HH0105 Entropy and the Second Law of Thermodynamics

The notes are in memory of disappearing
"slides" — once made of real materials
and now in virtual reality

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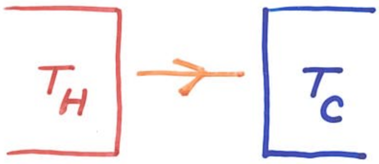
Entropy and the 2nd Law

- Introduction
- Heat engine / Refrigerator
- The Second Law
- Carnot Cycle
- Gasoline engine
- Entropy and disorder

Entropy and the Second Law

Our common senses tell us that:



Heat *always* flows from a hot body to a cold body.

Question: Is the above observation always true?

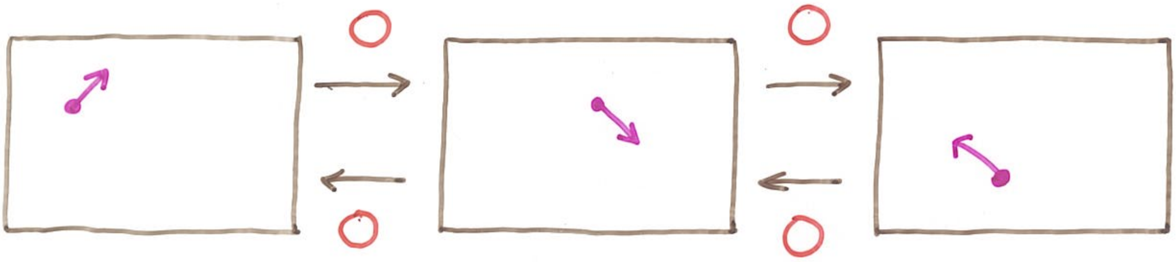
Let us go back a bit. The 1^{st} law of thermodynamics is

$$\boxed{Q = \Delta U + W}$$

- Nothing but energy conservation.
- Heat is another form of energy.

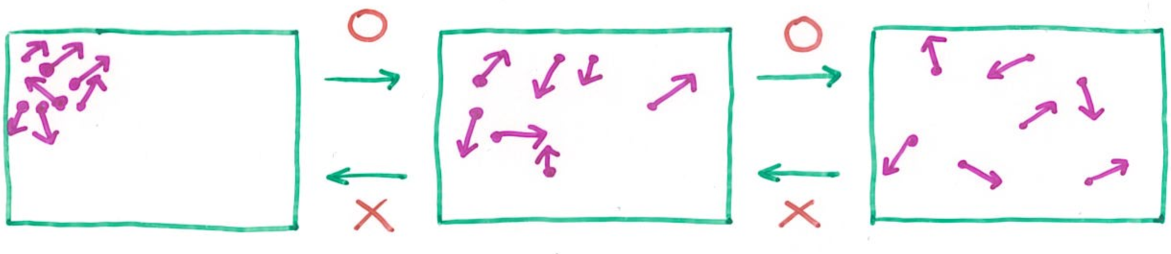
But the 1^{st} law does not tell us which thermal process is possible! Energy conservation alone does not determine the dynamics of the system.

Suppose we observe a single particle moving in a box



The processes look the same if the time t is reversed $t \to -t$ This agrees with the fundamental law down to microscopic scale.

However, if we put in many particles,



According to our common senses, the time sequence can be determined without doubt.

- Is this an illusion?
- How many is "many"?

This is what the 2nd law is about...

Heat Engine

1712 Newcomen: steam engine

1763 - 1782 Watt: great improvement.

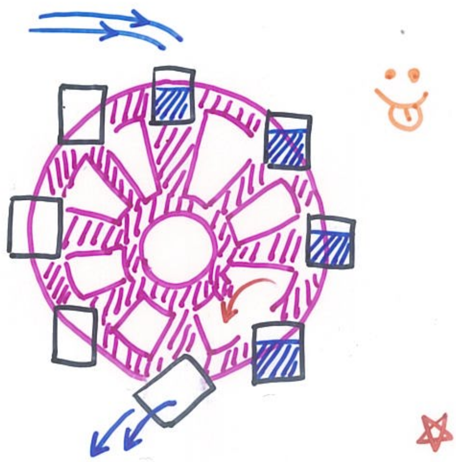
→ Industrial Revolution !

A heat engine is a device that converts heat into mechanical work.

$$\boxed{\epsilon \equiv \frac{W}{Q_{in}}}$$

thermal efficiency.

Carnot tried to understand the principle behind generic heat engines. His observation is how the watermill works.



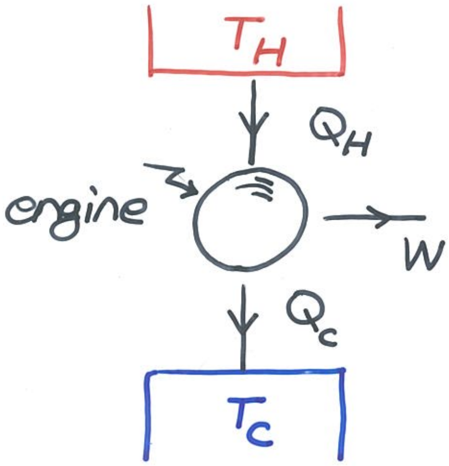
water filled at some height → discharged at lower level.

★ caloric filled at some high temperature reservoir

→ discharged into low temperature

Great observation !!

Now we are ready to introduce heat engine diagram. Here we assume that Q_H, Q_c, W are all <u>positive</u>



After a cycle, the engine returns to its initial state

$$\boxed{\Delta U = 0.}$$

According to the 1^{st} law.

$$\boxed{Q_H - Q_c = W}$$

We can compute the thermal efficiency

$$\epsilon = \frac{W}{Q_H} = \frac{Q_H - Q_c}{Q_H} = \boxed{1 - \frac{Q_c}{Q_H}}$$

- The efficiency is 100 % only if $Q_c = 0$.

impossible !

- Realistic gasoline engine

  $\epsilon \sim 20\%$

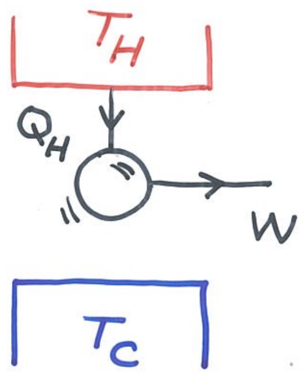
  diesel engine $\epsilon \sim 30\%$

The Second Law

The Kelvin-Plank Statement of the 2^{nd} law

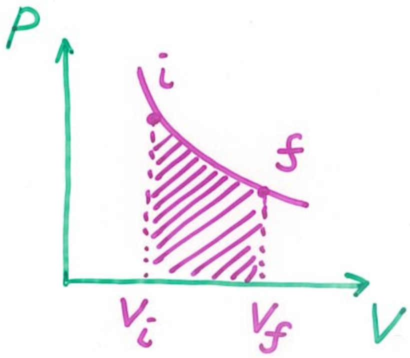
It is impossible for a heat engine that operates in a cycle to convert its heat input completely into work

Or it's simpler in terms of diagram



The ideally perfect heat engine with $\epsilon = 1$ does not exist!

Notice that "cycle" is important!



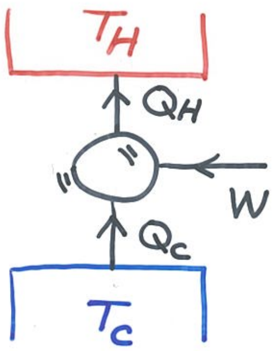
In isothermal expansion,

$$U(T) = \text{const.} \rightarrow \Delta U = 0$$

The absorbed heat Q is completely turned into the mechanical work W. But. the system is <u>not</u> the same anymore.

Refrigerator

Refrigerator is an inversed device of the heat engine. We input some mechanical work W to force the heat flows from the low temperature reservoir to the high T one.



According to the 1^{st} law, after each cycle $\Delta U = 0$

$$\boxed{Q_H = Q_c + W}$$

Define the coefficient of performance (COP)

$$\boxed{COP = \frac{Q_c}{W} = \frac{Q_H - W}{W} = \frac{Q_H}{W} - 1}$$

A practical refrigerator has $COP \approx 5$.

<u>Note.</u> If the heat engine is reversible, we can run it in the reverse direction.

$$COP = \frac{Q_H}{W} - 1 = \boxed{\frac{1}{\epsilon} - 1}$$

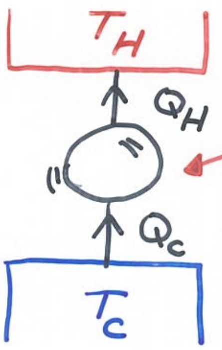
$$0 < \epsilon < 1 \quad \Leftrightarrow \quad 0 < COP < \infty$$

The Second Law, Again!

Clausius statement of the second law:

> It is impossible for a cyclical device to transfer heat continuously from a cold body to a hot body without the input of work or other effect on the environment.

Again, it is simpler in terms of diagram



impossible refrigerator!

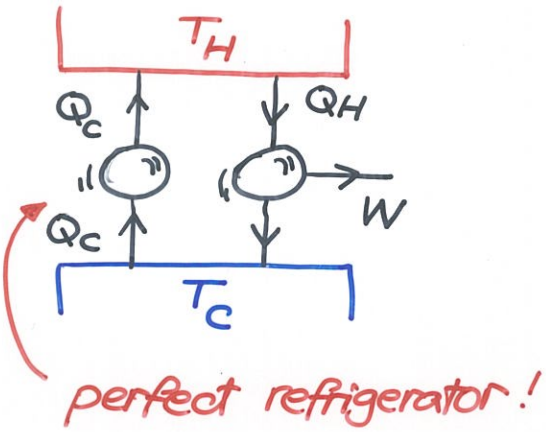
$$COP = \frac{Q_C}{W} \longrightarrow \infty \; !$$

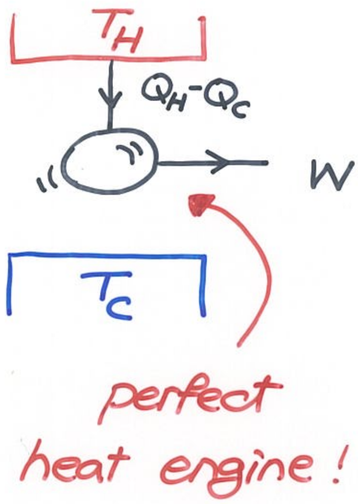
- This is just a sophisticated way to state our common senses that heat never flows from the cold body to the hot body without external manipulation!

- This statement is equivalent to the Kelvin-Plank statement.

Now we are going to show that Kelvin-Plank and Clausius statements are equivalent.

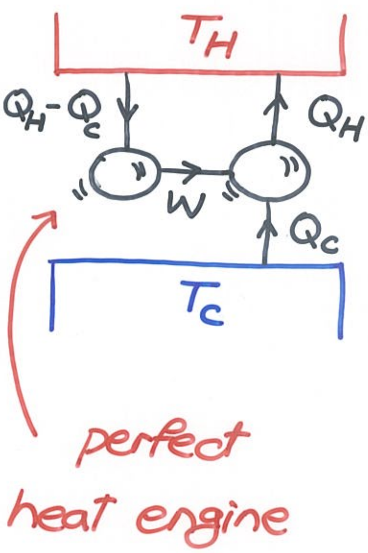
1°) First assume that Clausius statement is wrong $\longrightarrow$ perfect refrigerator!

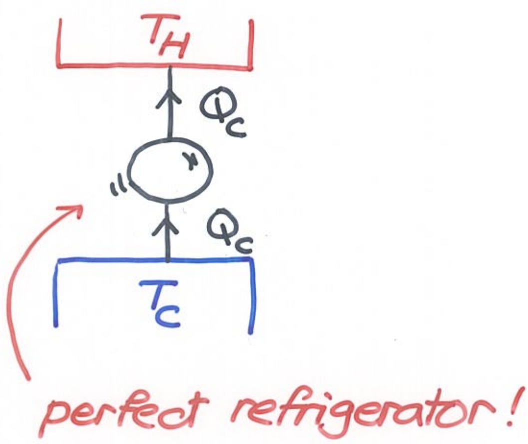




Therefore, Kelvin-Plank statement is also false.

2°) Assume Kelvin-Plank statement is false $\longrightarrow$ perfect heat engine

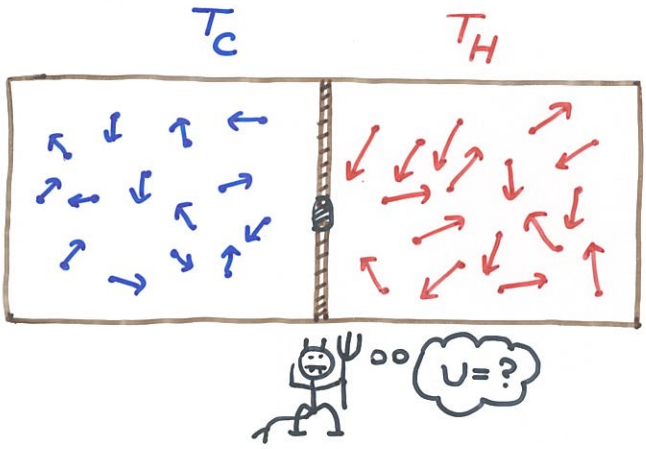


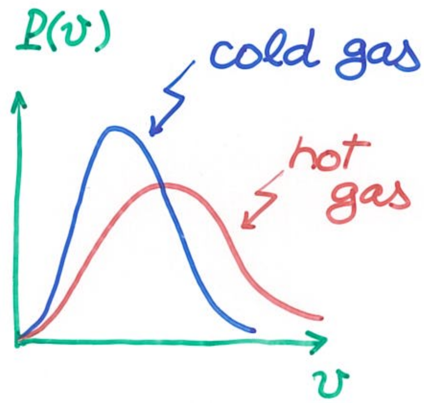


Maxwell Daemon

Maxwell posted a challenge to the 2^{nd} law by the following gedanken experiment.

Imagine a small daemon operates a tiny door between two gases with different temperature





Daemon lets the slow atoms in the hot gas to go into the cold gas. Besides, it also lets the fast atoms in the cold gas go to the hot gas.

> The cold gas becomes even colder and the hot gas hotter! The 2^{nd} law is violated ?!

Reversible v.s. Irreversible

When we perturb the system, it takes some time to reach equilibrium again. This time scale is called relaxation time. Quasistatic process is defined with respect to this time scale.

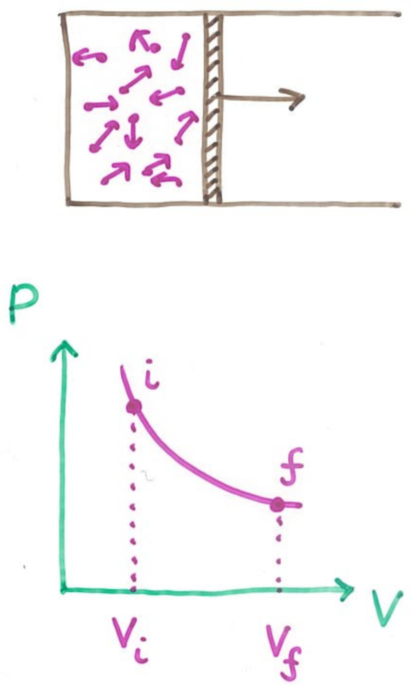
Reversible process:

(1) It must be quasistatic.

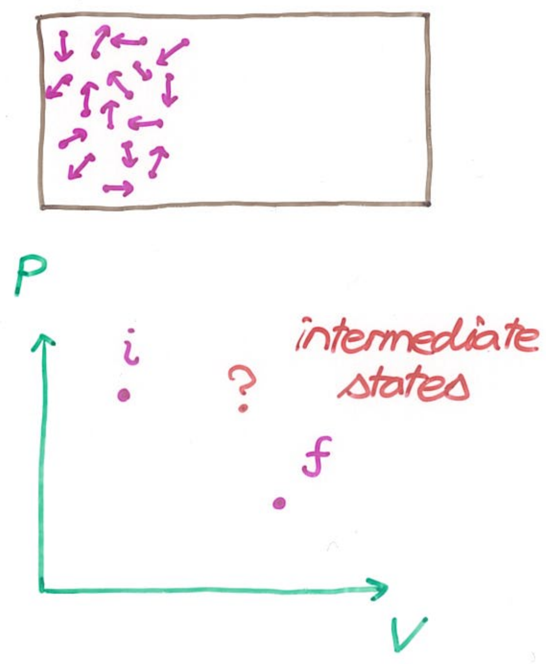
(2) There must be no friction.

(3) Any transfer of heat must occur at constant / infinitesmal different temperature.

Otherwise, it is called irreversible.



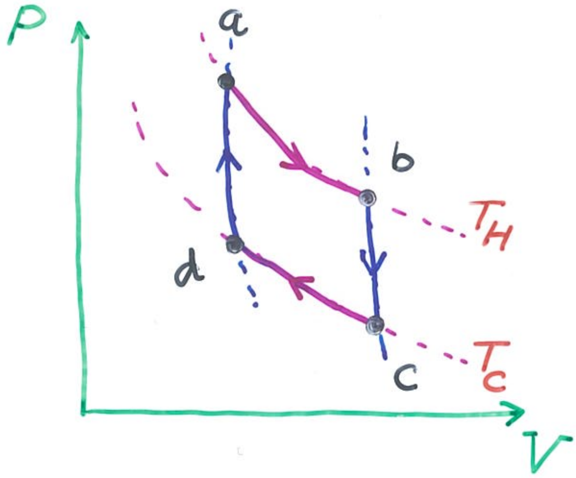
isothermal expansion



free expansion

Carnot Cycle

1824, Carnot devised a reversible cycle of operations.



$a \to b$: isothermal T_H

$b \to c$: adiabatic

$c \to d$: isothermal T_C

$d \to a$: adiabatic

Heat : $a \to b$ isothermal expansion

$$Q = \underbrace{\Delta U}_{= 0} + W = \int_{V_a}^{V_b} P\, dV$$

Apply the ideal gas law $PV = nRT$

$$P(V) = \frac{nRT}{V}$$

$$Q_H = \int_{V_a}^{V_b} P \cdot dV = nRT_H \int_{V_a}^{V_b} \frac{1}{V} dV$$

$$= nRT_H \left[\ln V_b - \ln V_a \right]$$

$$= \boxed{nRT_H \ln\left(\frac{V_b}{V_a}\right)}$$

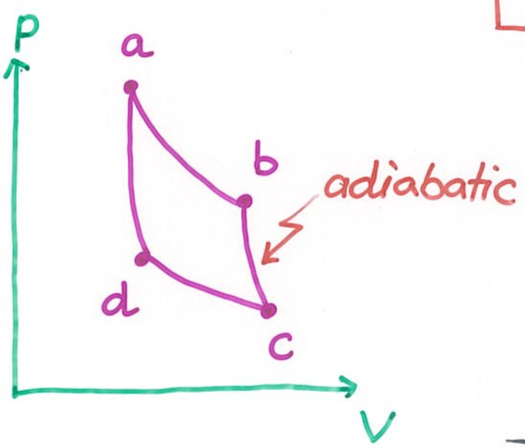
Similarly, during another isothermal process $c \rightarrow d$, heat is discharged into the cold reservoir.

$$\boxed{Q_c = -\int_{V_c}^{V_d} P\,dV = nRT_c \ln\left(\frac{V_c}{V_d}\right)}$$

Making use of $PV^{\gamma} = \text{const}$ for adiabatic process. Combined with $PV = nRT$,

$$PV^{\gamma} = \frac{nRT}{V} \cdot V^{\gamma} = nRTV^{\gamma-1} = \text{const}$$

therefore, $\boxed{TV^{\gamma-1} = \text{const}}$



$$T_H V_b^{\gamma-1} = T_c V_c^{\gamma-1}$$

$$T_H V_a^{\gamma-1} = T_c V_d^{\gamma-1}$$

$$\rightarrow \quad \left(\frac{V_b}{V_a}\right)^{\gamma-1} = \left(\frac{V_c}{V_d}\right)^{\gamma-1}$$

Furthermore,

$$\boxed{\frac{V_b}{V_a} = \frac{V_c}{V_d}} \quad \rightarrow \quad \ln\left(\frac{V_b}{V_a}\right) = \ln\left(\frac{V_c}{V_d}\right)$$

The heat $Q_H = nRT_H \ln(V_b/V_a)$

$$Q_c = nRT_c \ln(V_c/V_d)$$

The ratio of absorbed and discharged heat is

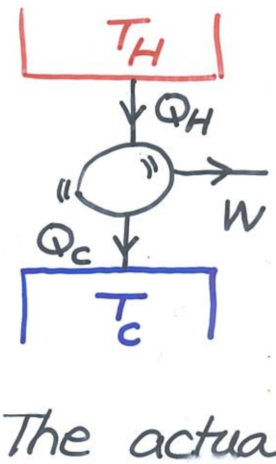
$$\frac{Q_H}{Q_c} = \frac{nRT_H}{nRT_c}\frac{\ln(V_b/V_a)}{\ln(V_c/V_d)} = \frac{T_H}{T_c}$$

It's surprising that the ratio is very simple and only depends on the temperature of reservoir.

$$\boxed{\frac{Q_H}{Q_c} = \frac{T_H}{T_c}}$$

simple but important!

Now we turn to calculate work W.



From the heat engine diagram, it is clear that

$$\boxed{W = Q_H - Q_c}$$

The actual amount of work can be computed as the enclosed area in the P-V diagram!

Now we are ready to evaluate the efficiency of a Carnot cycle.

$$\epsilon_C \equiv \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

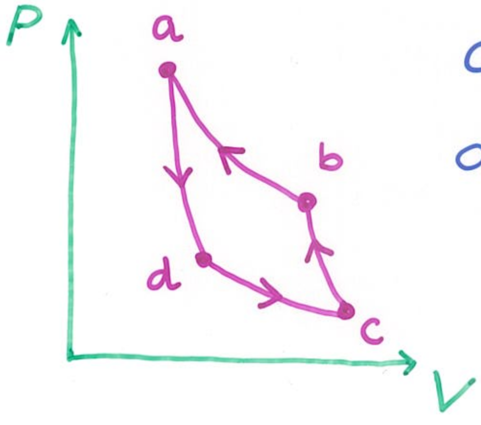
As computed previously, $Q_C / Q_H = T_C / T_H$

$$\boxed{\epsilon_C = 1 - \frac{T_C}{T_H}}$$

Reality:

- A real engine involves irreversible processes.
- A real engine aborbs / discharges heat at different temperatures, not just two constant temperature reservoir.

Question: What does the reversed Carnot cycle do? Is it possible at all?



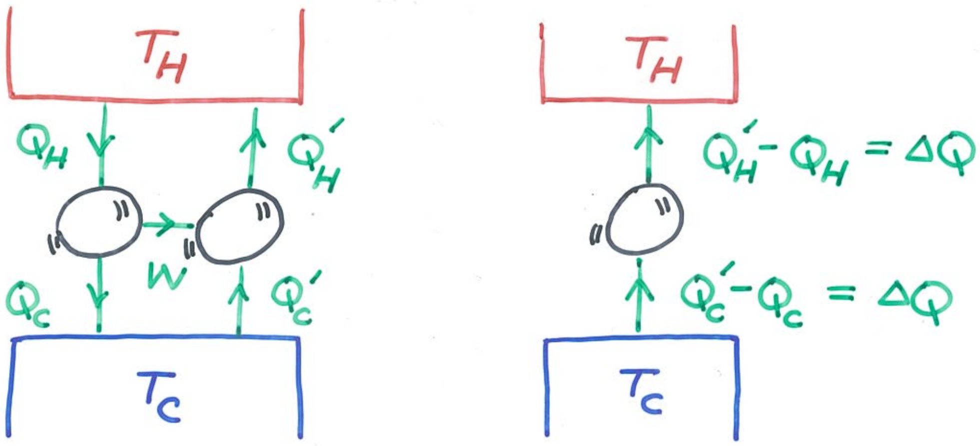
Carnot's Theorem

Carnot presented the following theorem:

(1) All reversible engines operating between two given reservoirs have the same efficiency

(2) No cyclical engine has a greater efficiency than a reversible engine operating between the same two temperatures.

Now we are going to prove the theorem ☺
Since the engines are reversible, let's reverse one of them as a refrigerator.



1^{st} law $\qquad \Delta Q = Q_H' - Q_H = Q_C' - Q_C$

2^{nd} law $\qquad \boxed{\Delta Q \leq 0}$

✲ heat must flow from T_H to T_C !

The efficiency is

$$\begin{cases} \epsilon = \dfrac{W}{Q_H} \\ \epsilon' = \dfrac{W}{Q'_H} \end{cases}$$

Since $\Delta Q \leq 0$ from the 2nd law, $Q'_H \leq Q_H$

Therefore, it is clear that $\boxed{\epsilon \leq \epsilon'}$

Since both engines are reversible, we can reverse the other engine as the refrigerator and conclude that $\boxed{\epsilon' \leq \epsilon}$

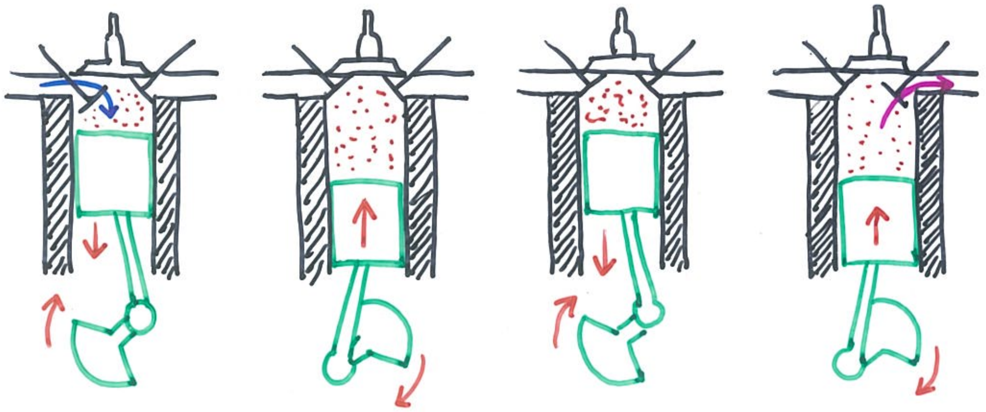
The only sensible conclusion is then $\boxed{\epsilon = \epsilon'}$

The second part can be proved in a similar fashion. We reverse the reversible engine to be the refrigerator.

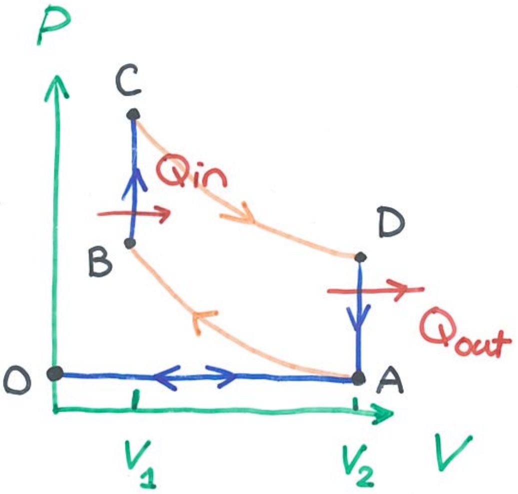
$$\boxed{\epsilon_{irrev} \leq \epsilon_{rev}}$$

Since the engine can not be reversed, this is the only criterion we get.

Gasoline Engine (Otto cycle)



Intake | Compression | Ignition/Power | Exhaust



(1) $O \to A$ (Intake stroke)

(2) $A \to B$ compression.

Adiabatic process

(3) $B \to C$ ignition

(4) $C \to D$ power stroke

Adiabatic again!

(5) $D \to A$ Exhaust

(6) $A \to O$ Exhaust stroke.

Notice that heat absorption/discharge does not occur at constant temperature!

Let's compute the efficiency for ideal Otto cycle. The heat transfer occurs at constant volume.

$$\boxed{\begin{aligned} Q_{in} &= nC_v(T_C - T_B) \\ Q_{out} &= nC_v(T_D - T_A) \end{aligned}}$$

Use the fact that (A, B) and (C, D) are related by adiabatic process respectively.

$$TV^{\gamma-1} = \text{const} \quad \text{or} \quad T = \frac{\text{const}}{V^{\gamma-1}}$$

Therefore, we can compute the ratio of T_A, T_B

$$\frac{T_A}{T_B} = \frac{\text{const}/V_A^{\gamma-1}}{\text{const}/V_B^{\gamma-1}} = \left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

Similarly, the ratio of T_C, T_D is

$$\frac{T_D}{T_C} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\boxed{\frac{T_A}{T_B} = \frac{T_D}{T_C} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}}$$

The thermal efficiency is

$$\epsilon = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

$$= 1 - \frac{nR(T_D - T_A)}{nR(T_C - T_B)} = 1 - \left(\frac{T_D - T_A}{T_C - T_B}\right)$$

Since $\frac{T_D}{T_C} = \frac{T_A}{T_B} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$

$$\epsilon = 1 - \frac{T_D - T_A}{T_C - T_B} = \boxed{1 - \frac{T_D}{T_C}}$$

$$= \boxed{1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}}$$

important result!

Introduce the compression ratio r

$$r \equiv \frac{V_1}{V_2} > 1 \quad \rightarrow \quad \epsilon = 1 - \frac{1}{r^{\gamma-1}}$$

- $r = 8$, $\gamma = 1.4$ efficiency $\epsilon = 56\%$

  The practical value is only about 20%

- For a Carnot cycle operating between the same extremal temperatures

  $$\epsilon_C = 1 - \frac{T_A}{T_C} > \epsilon = 1 - \frac{T_D}{T_C}$$

  More efficient as predicted!

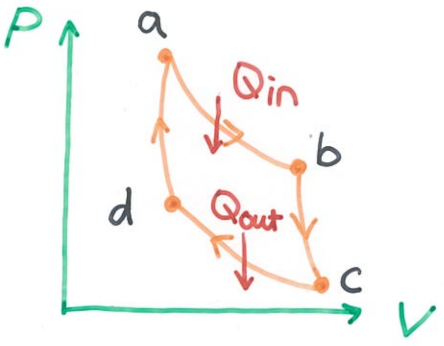
Entropy

zeroth law: T is a state variable.

first law: U is a state variable.

What about the second law?

Let us go back to the Carnot cycle again.



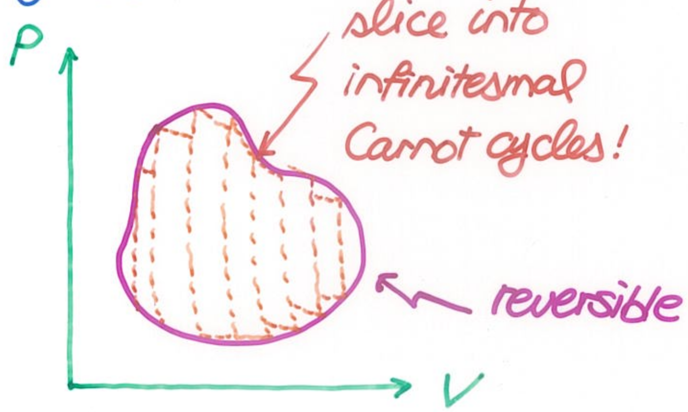
$$\boxed{\frac{Q_H}{T_H} = \frac{Q_C}{T_C}}$$

- $a \to b$ $\quad \frac{\Delta Q}{T} = \frac{Q_H}{T_H}$
- $b \to c$ $\quad \frac{\Delta Q}{T} = 0$
- $c \to d$ $\quad \frac{\Delta Q}{T} = -\frac{Q_C}{T_C}$, • $d \to a$ $\quad \frac{\Delta Q}{T} = 0$

We find that

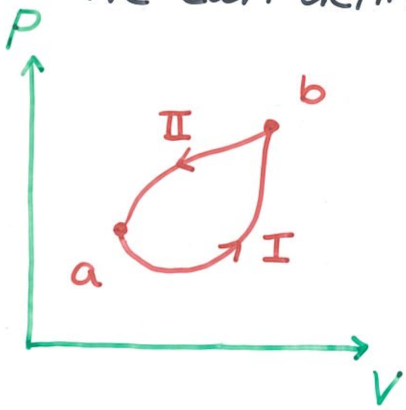
$$\boxed{\sum \frac{\Delta Q}{T} = 0}$$

Now generalize the above result for arbitrary cycles.



$$\boxed{\oint \frac{dQ}{T} = 0}$$

We can define a new state variable S entropy



According to previous theorem

$$\int_{a_{I}}^{b} \frac{dQ}{T} + \int_{b_{II}}^{a} \frac{dQ}{dT} = 0$$

But $\int_a^b = - \int_b^a$

$$\int_{a \atop I}^{b} \frac{dQ}{T} - \int_{a \atop II}^{b} \frac{dQ}{T} = 0 \Rightarrow \int_a^b \frac{dQ}{T} = F(b) - F(a)$$

Therefore, the entropy S is defined

$$\boxed{\Delta S = S_b - S_a = \int_a^b \frac{dQ_R}{T}}$$

Or, in infinitesmal form

$$\boxed{dS = \frac{dQ}{T}}$$

The change of entropy only depends on the initial and final states, but independent of the thermodynamic paths (which do not exist for irreversible processes!)

Reversible Process for Ideal Gas

With the definition of S, the first law can be re-written as

$$đQ = dU + đW$$

$$\rightarrow \quad \boxed{T\,dS = dU + P\,dV}$$

important!

Consider ideal gas, $PV = nRT$

$$dS = \frac{1}{T}\,dU + \frac{1}{T}P\,dV$$

$$= \frac{nC_v}{T}\,dT + \frac{nR}{V}\,dV$$

Integrate on both sides

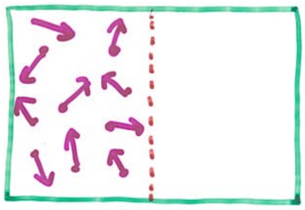
$$\int_i^f dS = nC_v \int_i^f \frac{dT}{T} + nR \int_i^f \frac{dV}{V}$$

$$\Delta S = nC_v\left(\ln T_f - \ln T_i\right) + nR\left(\ln V_f - \ln V_i\right)$$

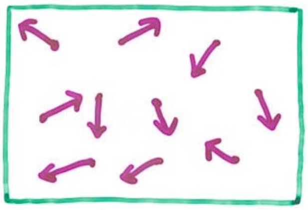
$$\boxed{\Delta S = nC_v \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{V_f}{V_i}\right)}$$

ONLY for ideal gas!

Adiabatic Free Expansion ← irreversible!



$t=0$

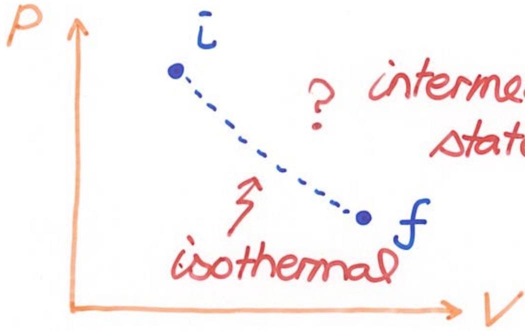


$t>t_e$

$\Delta U = 0$ T is constant!

$\Delta Q = 0$ No heat flow.

$\Delta W = 0$ No work done.



The change of the entropy is

$$\Delta S = n C_V \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{V_f}{V_i}\right)$$

$$\ln\frac{T_f}{T_i} = \ln 1 = 0 \;\longrightarrow\; \boxed{\Delta S = nR\ln\left(\frac{V_f}{V_i}\right)}$$

- Entropy increases even though that there is NO heat flow involved! It is important to notice that

$$\boxed{\Delta S \neq \frac{\Delta Q}{T}}$$

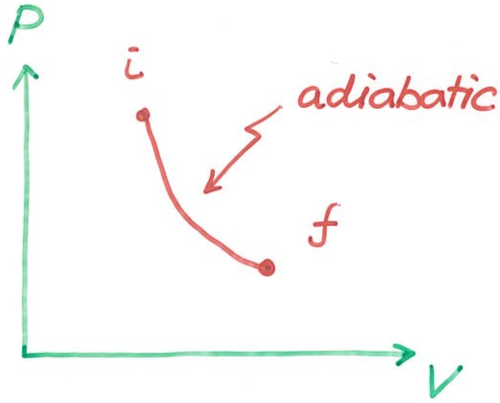
for irreversible process!

- For an <u>isolated</u> system

$\Delta S = 0$ reversible.

$\Delta S > 0$ irreversible.

Adiabatic Expansion (reversible process)



There are two ways to calculate the answer.

(1) $$\Delta S = \int_i^f \frac{dQ}{T}$$

$$= 0 \; !$$

(2) $$\Delta S = n C_v \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

Since $TV^{\gamma-1} = \text{const.}$ $\quad \dfrac{T_f}{T_i} = \left(\dfrac{V_f}{V_i}\right)^{1-\gamma}$.

The change of the entropy is

$$\Delta S = n C_v \ln\left(\frac{V_f}{V_i}\right)^{1-\gamma} + nR \ln\left(\frac{V_f}{V_i}\right)$$

$$= n \ln\left(\frac{V_f}{V_i}\right) \left[(1-\gamma) C_v + R \right]$$

Note that $$(1-\gamma) C_v = \left(1 - \frac{C_p}{C_v}\right) \cdot C_v = C_v - C_p$$

$$= -R$$

$$\longrightarrow \quad (1-\gamma) C_v + R = 0 \; !$$

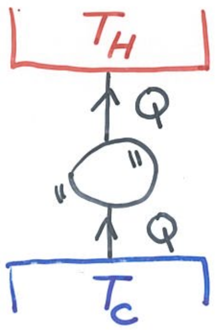
Therefore, we see that $\Delta S = 0$

Entropy and the Second Law, AGAIN!

The second law of thermodynamics:

$\Delta S \geq 0$ In a reversible process of an isolated system, the entropy stays constant. In an irreversible process, the entropy increases!

Example: A perfect refrigerator is impossible.



For the refrigerator, it completes a cycle and $\Delta S_r = 0$.

For the reservoirs,

$$\Delta S_E = \frac{Q}{T_H} - \frac{Q}{T_C} < 0$$

Therefore $\Delta S = \Delta S_r + \Delta S_E < 0$ impossible!

The entropy function S, first introduced in thermal physics, has close relation to probability distribution of the system.

$$\boxed{S = -\sum_n P_n \ln P_n}$$