8th Feb 2024

Clausius Inequality $\Rightarrow$

- A thermodynamic system performs a complete cycle. To do that, it interacts with reservoirs $R_1, \dots, R_n$ with temp $T_1, \dots, T_n$ and exchange heat $Q_1, \dots, Q_n$.
- Convention $\longrightarrow$ $Q \equiv +ve$, heat goes into system.

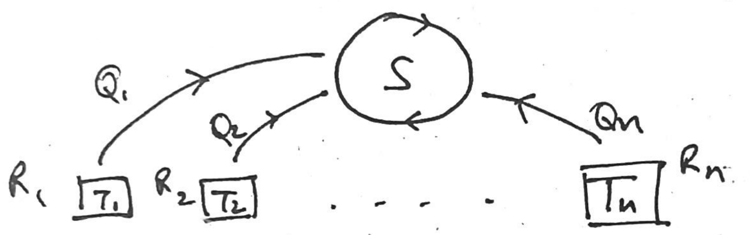
Statement $\longrightarrow$

$$\sum_{i=1}^{N} \frac{Q_i}{T_i} \leq 0 .$$

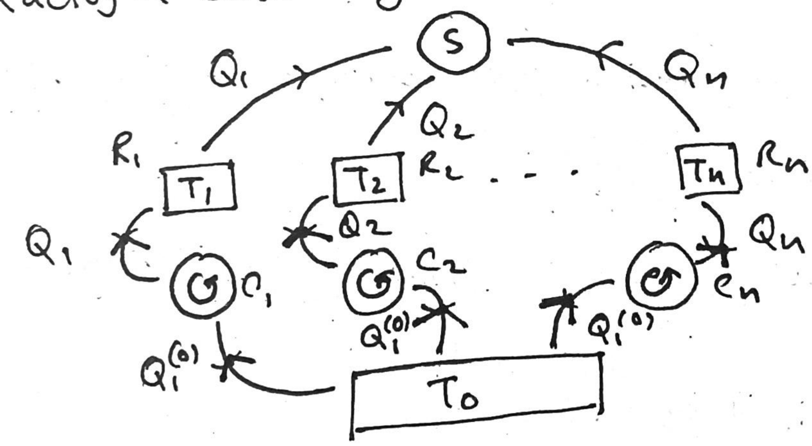
So for the carnot engine (a special subclass of this),

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

General case,



We introduce a reservoir with arbitrary temp T_0, and exactly n carnot engines.



⊛ C_1 supplies Q_i heat to R_1, the same heat that it ~~loses to~~ loses to S, and so on to n.

⊛ Note that this is possible due to the fact that Carnot engines are reversible and ~~cat~~ can act as heat engine as well as refridgerator.

① S and $R_1, \ldots, R_n$ goes back to same state

② T_0 reservoir 'loses' energy

$$Q_0 = \sum_{i=1}^{N} Q_i^{(0)}$$

Now we know that for the carnot engines,

$$\frac{Q_i^{(0)}}{Q_i} = \frac{T_0}{T_i}$$

$$\therefore \quad Q_0 = \sum_{i=1}^{N} Q_i^{(0)} = T_0 \sum_{i=1}^{N} \frac{Q_i}{T_i}$$

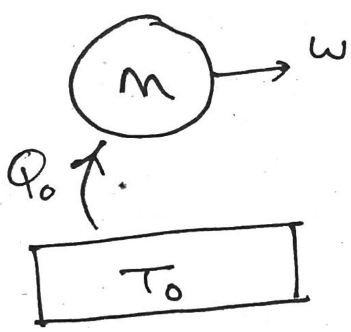
The process is cyclic for all the engines involved.
If we think of them as one engine, $\Delta U = 0$

Now, $\Delta U = \Delta Q + \Delta W$

$$\Rightarrow -\Delta Q = \Delta W$$

$$\Rightarrow \Delta W = -T_0 \sum_{i=1}^{N} \frac{Q_i}{T_i} \rightarrow \text{work done.}$$

Combining the engines,



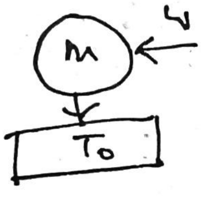
Obviously this engine cannot exist

$\Leftrightarrow$ Violates 2nd law

But this is okay if $Q_0 < 0$

Work $\rightarrow$ Heat conversion is never prohibited.

i.e, if work is done on system and ~~heat~~ heat is given to T_0 reservoir.



☑ Allowed

$$\Rightarrow Q_0 = T_0 \sum_{i=1}^{N} \frac{Q_i}{T_i} \leq 0$$

Consider S to be a reversible engine.

$\Rightarrow$ All engines / cycles are reversible.

Replace $Q_i \longrightarrow -Q_i$ (reverse the process)

$$\therefore T_0 \sum_{i=1}^{N} \frac{Q_i}{T_i} \geq 0$$

This can only be consistent if $T_0 \sum_{i=1}^{N} \frac{Q_i}{T_i} = 0$

$$\Rightarrow \boxed{\text{for reversible } \sum_{i=1}^{N} \frac{Q_i}{T_i} = 0} \quad \circledast$$

$$\Rightarrow \boxed{\text{for a cyclic process, } \sum_{i=1}^{N} \frac{Q_i}{T_i} \leq 0} \quad \circledast$$

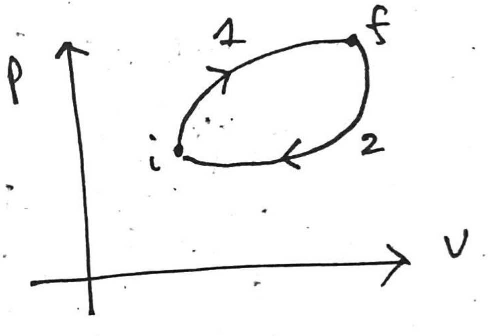
$\circledast$ equality for reversible, inequality otherwise.

This may be generalised to,

$$\oint \frac{đQ}{T} \leq 0$$

Consider a reversible cycle,

$$\oint \frac{đQ}{T} = 0$$



Now,
$$\int_i^f \frac{đQ_{rev}}{T}\bigg|_1 + \int_f^i \frac{đQ_{rev}}{T}\bigg|_2 = 0$$

$$\Rightarrow \int_i^f \frac{đQ_{rev}}{T}\bigg|_1 = + \int_i^f \frac{đQ_{rev}}{T}\bigg|_2$$

$\Rightarrow \frac{đQ_{rev}}{T}$ does not depend on path

$\Rightarrow$ It is a state function.

This will be called entropy.

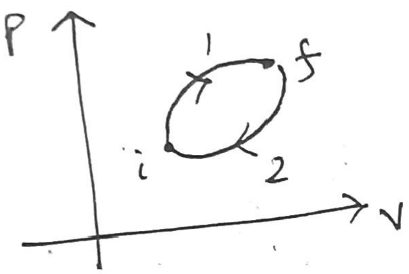
9th February 2024

o Clausius Inequality $\rightarrow$

$$\oint \frac{đQ}{T} \leq 0$$

Eqeality for reversible process

Entropy:



Reversible:

$$\int_{i1f2i} \frac{đQ_{rev}}{T} = 0$$

$$\Rightarrow \int_i^f \frac{đQ_{rev}}{T}\bigg|_1 + \int_f^i \frac{đQ_{rev}}{T}\bigg|_2 = 0$$

$$\Rightarrow \int_i^f \frac{đQ_{rev}}{T}\bigg|_1 = \int_i^f \frac{đQ_{rev}}{T}\bigg|_2$$

Does not depend on the path, clearly.

$\Rightarrow$ It is a state function.

So we define,

$$\int_1^2 \frac{đQ_{rev}}{T} = \int_1^2 dS \equiv S_2 - S_1$$

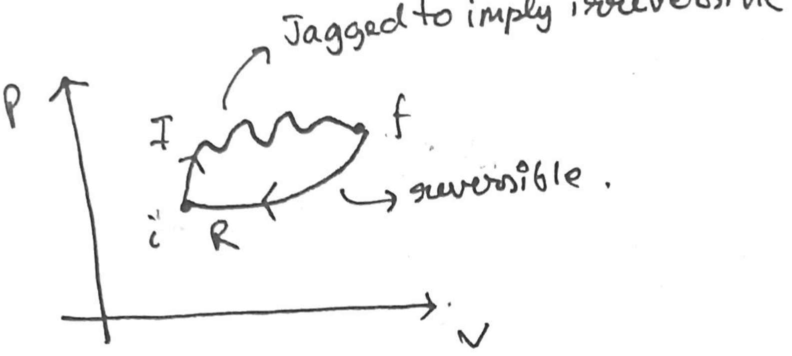
$S \equiv$ Entropy of the system.

Statement of entropy is related to reversible heat transfer only.

$\Rightarrow$ $\frac{đQ}{T}$ is not strictly correct,

it has to be $\frac{đQ_{rev}}{T}$.

Now,



Irreversible cycle $\rightarrow$ dissipation.

$$\oint \frac{đQ}{T} < 0$$

$$\Rightarrow \int_i^f \frac{đQ}{T}\Big|_I + \int_f^i \frac{đQ_{rev}}{T}\Big|_R < 0$$

$$\Rightarrow \int_i^f \frac{đQ}{T}\Big|_I < \int_i^f \frac{đQ_{rev}}{T}\Big|_R$$

$$\Rightarrow S_f - S_i > \int_i^f \frac{đQ}{T}\Big|_I$$

Words

$$\Rightarrow \Delta S \geq \frac{đQ}{T}$$

- If isolated system $đQ = 0$ (adiabatic)

$$S(f) \geq S(i)$$

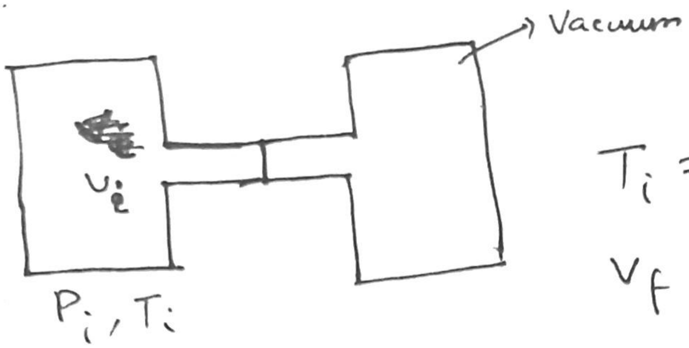
& For irreversible process,

$$S(f) > S(i)$$

Reversible process, $S(f) = S(i)$ (Isentropic)

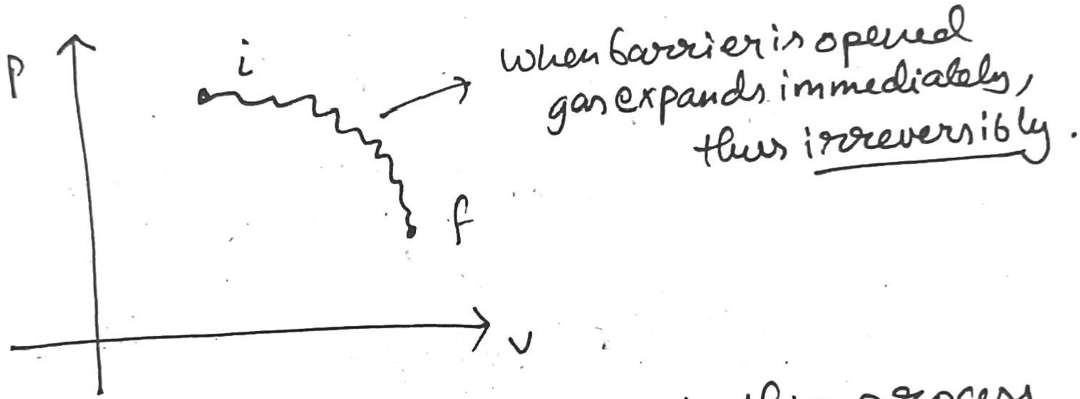
③ Entropy is an extensive parameter - if we scale system in contact with reservoir at temp T, the heat it exchanges with the reservoir also scales. T remains same.
$\Rightarrow$ Entropy is extensive.

o Joule Expansion:



$T_i = T_f$
$V_f = 2V_i$
$P_f = \frac{1}{2}P_i$

As temp / internal energy does not depend on V for ideal gas,
$T_i = T_f$



We want to find entropy change in this process.

$$\Delta S = S_2 - S_1 = \int \frac{dQ_{rev}}{T}$$

But the path is irreversible, how do we do this?
The entropy change is a state function! It has nothing to do with path. We may construct any hypothetical path which is reversible and calculate entropy change for that path - it is going to be the same for any path.
① S is state function - allows you to take any rev path.
② dS is defined for any reversible path.

We choose isotherm here.

$$\therefore \Delta S = \int_{V_0}^{2V_0} \frac{đQ_{rev}}{T} = \int_{V_0}^{2V_0} \frac{\cancel{du} + pdv}{T}$$

$$= \frac{1}{T} \int_{V_0}^{2V_0} pdv$$

$$= R \ln 2 > 0 \quad \therefore \text{(Positive semidefinite) quantity.}$$

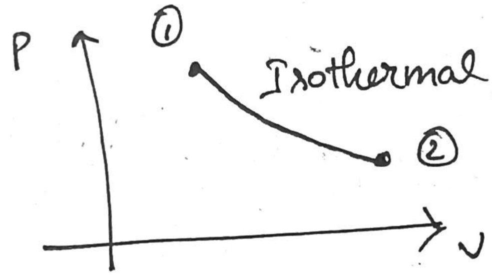
Note that here $đQ = 0$, so $\Delta S = \frac{đQ}{T} = 0$

But that is not reversible, so do not be fooled by this. It must be

- Any process of ideal gas —

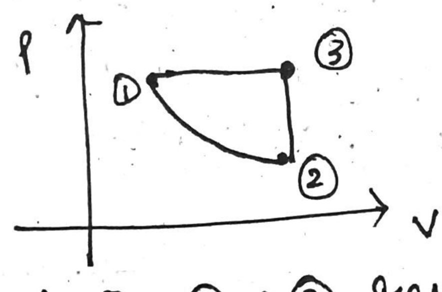
$$(P_1, V_1, T) \rightarrow (P_2, V_2, T)$$

$$\Delta S = NR \ln\left(\frac{V_2}{V_1}\right) \rightarrow \square \text{ Check}$$



We argue that this is the same for all reversible paths.

So we construct another 'reversible' path



$(P_1, V_1) \rightarrow (P_1, V_2)$ isobaric

$\downarrow$ isochoric

(P_2, V_2)

Hard to do ① → ③ → ② reversibly (req inf reservoirs)
but we do not care — we just assume it to be rev

① → ③ is not isothermal, it is isobaric

we use version of $đQ$ where p is constant.

$\therefore\ đQ = C_V\, dT + p\, dV$ $\boxed{\checkmark}$ we use this

$= C_p\, dT - V dp$ $\boxed{\checkmark}$ we use this.

$$\therefore\ \Delta S = \int \frac{đQ_{rev}}{T}$$

$$= \int C_p \frac{dT}{T} + \int C_V \frac{dT}{T}$$

$$= C_p \ln\left(\frac{T'}{T}\right) + C_V \ln\left(\frac{T}{T'}\right)$$

Show that,

$$\frac{T'}{T} = \frac{V_2}{V_1}$$

$$\Rightarrow \Delta S = C_p \ln\left(\frac{V_2}{V_1}\right) - C_V \ln\left(\frac{V_2}{V_1}\right)$$

$$= (C_p - C_V) \ln\left(\frac{V_2}{V_1}\right)$$

$$= NR \ln\left(\frac{V_2}{V_1}\right) \qquad \text{(Ideal gas)}$$

We can construct entropy some other way too —
we demand that dS is a state variable with the formula — axiomatically like Callen.

(*) So, we have redefined reversibility and irreversible with respect to entropy.