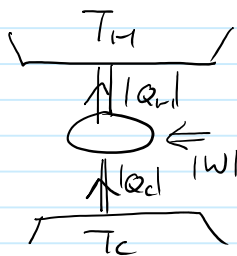
Not OK!

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

⇒ No engines could have 100% efficiency.

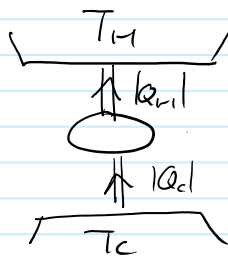
No ideal / perfect engines.

② Refrigerator Statement. (Clausius)



OK ✓

But



Not OK!

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

⇒ No perfect refrigerator with $K = \frac{|Q_C|}{W} \rightarrow \infty$

Both statements are referred to as the 2nd Law.

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

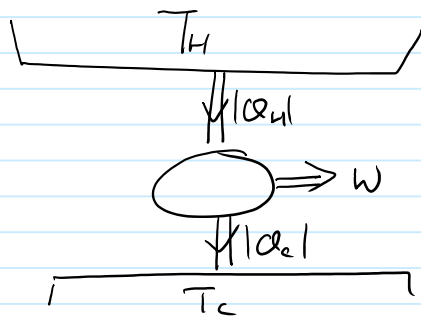
Let's prove ① $\Leftrightarrow$ ② by showing $\sim ① \Leftrightarrow \sim ②$
i.e. not ① $\Leftrightarrow$ not ②

Proof of equivalence between Engine Statement (1) and Refrigerator Statement (2):

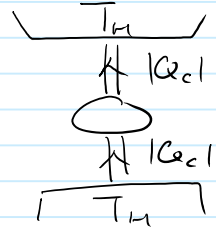
Proof: $\sim(2) \Rightarrow \sim(1)$

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

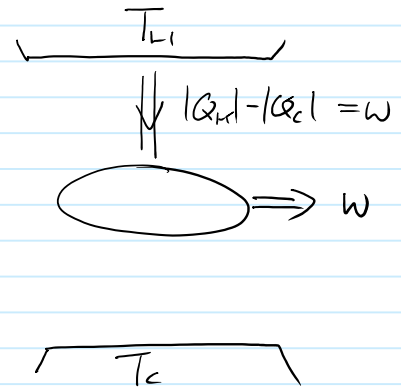
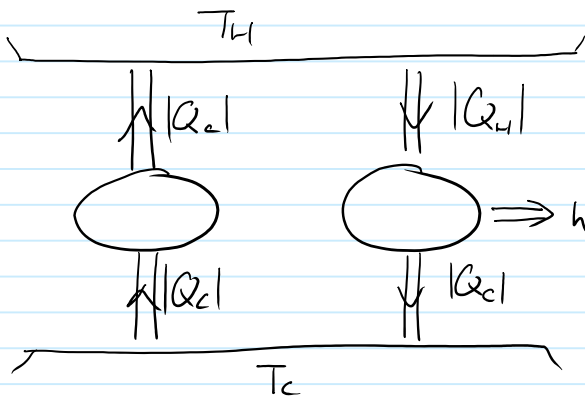
Consider an engine obeying (1)



We insert a perfect refrigerator to form a new engine.



We have:



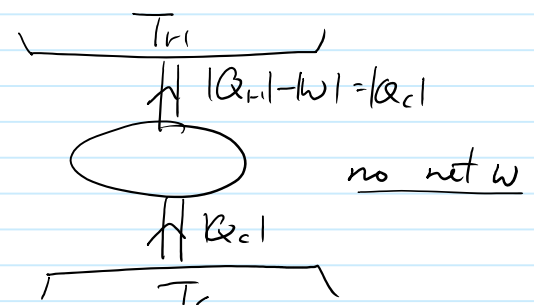
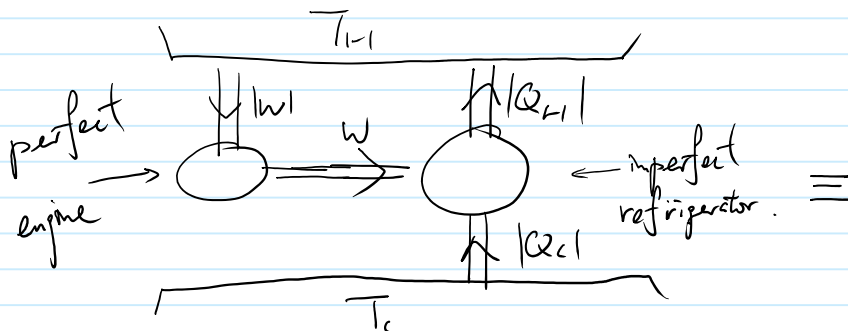
Perfect engine obtained!

$\sim(2) \Rightarrow \sim(1)$

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.



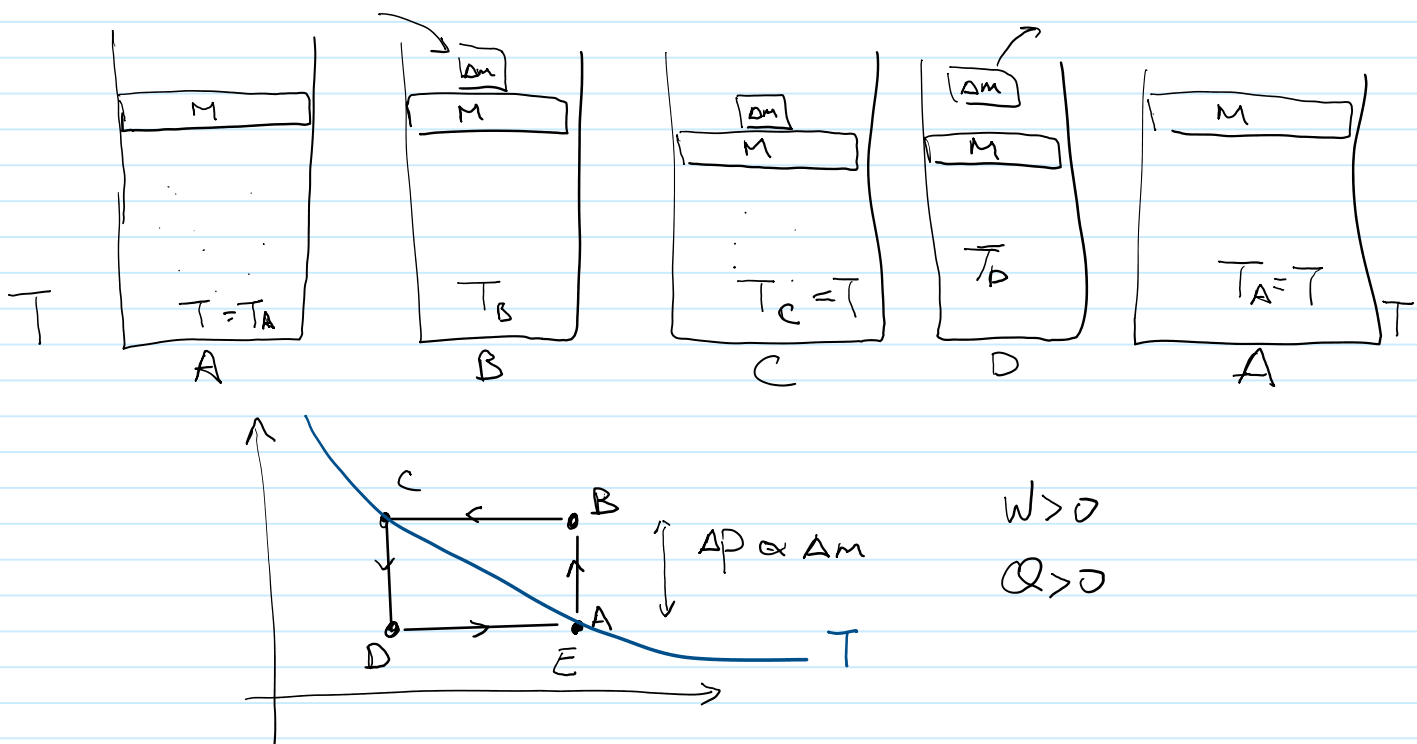
$\sim(1) \Rightarrow \sim(2)$

perfect refrigerator obtained!

Reversible Processes

A **reversible** thermodynamic process is an *idealized* process whose direction can be reversed by making only an infinitesimal change in the conditions of the system.

- ⚠ Throughout a reversible process the system must be very close to equilibrium at any instant, called an **equilibrium process** (*but not exactly in equilibrium, otherwise no change, no process*)
- ⚠ Heat flow due to a finite temperature difference is necessarily irreversible because an infinitesimal change in the temperatures cannot reverse heat flow.
- ⚠ How to understand reversible *isothermal* heat flow – the temperature difference must be *infinitesimal* so that as heat flows, the two bodies are still *infinitesimally* close to equilibrium. The rate of heat flow is *infinitesimally* small, and the time taken to finish the process is *infinitely* long!



Properties of Carnot cycle.

- Given only 2 reservoirs, Carnot cycle is the only reversible cycle working between two fixed temperature reservoirs.
- $\therefore$ 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 reservoirs.
 $\Rightarrow$ Only isothermal process & adiabatic process are reversible.
- Carnot engine is the most efficient engine operating between two reservoirs.

Proof: Consider a reversible Carnot engine $[A]$

$$\begin{array}{c} \Uparrow |Q_H| \\ [A] \Rightarrow W \\ \Downarrow |Q_C| \end{array} \quad e_A = 1 - \frac{|Q_C|}{|Q_H|}$$

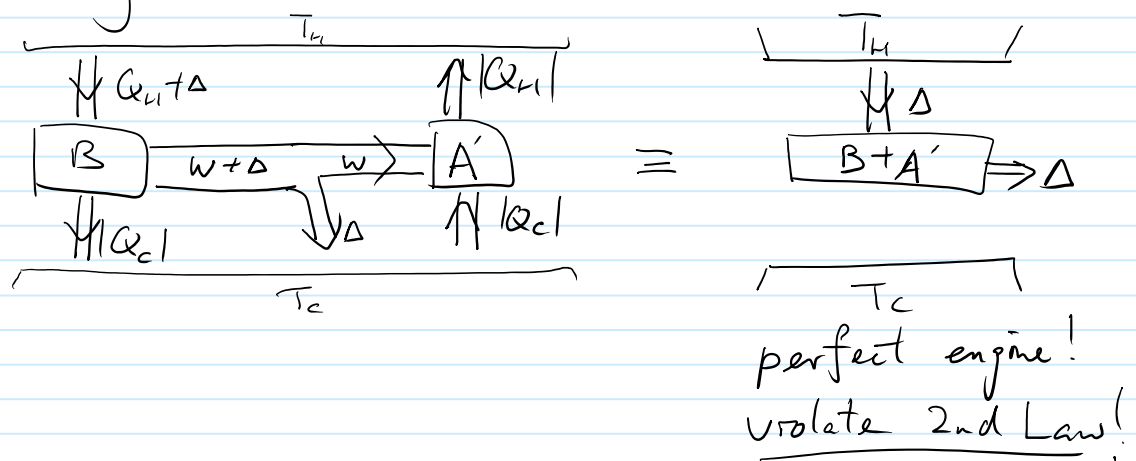
We can run $[A]$ backward and refer it as $[A']$

$$\begin{array}{c} \Uparrow |Q_H| \\ [A'] \Leftarrow W \\ \Downarrow |Q_C| \end{array} \quad \text{Refrigerator } [A']$$

Suppose there is an engine $[B]$ which has a higher efficiency than $[A]$ does.

$$\begin{array}{c} \Uparrow Q_H + \Delta \\ [B] \Rightarrow W + \Delta \\ \Downarrow Q_C \end{array} \quad e_B = 1 - \frac{|Q_C|}{|Q_H| + \Delta} > e_A$$

Combining A' and B , we have



$\Rightarrow$ 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 substance independent, it is more objective than any scale defined by state of a particular matter, such as freezing pt & boiling pt. of water.

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

Suppose we know T_C already and want to measure the temperature of T_H .

One can run a Carnot cycle between the two reservoirs, then measure the efficiency e_{Carnot} .

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

Carnot engine serves as a thermometer.

Entropy and reversibility. (Excluded from Final Exam)

on Carnot cycle we have

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

$\therefore Q_c < 0$
release heat.

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

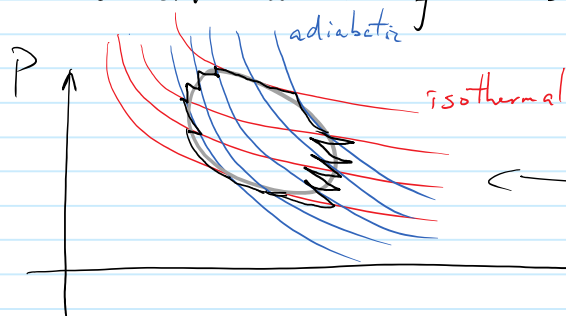
$$\Rightarrow \frac{Q_c}{T_c} + \frac{Q_H}{T_H} = 0 \quad \text{over Carnot cycle.}$$

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

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

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.

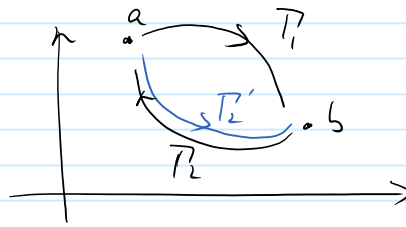


The cycle is approximated by a set of isothermal and adiabatic processes.

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

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

Since $\oint \frac{dQ_{rev}}{T} = 0$
any cycle



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

$$\Rightarrow \int_{T_1} \frac{dQ_{rev}}{T} - \int_{T_2'} \frac{dQ_{rev}}{T} = 0 \Rightarrow \int_{T_1} \frac{dQ_{rev}}{T} = \int_{T_2'} \frac{dQ_{rev}}{T}$$

$a \rightarrow b$ $c \rightarrow b$

$$\int_a^b \frac{dQ_{rev}}{T} \text{ is independent of path!}$$

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

$S \equiv \text{entropy (state function, similar to potential energy)}$

Relation to Reversibility:

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

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.



Suppose net heat Q is transferred from A to B.

$$\begin{aligned}\text{Entropy change} = \Delta S_{\text{tot}} &= \Delta S_A + \Delta S_B \\ &= \frac{-Q}{T_A} + \frac{Q}{T_B} \\ &= Q \left(\frac{T_B - T_A}{T_A T_B} \right)\end{aligned}$$

Calculation of ΔS_{tot}

If $T_A > T_B$, $\Delta S_{\text{tot}} > 0$

Reality check

It happens but irreversible.

Agree with 2nd Law

✓

If $T_A = T_B$, $\Delta S_{\text{tot}} = 0$

Isothermal heat transfer is reversible.

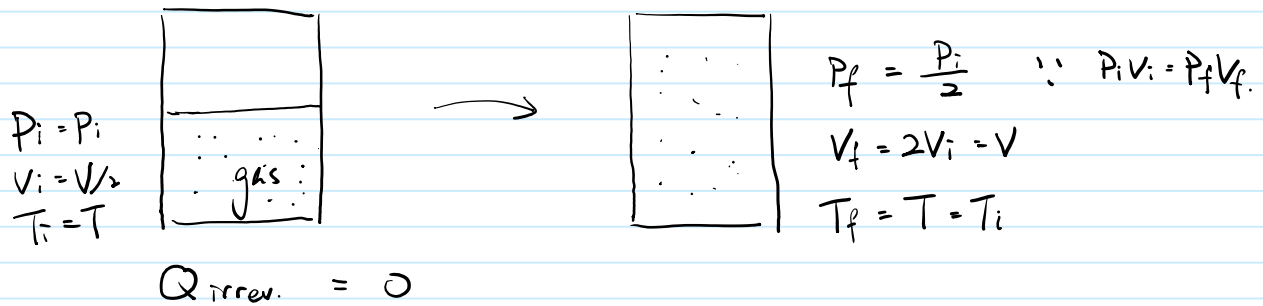
✓

If $T_A < T_B$, $\Delta S_{\text{tot}} < 0$

Heat never transfer from hot object to cold object.

✓

Example : Free Expansion

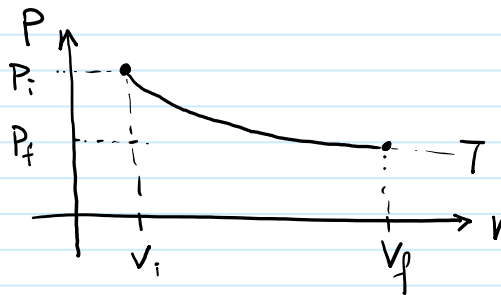


To calculate entropy change, we need to find a reversible process that connects the same initial and final state of the gas in the free expansion.

$$P_i \longrightarrow \frac{P_i}{2}$$

$$V_i = \frac{V}{2} \longrightarrow V$$

$$T_i \longrightarrow T$$



These pair of states can be connected by isothermal process which is reversible.

$$dQ_{\text{rev}} = dW = \frac{nRT}{V} dV$$

$$\Delta S_{\text{gas}} = \int_{V_i}^{V_f} \frac{dQ_{\text{rev}}}{T} = \int_{V_i}^{V_f} \frac{nR}{V} dV = nR \ln(2) > 0$$

$$\Delta S_{\text{surrounding}} = 0$$

Proof of Carnot engine is the most efficient engine allowed by 2nd Law.

The 2nd law tells us that the total entropy of the engine plus its surroundings can only increase but not decrease.

The entropy of the engine = $\Delta S_{\text{engine}} = 0$

$\because$ engine runs in cycles. $S_f = S_i$
 $\Rightarrow \Delta S = 0$

The entropy of the hot reservoir = $\Delta S_H = \frac{-|Q_H|}{T_H} < 0$

The entropy of the cold reservoir = $\Delta S_C = \frac{+|Q_C|}{T_C} > 0$

The 2nd law requires that $\Delta S_{\text{tot}} \geq 0$

$$\Rightarrow \Delta S_{\text{tot}} = \Delta S_{\text{engine}} + \Delta S_H + \Delta S_C \geq 0$$

$$\Rightarrow 0 + \frac{-|Q_H|}{T_H} + \frac{|Q_C|}{T_C} \geq 0$$

$$\Rightarrow \frac{|Q_C|}{|Q_H|} \geq \frac{T_C}{T_H}$$

Efficiency of any engine : $e_{\text{any engine}} = 1 - \frac{|Q_C|}{|Q_H|} \leq 1 - \frac{T_C}{T_H} = e_{\text{Carnot}}$

We have ,

$$\boxed{e_{\text{any engine}} \leq e_{\text{Carnot}}}$$

implied by 2nd Law $\rightarrow$

