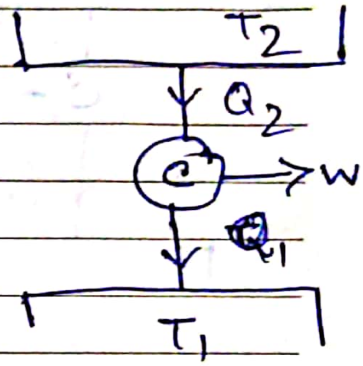
Entropy:

Carnot Th:

$$\eta \leq \eta_R$$

Equal only in the case of reversible.

$$\Rightarrow \quad 1 - \frac{Q_1'}{Q_2'} \leq 1 - \frac{Q_1}{Q_2}$$



$$\Rightarrow \quad \frac{Q_1'}{Q_2'} \geq \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

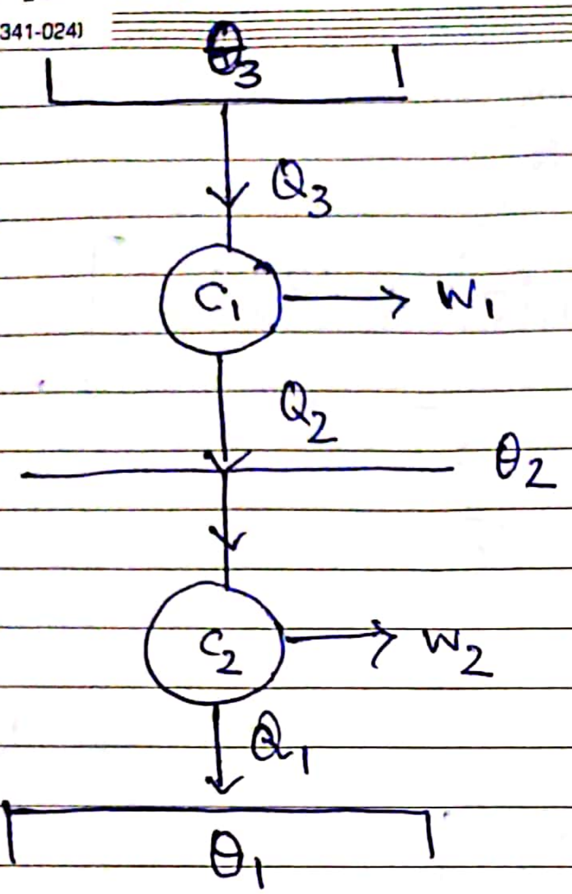
$$\Rightarrow \quad \frac{Q_1'}{T_1} - \frac{Q_2'}{T_2} \leq 0.$$

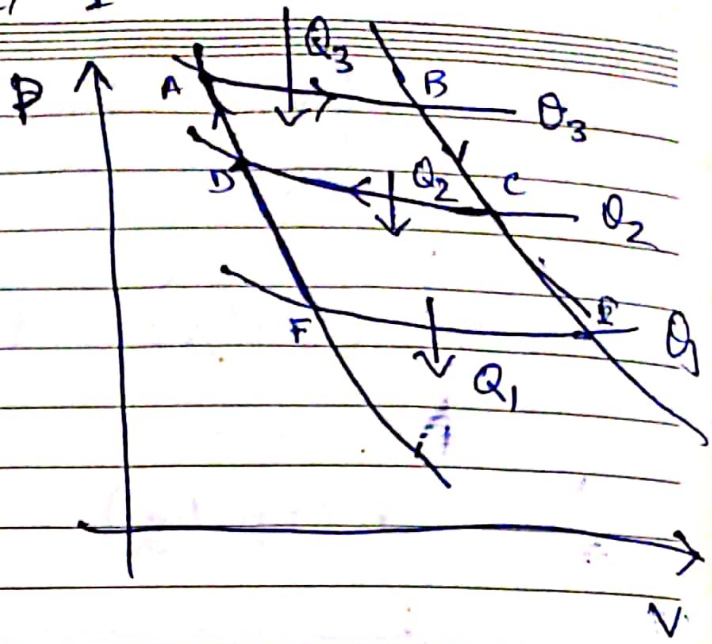
$$\Rightarrow \quad \sum \frac{Q}{T} \leq 0.$$

Equal for reversible only.

Absolute Temp:

$\theta_3 > \theta_2 > \theta_1$





$$\eta_1 = 1 - \frac{Q_2}{Q_3} = 1 - \frac{\theta_2}{\theta_3} = f(\theta_2, \theta_3)$$

$$\Rightarrow \frac{Q_2}{Q_3} = f(\theta_2, \theta_3)$$

$$\eta_2 = 1 - \frac{Q_1}{Q_2} = 1 - \frac{\theta_2}{\theta_2} \Rightarrow \frac{Q_1}{Q_2} = f(\theta_1, \theta_2)$$

$$\Rightarrow \frac{Q_1}{Q_3} = f(\theta_1, \theta_3)$$

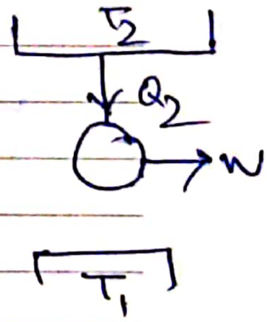
$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \cdot \frac{Q_2}{Q_3}$$

$$\Rightarrow \boxed{f(\theta_1, \theta_3) = f(\theta_1, \theta_2)\, f(\theta_2, \theta_3)}$$

$$f(\theta_1, \theta_2) = \frac{T(\theta_1)}{T(\theta_2)}$$

$$\boxed{T_1 = T(\theta_1)}$$

$$\Rightarrow \boxed{\frac{Q_2}{Q_1} = \frac{T_2}{T_1}}$$



$\Rightarrow Q_1 \propto T_1$

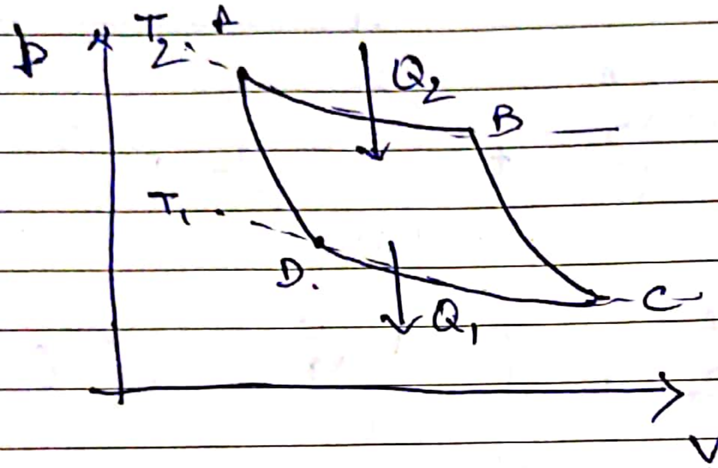
$\eta = 1 - \frac{T_1}{T_2}$

$\Rightarrow T_1 \to 0 \Rightarrow Q_1 \to 0 \Rightarrow \boxed{\eta = 1}$

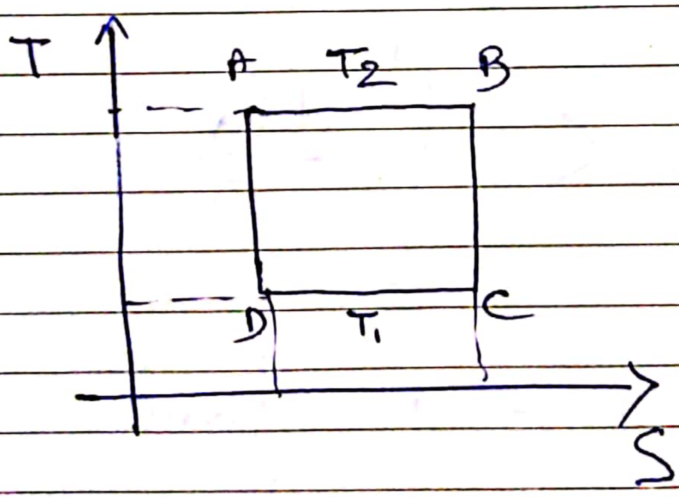
$\Rightarrow$ 2nd Law is violated.

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

$$\oint dS = 0.$$ $$dS = \frac{dQ_r}{T}$$



$$S_B - S_A = S_C - S_D$$



Clausious inequality:

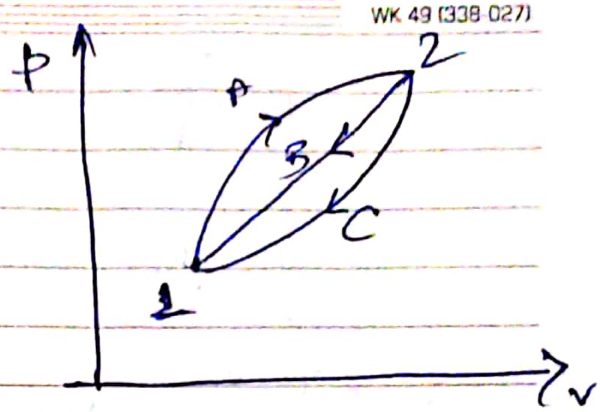
$$\eta_{irr} \leq \eta_{re}$$

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

Irreversible Process:

A, B ⇒ reversible

C ⇒ irreversible



$$\oint \frac{dQ_r}{T} = 0 = \int_1^2 \frac{dQ_r^A}{T} + \int_2^1 \frac{dQ_r^B}{T} = 0.$$

$$\oint \frac{dQ}{T} = \int_1^2 \frac{dQ_r^A}{T} + \int_2^1 \frac{dQ_I^C}{T} < 0.$$

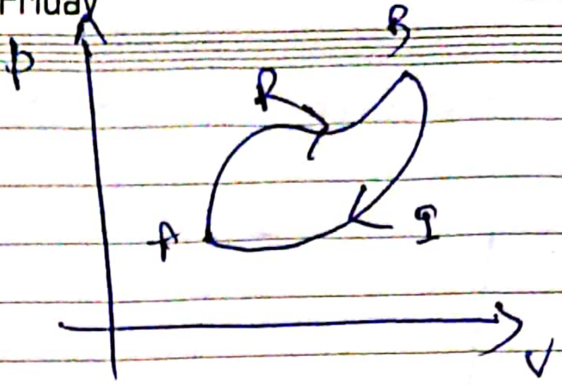
$$\Rightarrow \int_2^1 \frac{dQ_I^C}{T} < \int_2^1 \frac{dQ_r}{T}$$

However Entropy is a state func

$$\Rightarrow S_1 - S_2 = \int_2^1 \frac{dQ_R}{T} = \int_2^1 dS_B = \int_2^1 dS_C$$

$$\Rightarrow \int_2^1 dS_C > \int_2^1 \frac{dQ_I}{T}$$

$\Delta S \geq \frac{dQ}{T}$ equal only for rev.



From Clausious inequality we have

$$\oint \frac{dQ}{T} \leq 0.$$

$$\int_A^B \frac{dQ_r}{T} + \int_B^A \frac{dQ}{T} \leq 0.$$

$$\Rightarrow \int_B^A \frac{dQ}{T} \leq \int_B^A \frac{dQ_r}{T}$$

$$\Rightarrow dS = \frac{dQ_r}{T} \geq \frac{dQ}{T}$$

For Thermally isolated system $dQ = 0$.

$$\rightarrow dS \geq 0$$

$\Rightarrow$ Entropy of an thermally isolated system either staying same or increasing.

$\Rightarrow$ Entropy of an isolated system $\rightarrow$ maximum

Principle of increase of entropy:

Sys T_{sys}	Surr. T_{surr}

dQ flow from system → surrounding
from Clausious inequality,

$$\Delta S_{sys} \geq -\frac{dQ}{T_{sys}}.$$

$$\Delta S_{surr} = +\frac{dQ}{T_{surr}}.$$

$$\Delta S_{u} = \Delta S_{sys} + \Delta S_{surr}.$$

$$\geq -\frac{dQ}{T_{sys}} + \frac{dQ}{T_{surr}} = dQ\left(-\frac{1}{T_{sys}} + \frac{1}{T_{surr}}\right)$$

$$T_{surr} < T_{sys}.$$

$$\Delta S_{u} \geq 0$$

First Law:

$$dU = \text{đ}Q + \text{đ}W$$

$$dU = T\,dS - P\,dV \quad \Rightarrow$$ Holds for irreversible process also

$$U = U(S, V)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\left.\begin{aligned} T &= \left(\frac{\partial U}{\partial S}\right)_V \\ P &= -\left(\frac{\partial U}{\partial V}\right)_S \end{aligned}\right\} \Rightarrow \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_U$$