

- Reversible vs Irreversible process
  - History of Thermodynamics entropy (before Boltzmann)
    - Carnot's engine
    - Kelvin's temperature
    - Clausius's entropy function
  - Example of entropy's application
- 

### Process's irreversibility

A reversible process is usually

} Quasi-static  
No "un-intentional" loss of W.D.

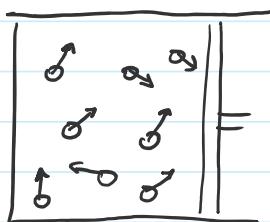
### Quasi static

Quasi static = Half equilibrium - Half transitioning

### Example : Gas compression

#### ① Before Compression

Can assume the gas being evenly distributed

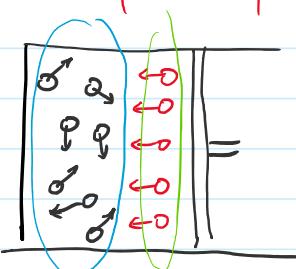


Gas particles are more or less evenly distributed

⇒ Pressure is well-defined

#### ② At the beginning of the push

Only the gas near the piston know the piston is pushing

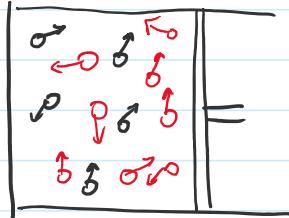


Pressure remain original value      Pressure near piston is higher

⇒ Pressure become not so well defined

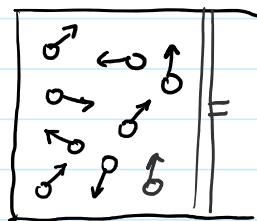
③ Piston stop moving

Gas originally near piston  
start to mix with the remaining gas



④ Wait for a long time

All particles are well mixed

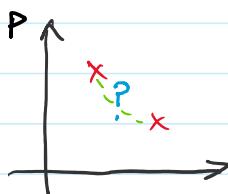


Pressure is still not well-defined

Gas particles are more or less evenly distributed  
⇒ Pressure become well-defined

In reality, rate of change in pressure depends on position

So the transition from one state to another shall not be described by a single line in the phase space.



The transition path between 2 state  
is ambiguous.

BUT if the process is so slow, such that

- The piston only compresses a very tiny volume each time
- Time allowed for the gas to fully mix is extremely long

Such that the differences between 2 states are infinitesimal.

IF we carry out such transition for many times, we can "approximate"

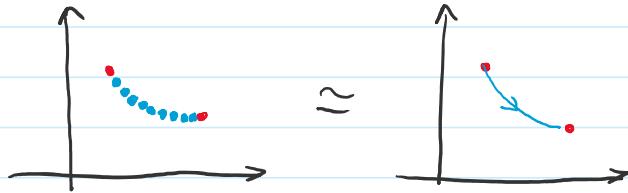
the state parameters to be changing continuously in the process

Such process = Quasi-Static

= Half equilibrium - Half transitioning

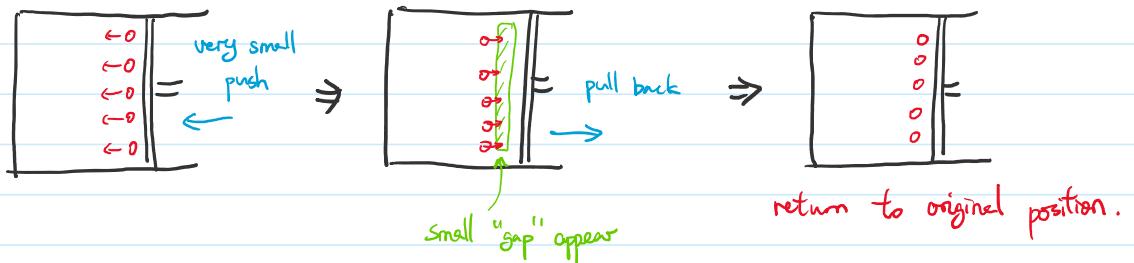
Made of infinitely many intermediate states  
so state parameters are always  
well-defined

Made of infinitely many processes  
so state parameters are always  
smoothly changing



★ Quasi-static is not practical in reality, but they are reversible

E.g.



### Irreversible process

Consider a close system (Total energy in the box is a constant)

We observe that any irreversible process happening inside the system is either one of these cases :

Case 1 : Not quasi-static

= Drastic change in state parameter

= No line can be drawn on the state space



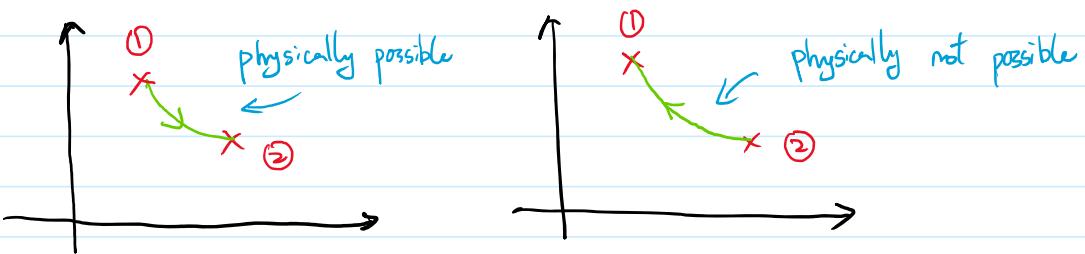
Case 2 : Objects in the system interact in a way

such that W.D. is lost as heat "un-intentionally"

E.g. Friction exists between piston head & container wall

⇒ W.D. by piston lost as heat

→ The line connecting 2 states can only be drawn as bidirectional



But how can we tell if a process is reversible or not?

We need to find it out from the entropy function

### Brief history of thermodynamics

- Carnot Theorem + Carnot Engine (1824)  
(Carnot died in 1832)

- The first 2 statements of thermo. 2<sup>nd</sup> law.

- Kelvin statement (1850)
- Clausius statement (1851)

- - - - Statistical Physics begins - - - - -

- Boltzmann's Entropy (1859)

↑ thermodynamics

↓ statistical mechanics

### Achievement of Carnot

- The first person who suggested that one can extract energy for our use, in the process when heat flow from hot object to cold object. Just like we can extract KE from object that falls from high place to low place

⇒ i.e. The concept of heat engine =

Any cyclic process that can be used to extract W.D. out

of the natural heat flowing from hot to cold object

meaning it can be reused indefinitely

### - Carnot Theorem

For any heat engines that operate between 2 heat reservoirs at 2 fixed temperature. The engine that runs reversible processes is the most efficient in converting heat into W.D.

⇒ Propose Carnot engine in his proof of the theorem.

However his arguments were derived from 1<sup>st</sup> Law and involved

circular reasoning , ie. logically incorrect .

After years , scientists finally realized Carnot Theorem is impossible to be derived from 1<sup>st</sup> law . It should not be described as a theorem , but a new law itself

Theorem = Consequence that we can logically derive from known results

Law = A rule decided by the nature . We can conclude such rule only by observations .

Carnot Theorem is in fact an alternative statement / description to

the 2<sup>nd</sup> Law of thermodynamics - Irreversibility of processes

## The first 2 statements of 2<sup>nd</sup> Law

Kelvin & Clausius independently formulate their own

statement of the law about irreversibility:

$$\left\{ \begin{array}{l} \text{Kelvin : No W.D.} \rightarrow \text{No reverse heat flow} \\ \text{Clausius : Heat} \xrightarrow[100\%]{\times} \text{W.D.} \end{array} \right.$$

= Their observation to how irreversibility can be described

NOT explanation of why irreversibility occurs.

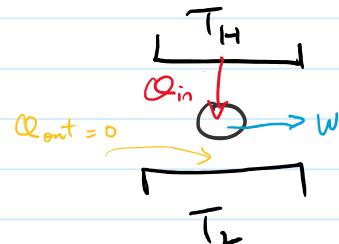
Their statements can be proven to be logically equivalent

Proof : By contradiction (If one fails, the other must also fail)

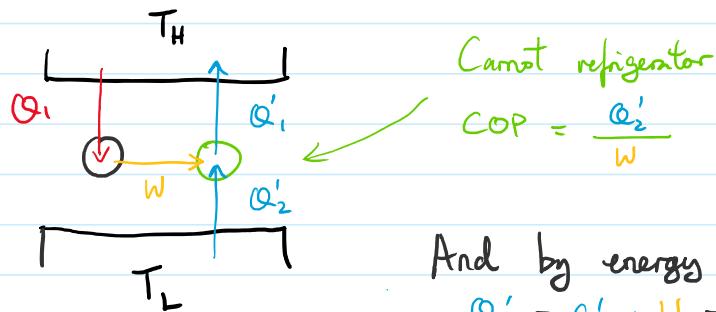
(1) Clausius fails  $\Rightarrow$  Kelvin fails

[1] Suppose Clausius statement is wrong

i.e. there exists an engine that  
can convert 100% of heat to W.D.



[2] We can operate it together with a Carnot refrigerator

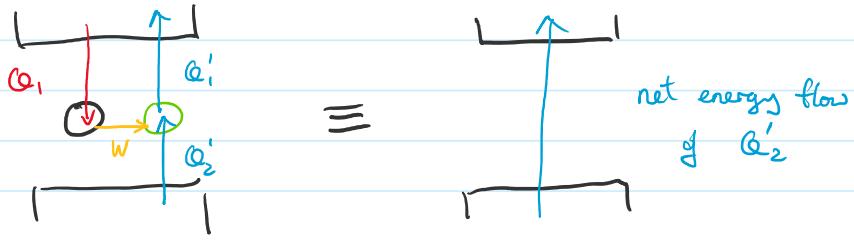


And by energy conservation

$$Q_1' = Q_2' + W = Q_2' + Q_1$$

[3] The whole process is equivalent to net heat flow from

colder reservoir to hotter reservoir without external W.D.

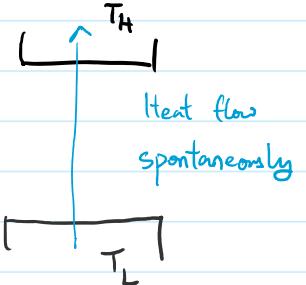


$\Rightarrow$  This is forbidden by Kelvin's statement

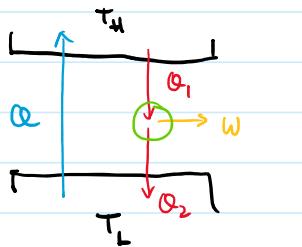
### ② Kelvin fails $\Rightarrow$ Clausius fails

① Suppose Kelvin statement is wrong

i.e. Heat can flow from a colder place to a hotter place without applying W.D.



② We can operate it together with a Carnot engine



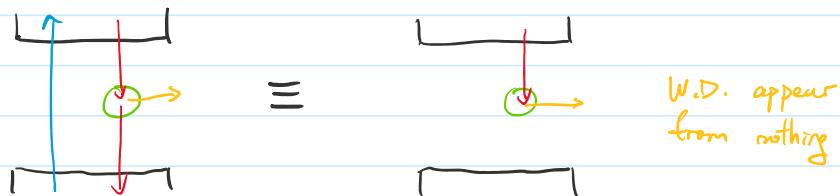
Carnot engine.  
efficiency =  $1 - \frac{Q_2}{Q_1} = \frac{W}{Q_1}$

If we make the rate of  $Q$  flowing out of colder reservoir equal to the rate of  $Q_2$  pumping into colder reservoir such that  $T_2$  is kept constant. Then we can write

$$Q = Q_2 = Q_1 - W$$

③ The whole process is equivalent to extracting W.D.

without any heat exchange between 2 reservoir



$\Rightarrow$  This is forbidden by Kelvin's statement

## Carnot's "Theorem"

Carnot's theorem can be proven as another statement about the law of irreversibility equivalent to Kelvin's & Clausius's

All engines that work between the same 2 heat reservoir

must operate at an efficiency no higher than a  $\text{Carnot engine's}$

\* Carnot engine = Any engine that runs with reversible cycle

Not just those with Carnot cycle

Proof: Again by contradiction

Suppose there is an engine with efficiency  $\eta$  > Carnot engine's  
 $(\eta_1)$   $(\eta_2)$

We already know Carnot cycle is a reversible process.

\* i.e. This engine runs on irreversible process and we assume that it can convert a larger portion of heat input to W.D. But since all its processes are irreversible, running the cycle in the opposite direction as a refridgerator with the same efficiency / COP is not possible

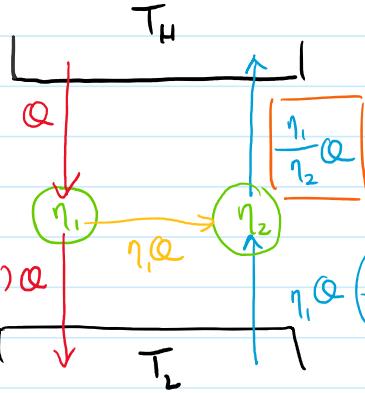
⇒ Operate this engine with a Carnot refrigerator

Recall : Def. of efficiency

$$\eta = \frac{W}{Q_{in}} = \frac{\text{energy convert to W.D.}}{\text{heat input}}$$

Energy not convert  
to W.D. =  $(1-\eta)Q$

$$(1-\eta_1)\alpha$$



Recall : Def. of COP

$$COP = \frac{1-\eta}{\eta} = \frac{\text{energy removed}}{\text{W.D.}}$$

Look at the net heat flow into  $T_H$  :

$$= \frac{\eta_1}{\eta_2}Q - Q > 0 \quad \text{if } \eta_1 > \eta_2$$

= Net inflow of heat to  $T_H \Rightarrow$  Forbidden by Kelvin's statement



Summary of the logic :

- Carnot cycle is made of reversible processes, and is operating solely in between 2 heat reservoir of constant temperature
- We know the efficiency of Carnot cycle very well =  $1 - \frac{T_L}{T_H}$
- We know that a Carnot engine can be used as a refrigerator

Then any engine that is also operating solely in between the same 2

heat reservoir must have an efficiency  $\leq 1 - \frac{T_L}{T_H}$

or else we can make heat flow from  $T_L$  to  $T_H$  spontaneously

P.S. Not all types of engine operate with 2 reservoirs

those are not comparable with Carnot engine

## Kelvin Temperature

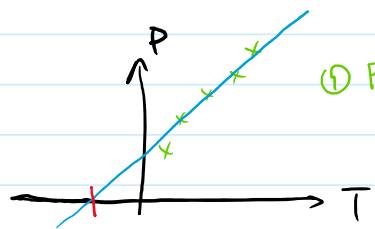
### Temperature Scale before Kelvin

E.g. Celsius = Measure length expansion of mercury / alcohol column  
 (1701 - 1744)  
 between water's freezing & boiling point

Then divide the expansion into 100 grids

At that time, P vs T relation of ideal gas is found purely by experiment

- ② Find P & T in a linear relation  
 $\Rightarrow$  Draw a fitting line to find the equation



- ① Plot data from experiment

- ③ Find the line cut  $P = 0$  when  $T = -273^{\circ}\text{C}$

3 Experiment cannot tell what will happen when T is below  $-273^{\circ}\text{C}$

## Thermodynamic temperature scale

- = Define temperature scale by measuring Carnot engine efficiency
- = Theoretical approach showing that there cannot be anything below  $-273^{\circ}\text{C}$

Idea: Because efficiency of Carnot cycle is purely determined by the "relative hotness" between 2 reservoir

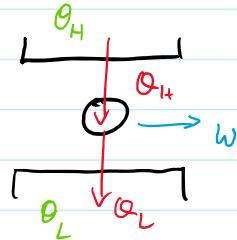
$\Rightarrow$  Measure efficiency = Measure how hotter the hot reservoir relative to the cold reservoir

Let's say the 2 reservoirs have "relative hotness"  $\theta_H, \theta_L$

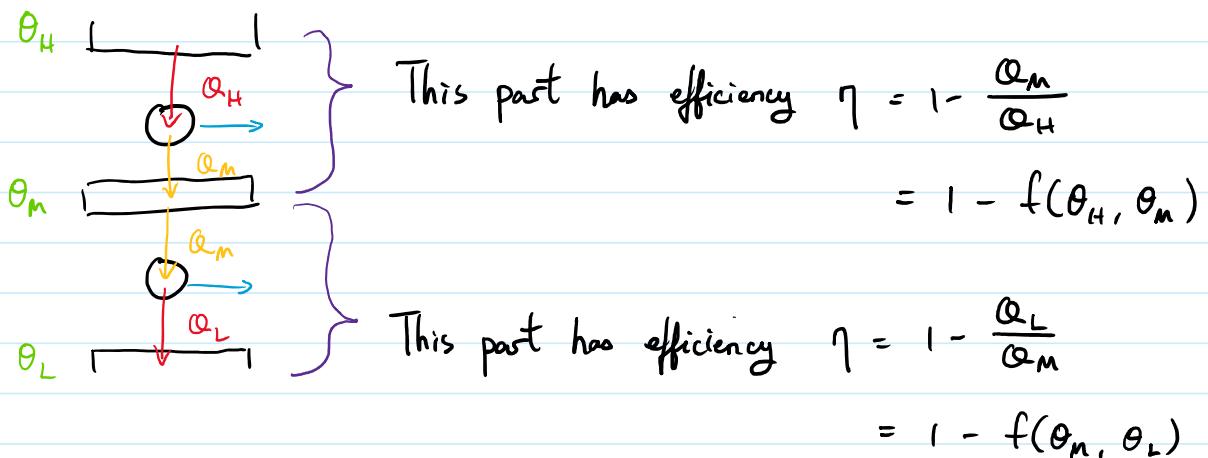
① Assume the efficiency can be written as a function of  $\theta_H, \theta_L$

$$\eta = 1 - \frac{\Omega_H}{\Omega_L}$$

$$= 1 - f(\theta_H, \theta_L)$$



② Insert a 3<sup>rd</sup> reservoir M in between, with hotness  $\theta_H > \theta_M > \theta_L$



③ Because of these mathematical relations

III

$$\frac{\Omega_L}{\Omega_H} = \frac{\Omega_L}{\Omega_M} \times \frac{\Omega_M}{\Omega_H}$$

$\Rightarrow$   $f(\theta_H, \theta_L) = f(\theta_M, \theta_L) \times f(\theta_H, \theta_M)$

IV

$$\frac{\Omega_L}{\Omega_H} = \frac{1}{\frac{\Omega_H}{\Omega_L}}$$

$\Rightarrow$   $f(\theta_H, \theta_L) = \frac{1}{f(\theta_L, \theta_H)}$

What kinds of function f satisfy these relations?

There are infinitely many choices :

$$\text{E.g. } f(\theta_1, \theta_2) = \frac{\theta_2}{\theta_1}, \quad f(\theta_1, \theta_2) = e^{\theta_1 - \theta_2}, \dots$$

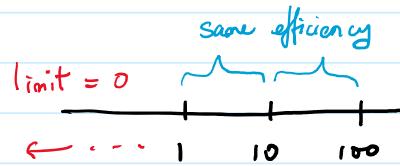
But they differ only in a matter of the choice of scale.

- If you prefer  $f(\theta_1, \theta_2) = \frac{\theta_2}{\theta_1}$

Carnot engines between  $(\theta_H, \theta_L) = (10, 1)$

&  $(\theta_H, \theta_L) = (100, 10)$  are the same.

⇒ The measure of hotness is in an exponential scale

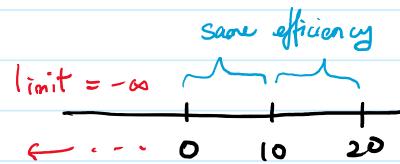


- If you prefer  $f(\theta_1, \theta_2) = e^{\theta_2 - \theta_1}$

Carnot engines between  $(\theta_H, \theta_L) = (0, 10)$

&  $(\theta_H, \theta_L) = (10, 20)$  are the same

⇒ The measure of hotness is in a linear scale



★★ Because people at that time already know ideal gas law

- Ideal gas measurement is using the scale of  $(T + 273)^\circ\text{C}$
- The theory of Carnot engine is built based on ideal gas

$\Rightarrow$  It is simply a convenient choice to continue using the existing one  
 so the modern temperature scale is actually an exponential scale

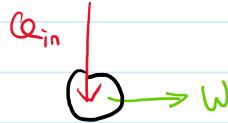
The Kelvin scale 
$$\left[ \frac{\theta_2}{\theta_1} \right] = \left[ \frac{T_2 + 273}{T_1 + 273} \right]$$
 from the theory of Carnot engine

The consequence : Unable to reach absolute 0 ( $\theta = 0$ )

We can see that the  $\text{absolute } 0$  in an exponential scale  
 is corresponding to  $-\infty$  in a linear scale.

So it makes sense mathematically that we are unable to past  $\theta = 0$   
 Also in terms of Carnot engine theory, being able to reach  $\theta = 0$   
 meaning we can violate 2<sup>nd</sup> Law.

Some  $\theta_H > 0$



Efficiency of a Carnot engine if colder side  $\theta = 0$  :

$$\eta = 1 - \frac{0}{\theta_H} = 1$$

$\theta_L = 0$

Meaning all heat input becomes W.D.

$\Rightarrow$  Violating Clausius statement

## Clausius Entropy

- Clausius : The first guy invented the term "Entropy"

$$-\text{Clausius Theorem} : \sum_{\substack{\text{all object involved} \\ \text{in heat exchange}}} \int \frac{dQ_{in}}{T} \geq 0$$

any process

★ Note that Clausius Theorem is only a consequence of 2<sup>nd</sup> law

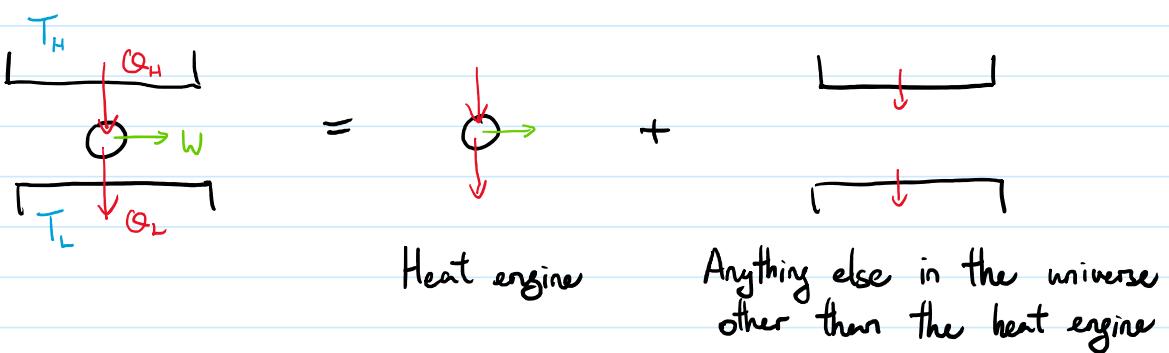
if 2<sup>nd</sup> law is correct. It does not explain why it is true.

## Proof of Clausius Theorem

Rundown of the proof : Show , after 1 engine cycle

$$\textcircled{1} \quad \oint \frac{dQ_{in}}{T} \text{ of reversible } \underline{\text{heat engine}} \text{ after heat exchange} = 0$$

$$\textcircled{2} \quad \oint \frac{dQ_{in}}{T} \text{ of } \underline{\text{anything else}} \text{ after heat exchange} \geq 0$$



Part 1 : Proving  $\oint \frac{dQ}{T} = 0$  for any engine running a cycle

□ In a Carnot engine

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \Rightarrow \frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

Adopting the notation  $\begin{cases} Q > 0 & \text{as heat input} \\ Q < 0 & \text{as heat output} \end{cases}$  to engine

$$\Rightarrow \frac{Q_{H,in}}{T_H} - \frac{(-1) Q_{L,in}}{T_L} = 0$$

$Q_L$  is flowing out  
so need a minus sign

heat exchange  
only occur in  
the isothermal process  
in a Carnot cycle

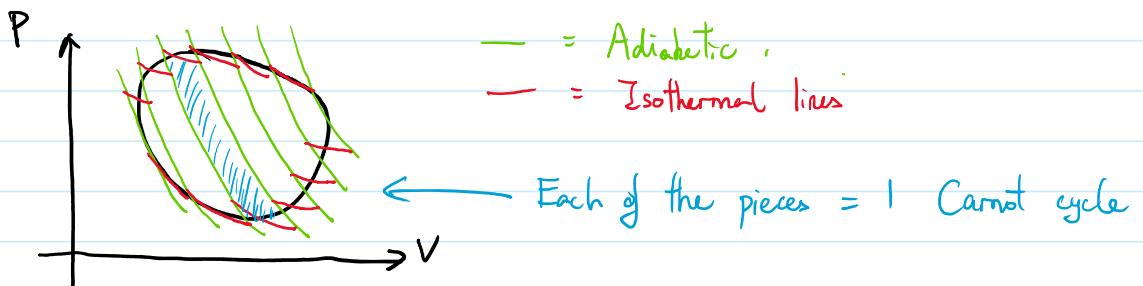
$$\left| \frac{Q_{H,in}}{T_H} \right| + \left| \frac{dQ}{T_{\text{adiabatic}}} \right| + \left| \frac{Q_{L,in}}{T_L} \right| + \left| \frac{dQ}{T_{\text{adiabatic}}} \right| = 0$$

↑ const. ↑ const. (By definition,  $dQ = 0$  on any adiabatic process)

Then we have found the  $\oint \frac{dQ}{T}$  of a Carnot cycle :

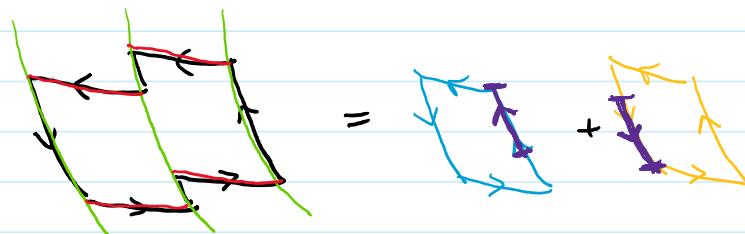
$$\Rightarrow \sum_{i=1 \text{ to } 4} \frac{Q_{\text{in, path } i}}{T_{\text{path } i}} = 0 \Rightarrow \oint_{\text{Carnot cycle}} \frac{dQ_{\text{in}}}{T} = 0$$

② Any engine cycle can be cut into many Carnot cycle



Then we can use the property of line integral on scalar function

$$\oint_{\text{black loop}} \frac{dQ}{T} = \oint_{\text{blue loop}} \frac{dQ}{T} + \oint_{\text{yellow loop}} \frac{dQ}{T}$$



Integration along purple lines  
cancel because of opposite direction

So we can conclude

$$\oint \frac{dQ_{in}}{T} = \sum \left( \oint \frac{dQ_{in}}{T} \right)_{\substack{\text{any} \\ \text{reversible} \\ \text{cycle}}} + \sum \left( \oint \frac{dQ_{in}}{T} \right)_{\substack{\text{many} \\ \text{Carrot} \\ \text{cycle}}} = 0$$

Part 2: Proving  $\oint \frac{dQ}{T} \geq 0$  for the environments that have heat exchange with the engine.

When a natural heat exchange occurs,

① Heat only naturally flows from hotter object to colder object  
(IF Kelvin's statement is true)

$$\because T_H > T_L \text{ and } (dQ_{out})_{\substack{\text{hotter} \\ \text{object}}} = (dQ_{in})_{\substack{\text{colder} \\ \text{object}}}$$

$$\Rightarrow \left( \frac{dQ_{out}}{T_H} \right)_{\substack{\text{hotter} \\ \text{object}}} < \left( \frac{dQ_{in}}{T_L} \right)_{\substack{\text{colder} \\ \text{object}}}$$

$$\Rightarrow \left( \frac{dQ_{in}}{T_L} \right)_{\substack{\text{colder} \\ \text{object}}} + \left( \frac{-dQ_{in}}{T_H} \right)_{\substack{\text{hotter} \\ \text{object}}} > 0$$

Generalized as :  $\sum \left( \frac{dQ_{in}}{T} \right)_{\substack{\text{all objects involved} \\ \text{in heat exchange}}} > 0$

② We can reduce the amount of heat flowing into the colder object by inserting a reversible heat engine.

i.e. make  $(dQ_{out})_{\substack{\text{hotter} \\ \text{object}}} > (dQ_{in})_{\substack{\text{colder} \\ \text{object}}}$  by using

part of the output heat to do work.

However, engine on reversible cycle must have  $\int_{\text{cycle}} \frac{dQ}{T} = 0$

$$\therefore \sum_{\text{all heat exchange}} \left( \frac{dQ_{in}}{T} \right)$$

$$= \left( \frac{-dQ_{in}^{(1)}}{T_H} \right)_{\text{hotter object}} + \left( \frac{dQ_{in}^{(1)}}{T} \right)_{\text{engine}} + \left( \frac{-dQ_{in}^{(2)}}{T} \right)_{\text{engine}} + \left( \frac{dQ_{in}}{T_L} \right)_{\text{colder object}}$$

$$\geq 0$$

$\int_{\text{cycle}} \frac{dQ}{T} = 0$

Equal sign occur only if  $dQ_{in} = 0$ , which occur only if

- No heat exchange at all
- Work done by engine is used to operate another mechanism (e.g. refrigerator) s.t. net heat flow in all objects is 0.

→ In this case, we can think of a "battery"

that can store the W.D. produced by the engine

- When engine operate
  - $S \uparrow$  in reservoirs.
  - $S \downarrow$  in battery
  - $\text{total } \Delta S = 0$

- When refrigerator operate
  - $S \downarrow$  in reservoirs
  - $S \uparrow$  in battery
  - $\text{total } \Delta S = 0$

## Summary of Clausius Theorem

In any close system.

(In open system,  $\sum \Delta S$  can be anything)

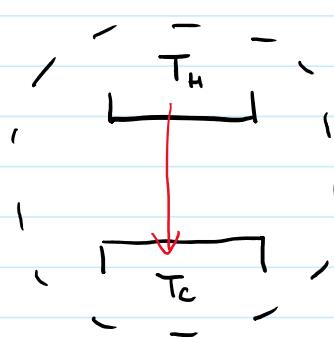
- Through any processes with heat exchanges.

$\Delta S$  of each object can be +ve or -ve

- But the sum of all  $\Delta S$  must be  $\geq 0$

The special case  $\sum \Delta S = 0$  is when all the heat exchange processes are reversible.

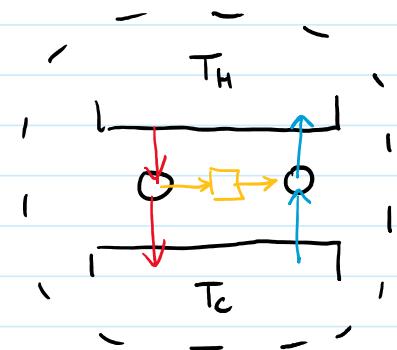
- Whether a process is "reversible" is determined by if the system contain a process to revert such state change



There is no process to  
revert the heat flow

So it must have  $\sum_{\text{all object}} \Delta S > 0$

= Not a reversible system



Any change in this system  
are reversible because revert

processes exist.  $\sum_{\text{all object}} \Delta S = 0$

= A reversible system

## Entropy as a state function

In a reversible system,  $\sum_{\text{all object}} \Delta S = 0$  is guaranteed.

Then if we change the states of some objects and revert them,  $\Delta S$  of those objects should be 0.

$\Rightarrow S$  is a state function for each object

$$S(\text{state 2}) - S(\text{state 1}) = \int_{\substack{\text{state 1} \rightarrow \text{state 2} \\ \text{in a reversible system}}} \frac{dQ_{\text{in}}}{T}$$

Or else we can repeat and revert the processes infinite many times to make some objects with  $\Delta S = +\infty$  and some with  $\Delta S = -\infty$

Question : Is this allowed ?

What is the actual physical meaning of  $S$  ?

## Example of using entropy

Given 2 states of the same materials, which one is "naturally preferred" ?

state 1  $\rightleftharpoons$  state 2 . eg. phase change, chemical reaction

Naturally preferred :

In an environment, will the material spontaneously shift to another state, if the reverse process does not exist / cannot occur

We can determine this by calculating the entropy change

- Suppose we start with the material at state 1  
(E.g. object is in the "hot" state)
- The material will interact with the environment in some process and become state 2  
(E.g. it can cool down to the "cold" state)

- The process can be spontaneous only if  $\sum_{\text{object}} \Delta S \geq 0$

(E.g. Naturally cooling down is possible only if  $T_{\text{object}} > T_{\text{envr.}}$ )  
which mathematically yield  $\Delta S > 0$

The calculation as follow :

Check the sign of  $\Delta S_{\text{material}} + \Delta S_{\text{envr.}}$

$\begin{cases} > 0 & \text{prefer final state} \\ = 0 & \text{Equilibrium} \\ < 0 & \text{prefer initial state} \end{cases}$
--

along a reversible process that connects the 2 states.

$$\Delta S_{\text{material}} = \int_{\text{reversible process}} \frac{dQ_{\text{in}}}{T} \quad \begin{array}{l} \text{may be a complicate integral} \\ \text{depends on how Q change with T} \end{array}$$

$$\Delta S_{\text{envr.}} \approx \int_{\text{reversible process}} \frac{dQ_{\text{in}}}{T_{\text{const.}}} \quad \begin{array}{l} \text{State of environment is usually} \\ \text{considered as constant because it} \\ \text{is much bigger than the material} \end{array}$$

★★ Choosing reversible process because  $\Delta S$  is the smallest among all theoretically possible processes.

⇒ If the reversible process yield  $\Delta S > 0$ , any process in that direction must also yield  $\Delta S > 0$

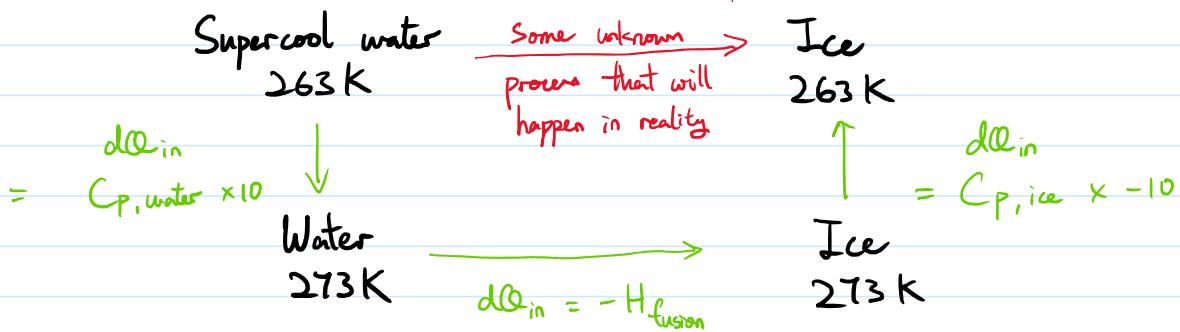
Example : Supercool water vs Ice (at 263 K, atm pressure)

Given  $C_p$  of ice = 36 J/K/mol

$C_p$  of water = 75 J/K/mol

Latent heat of fusion = 6000 J/K

① Construct a theoretical process that is reversible



Total  $\Delta S$  in the reversible process is

$$\Delta S_{\text{rev}} = \Delta S_{\text{heat up}} + \Delta S_{\text{fusion}} + \Delta S_{\text{cool again}}$$

$$= \int_{263}^{273} \frac{C_p, \text{water } dT}{T} + (-1) \frac{H_{\text{fusion}}}{273} + \int_{273}^{263} \frac{C_p, \text{ice } dT}{T}$$
$$\approx -20.52 \quad (\text{in the reversible process})$$

②  $\Delta S$  of the environment

Note :

①.  $dQ_{in}$  of material =  $-dQ_{in}$  of environment

(energy conservation)

②. T of environment is unchanged in the real process

⇒ should be kept at 263 K

$$\therefore \Delta S_{\text{env.}} = - \frac{C_p, \text{water} \times 10 + H_{\text{fusion}} + C_p, \text{ice} \times 10}{263}$$

$$\approx 21.32$$

③ Total  $\Delta S$  of water + environment

$$= 21.32 - 20.52$$

$$= 0.80 > 0$$

So a reversible process of supercool water  $\rightarrow$  ice at 263 K can happen spontaneously

$\Rightarrow$  Any non reversible process in the same direction can also happen spontaneously.

$\Rightarrow$  Nature prefer ice at 263 K atm pressure.