Second law & its Corollaries.

1st law for closed system & open system

2nd law = Most important law of nature in all branches of physical sciences.

This is the law which puts directional constraint or unidirectional characteristic of all natural processes.

These directional constraints may be in various forms hence 2nd law expressed in various forms though they originate from same concept.

- wide, various forms, originate.
- Directional constraint.

spontaneous process always proceed towards equilibrium and take place in a particular direction.

- Eg liquid flows from higher to lower elevation. Spontaneously.
- heat flows from high temp to low temp.
- Materials always diffuse from high conc to low conc.

Reverse never happen (external energy or source needed)

- A moving wheel stops due to friction of brakes and gets hot.
KE → intermolecular

Reverse → cooling the wheel & brake will not move the wheel, by any external agent.

— Wire becomes hot when current passes but cooling the wire will not give ~~ele~~ electrical work.

Some processes take place in both direction → eg heat & cool a body from high T to low T.

— Expand gas from high P to low P (work is delivered) or compress Gas from ~~high~~ low P to high P. (work is given)

→ Heat engine or heat pump
source & sink.

Process may have come back

to its original state but surrounding suffers

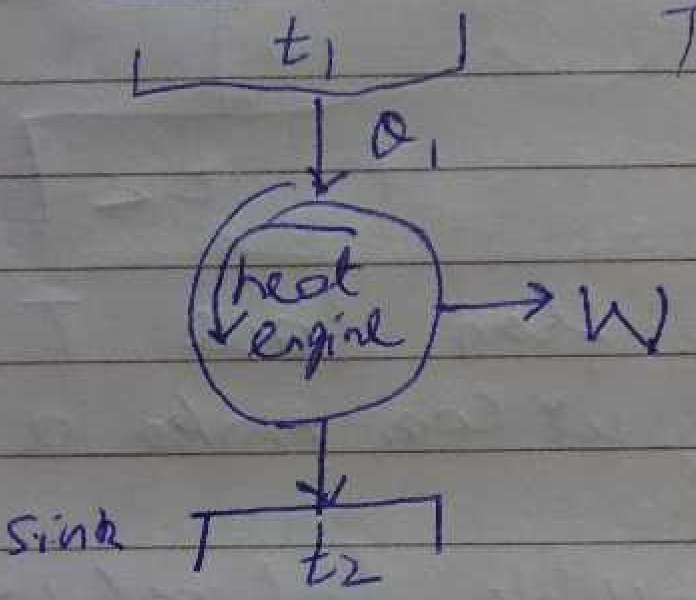
Directional constraints in various forms.

- Engineering point of view, heat / work

D

Heat engine : (cycle)

Thermal reservoir / Source
(infinite capacity)
T remain same



$t_2 < t_1$

$W = Q_1 - Q_2$ $\quad$ $W = Q_1$ ✗

$Q_2 \neq 0$

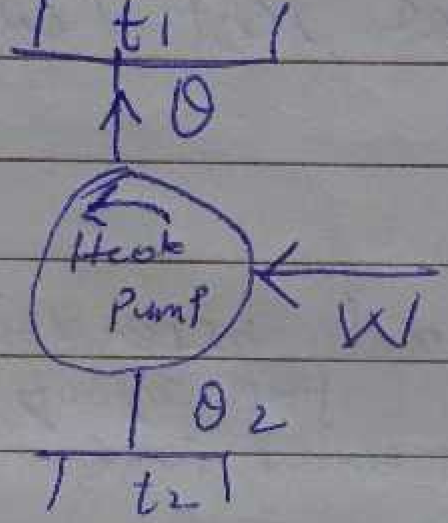
$$\eta_t = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

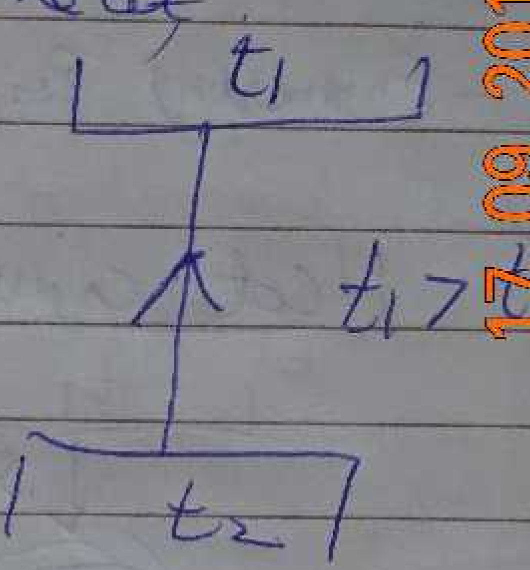
Second law tells Q_2 cant be zero even if the process is ideal (no friction etc)

$\eta_t \neq 1$ (no 100% efficiency)

Kelvin Planck statement :

Take heat & reject heat

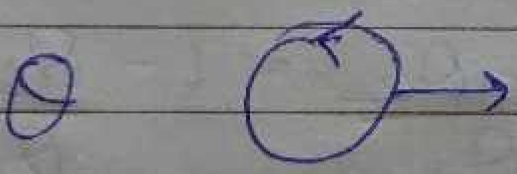




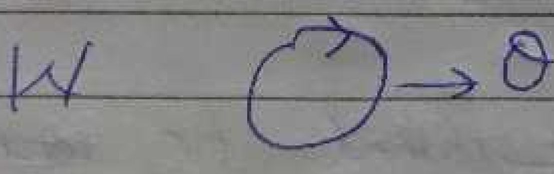
heat cant flow from low T to high T. but we can make a device

Pump heat is possible (absorb work)

$Q_1 = W + Q_2$



(W < Q)



(Q = W)

heat → low Grade

Work → high grade

⑤ Date ______

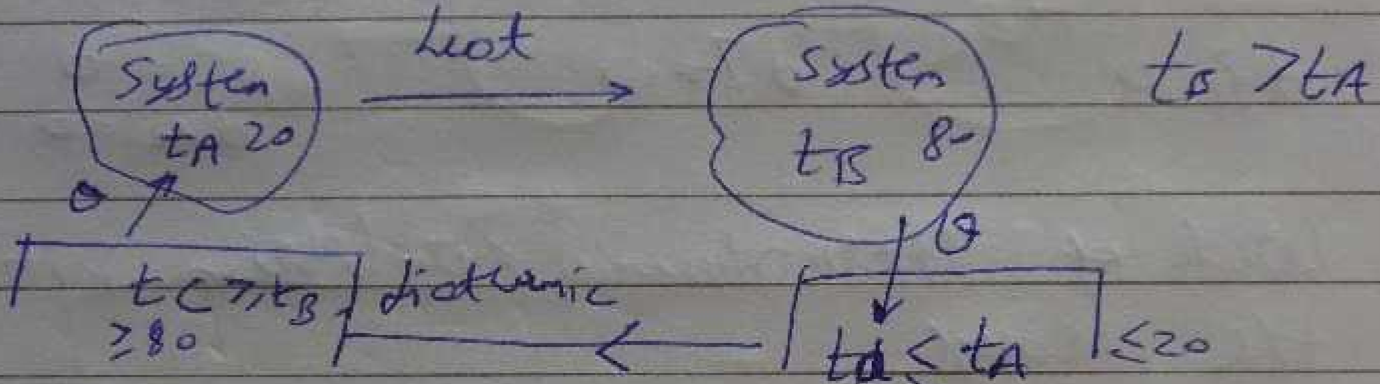
Clausius statement =

Reversible Process -

Mechanical → intermolecular

wire heating

no effect on surrounding restore to initial condition.



System back to initial state
but not surrounding

heating cooling → irreversible

Compression / Expand Gas (Adiabatic)

Work obtained / required will not be same in both case.

Surrounding suffers

Causes of Irreversibility

Lack of thermodynamic equilibrium

Mechanical eq
dP
(Work)

Thermal eq
dT
(heat)

Chemical eq
dC, dsc
(conc diffusion)

Heat transfer requires temperature difference.
Diffusion " conc "

Work transfer requires pressure difference.
Chemical potential difference for chemical reaction to take place.

$dP = 0$ $dT \neq 0$ $dC = 0$
$d\mu = 0$

Lack of Thermodynamic equilibrium initiates the process.

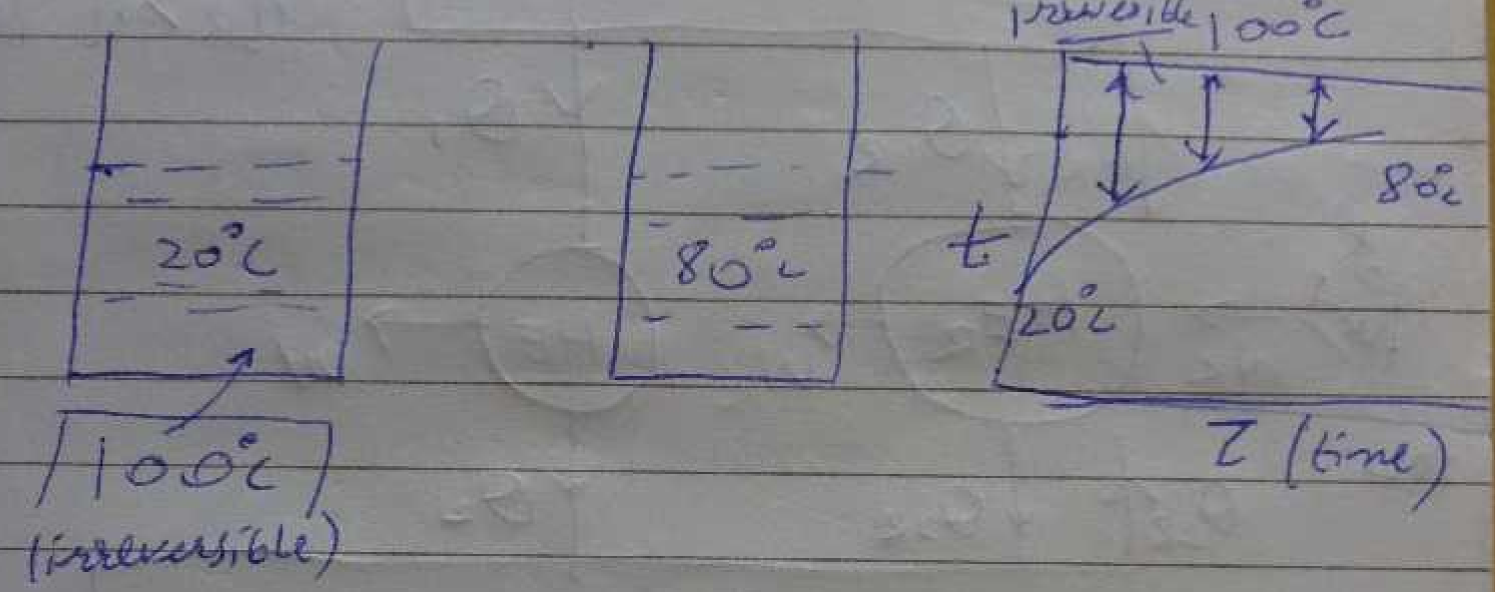
- Dissipative effects.
  - mechanical friction, fluid viscosity, magnetic hysteresis, inelasticity, electrical resistance.

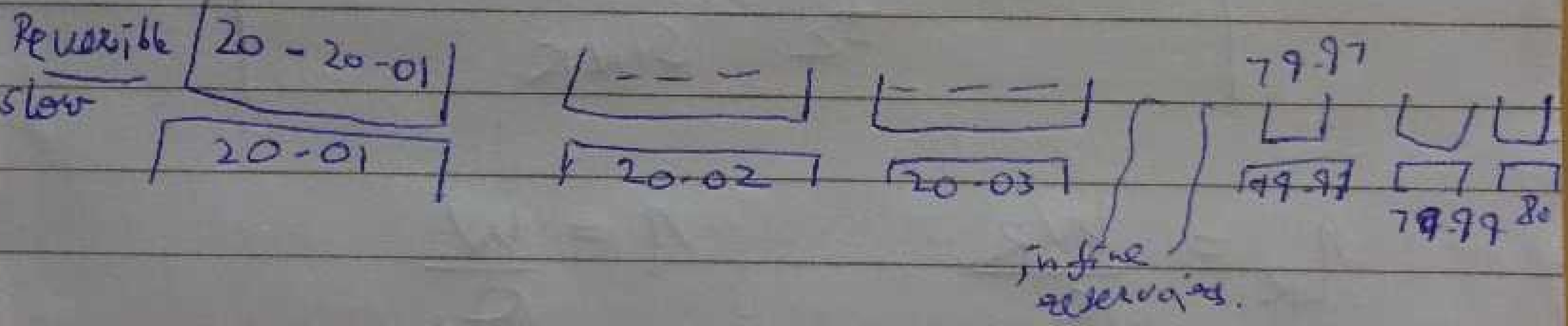
All natural processes are irreversible causes initiate the process.

Process:	Perfectly Reversible	Reversible in a limit
mechanical work Work transfer	~~$dP=0$~~ $\Delta P = 0$	$\Delta P \to 0$ (dP)
Heat transfer	$\Delta T = 0$	$\Delta T \to 0$ (dT)
Mass transfer	$\Delta C = 0$	$\Delta C \to 0$ (dC)
Chemical rxn	not possible	
NO dissipative effect	$\Delta \mu_c = 0$	$\Delta \mu \to 0$ $(d\mu)$

Work transfer with small Pressure then dissipation will be less.

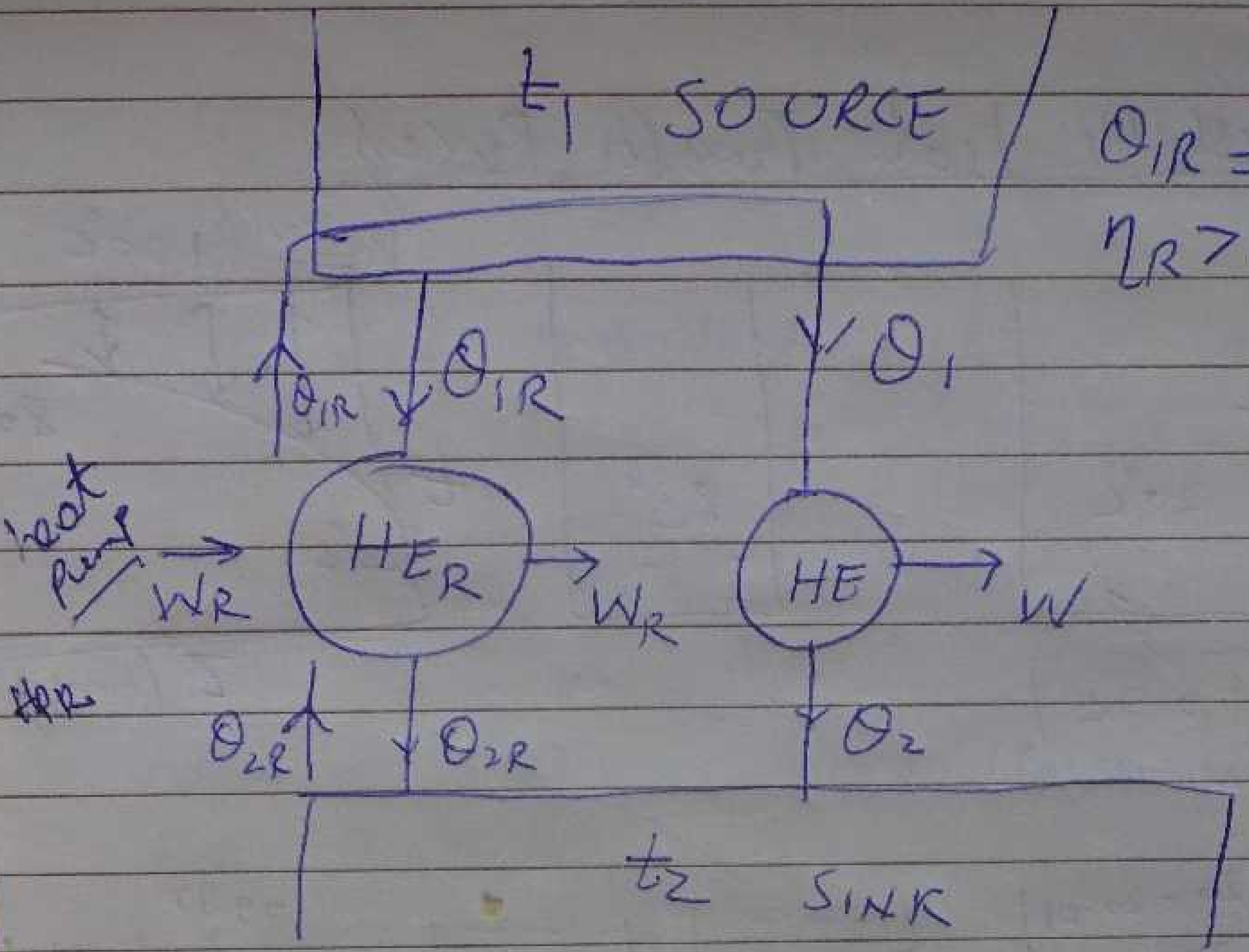
Reversible heat Transfer Process





Reversible ~~heat~~ cycle
Reversible heat engine
Reversible heat Pump.

Carnot's Theorem: No heat engine can be more efficient than a reversible engine operating between same temperature limits. & all reversible heat engines operating between same temperature limits have same efficiency.



$Q_{1R} = Q_1$

$\eta_R > \eta$ prove

$\eta_R = \frac{W_R}{Q_{1R}}$ $\eta = \frac{W}{Q_1}$

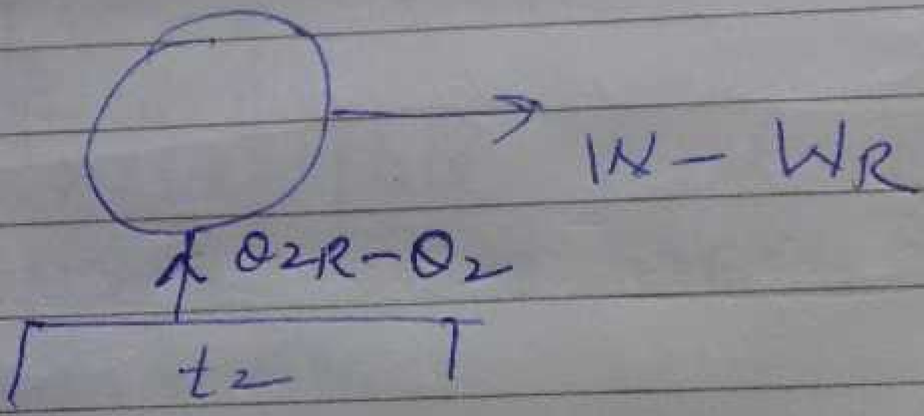
Prove $W_R > W$

Assume $\eta > \eta_R$ hence $W > W_R$

Now Reverse the Reversible engine to act as heat Pump.

We can connect & get work $W - W_R$

~~No heat~~



Operates with single fixed temperature and provides $W - W_R$

Violates Kelvin Plank statement.

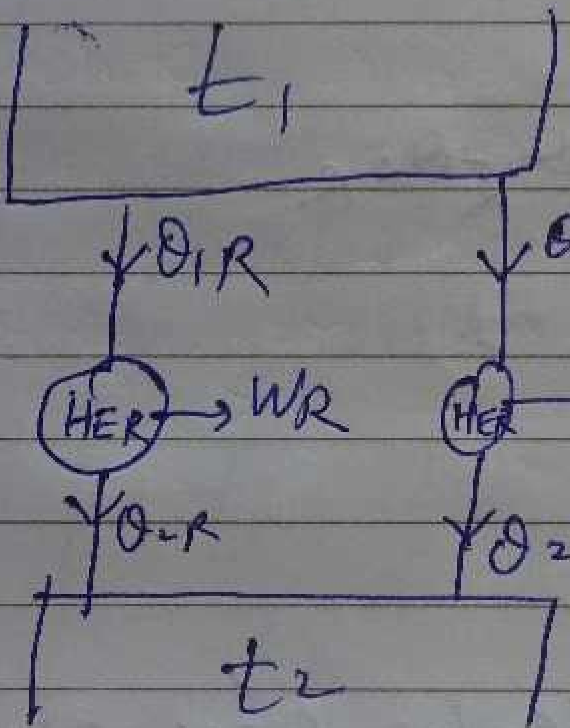
Hence wrong assumption.

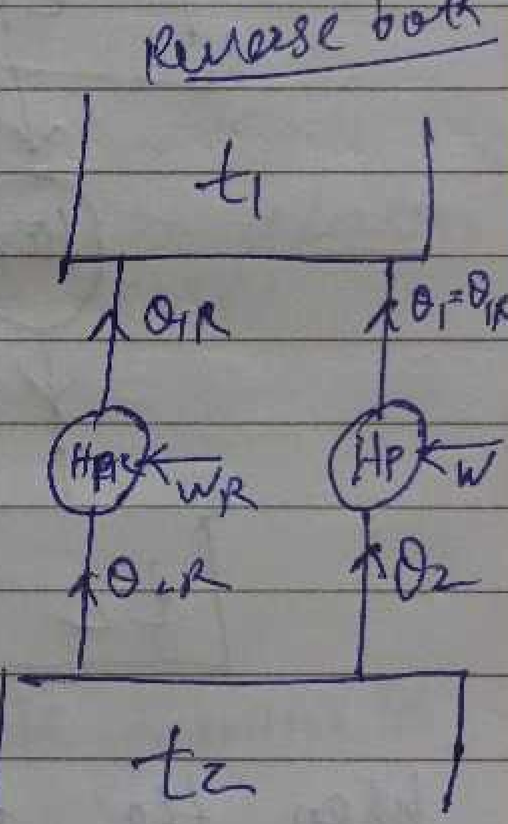
$$\eta_R > \eta$$

Second law and its Corollaries II

$\eta_R > \eta$

All reversible heat engines operating between same reservoirs have same efficiencies.





Both Reversible

$\eta_R = \eta$ (to be proved)

Assume $\eta_R < \eta$ $\quad W_R < W$

as earlier, reverse 1 and prove contradiction.

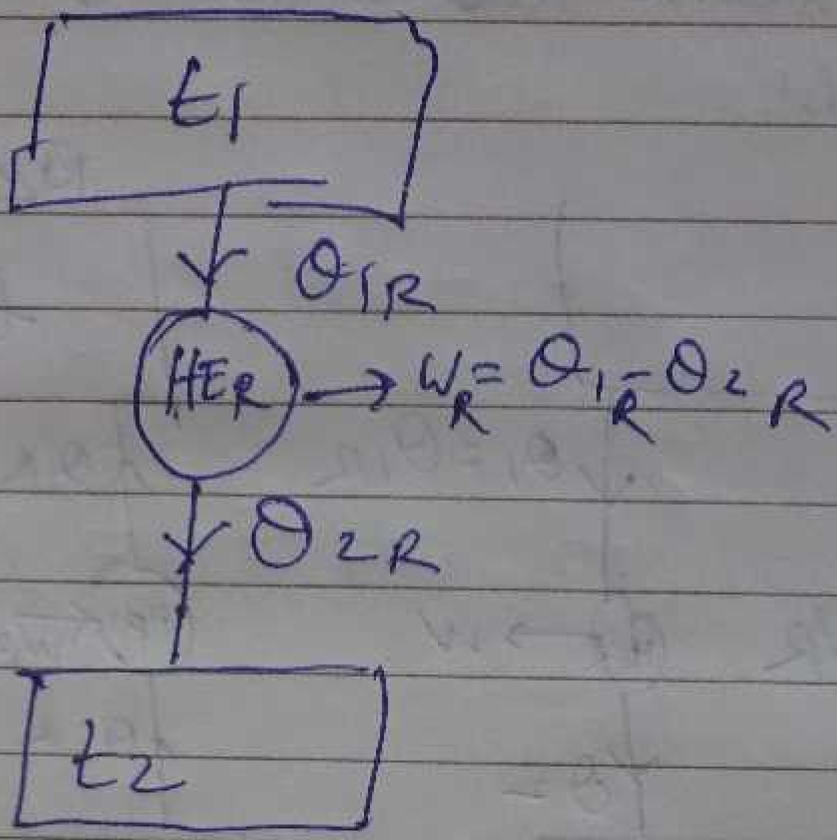
$\eta < \eta_R$ $\quad W_R > W$

reverse 2 this time.

$(W_R - W)$ Prove violation of Kelvin Planck

hence only possibility is $\eta = \eta_R$

Absolute Thermodynamic Scale of Temperature



When the two temperatures are fixed, then efficiency of ~~de~~ reversible heat engine is unique.

All reversible H.E have same eff.

$$\eta_R = f(t_1, t_2)$$

$$\eta_R = \frac{W_R}{Q_{1R}} = \frac{Q_{1R} - Q_{2R}}{Q_{1R}}$$

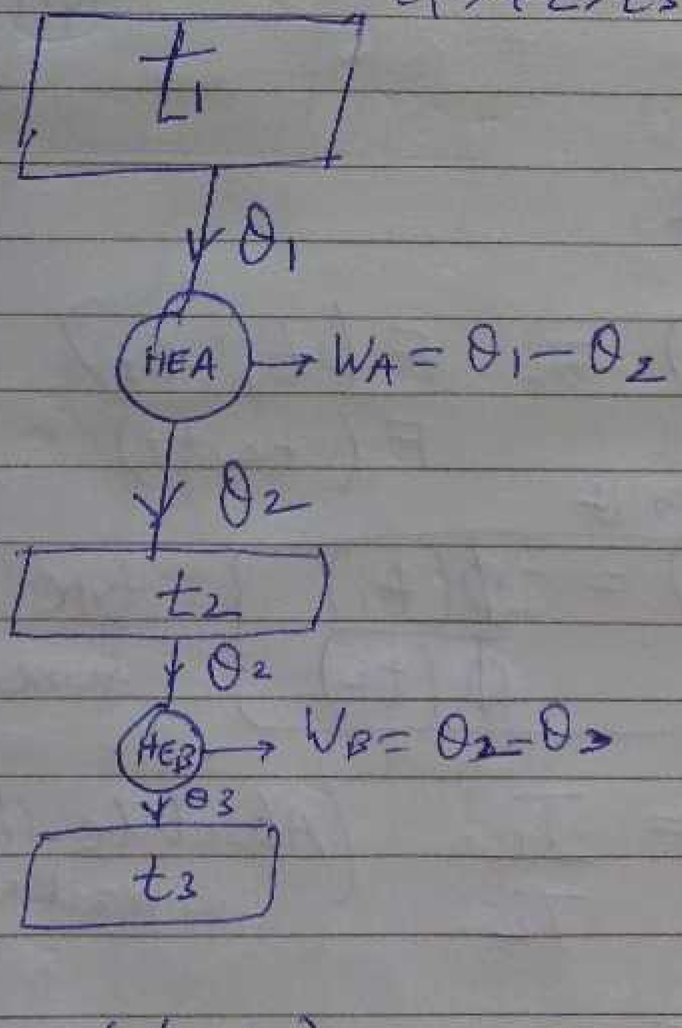
$$f(t_1, t_2) = 1 - \frac{Q_{2R}}{Q_{1R}}$$

$$\boxed{\frac{\theta_{1R}}{\theta_{2R}} = F(t_1, t_2)}$$ (for reversible)

not for irreversible heat engines.
All reversible H-E's have same efficiency when t_1, t_2 are fixed.

We will exploit this relation to develop absolute scale.
Function still unknown.

$t_1 > t_2 > t_3$



A & B are Reversible H-E

$$\frac{\theta_1}{\theta_2} = F(t_1, t_2) = \frac{\phi(t_1)}{\phi(t_2)}$$

$$\frac{\theta_2}{\theta_3} = F(t_2, t_3) = \frac{\phi(t_2)}{\phi(t_3)}$$

Remove t_2 as θ_2 rejected by A is taken up by B.
And Combine the two engines A & B.

$$W = W_A + W_B$$

interacts t_1 & t_3

$$\frac{\theta_1}{\theta_3} = F(t_1, t_3) = \frac{\phi(t_1)}{\phi(t_2)}$$

~~$F(t_2, t_3)$~~

$$F(t_1, t_2) = \frac{F(t_1, t_3)}{F(t_2, t_3)}$$

This can only happen if

$$\boxed{F(t_1, t_2) = \frac{\phi(t_1)}{\phi(t_2)}}$$ type of function.

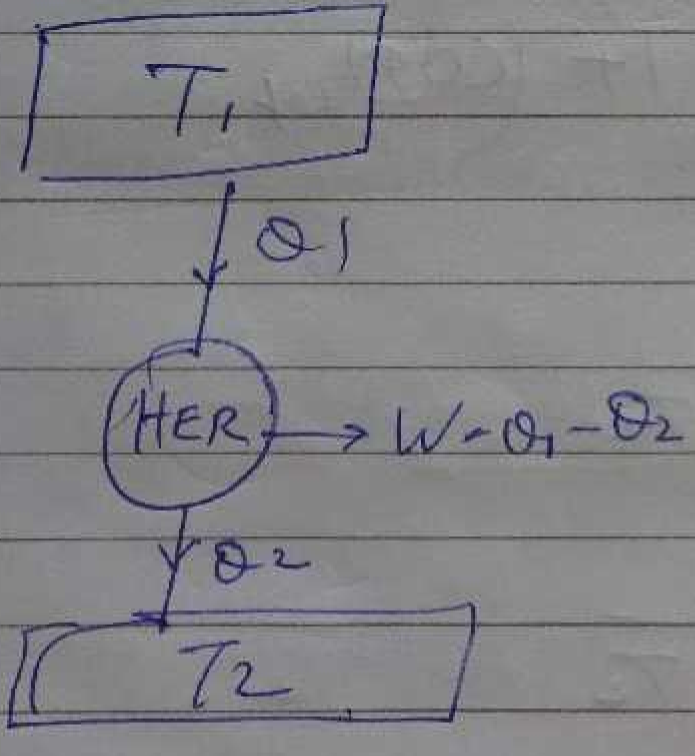
$$= \frac{T_1}{T_2}.$$ (Absolute Thermodynamic temperature scale)

$$\frac{\theta_1}{\theta_2} = \frac{T_1}{T_2}$$

This function ϕ is defined as Absolute thermodynamic temperature scale.

This is the definition of Absolute thermodynamic temperature scale.

Later it will be shown equal to ideal Gas scale.



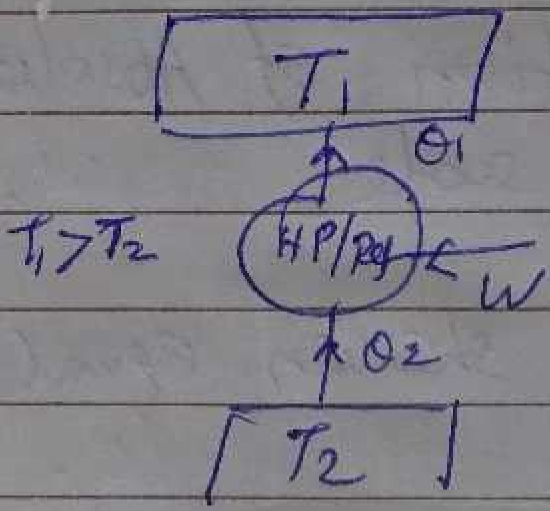
$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$\boxed{\eta_{Rev} = 1 - \frac{T_2}{T_1}}$$

(mean temperature take if T varies)

For a heat Pump or Refrigerator



$$Q_1 = Q_2 + W$$

$$(COP)_{HP} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2}$$

$$(COP)_{Ref} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

$$(COP)_{HP} = 1 + (COP)_{Ref}$$

$$(COP)_{R\,HP} = \frac{T_1}{T_1 - T_2}$$

$$(COP)_{R\,Ref} = \frac{T_2}{T_1 - T_2}$$

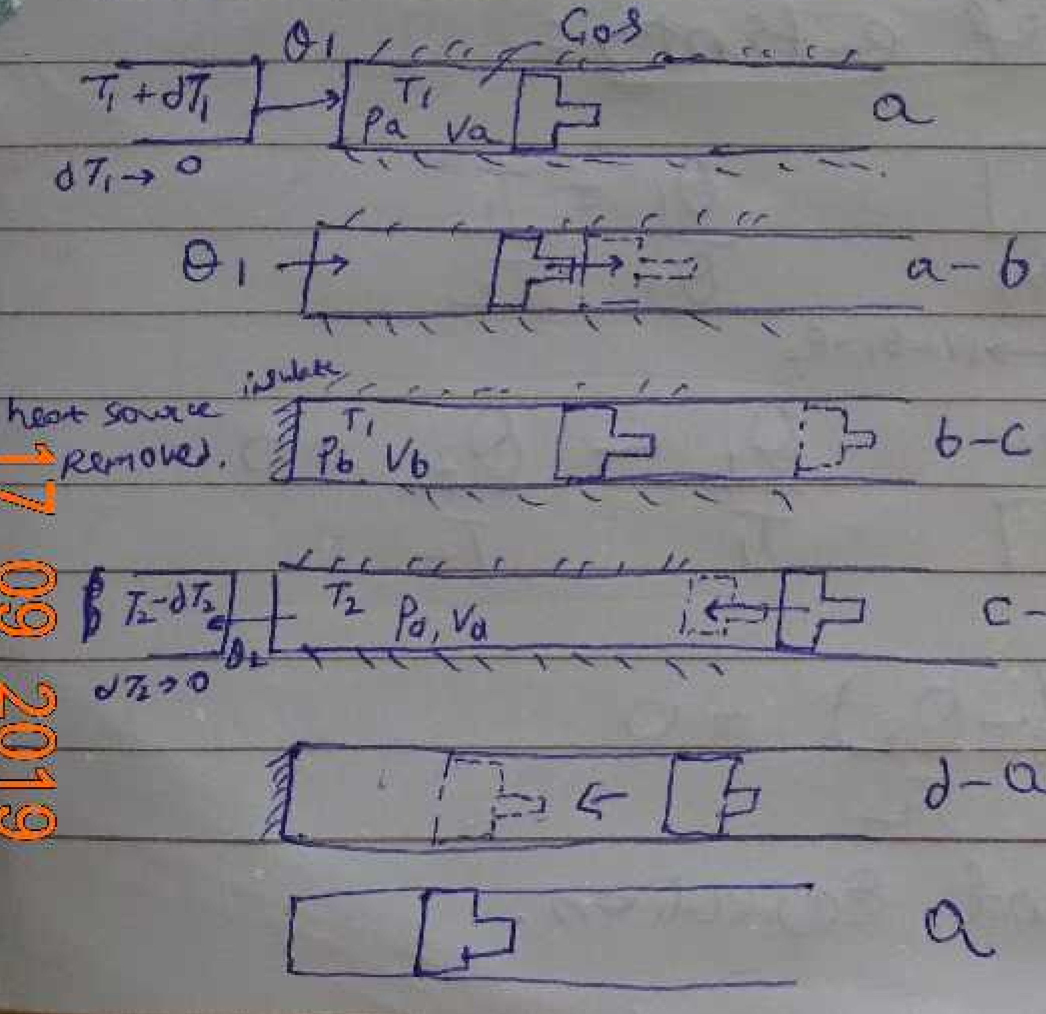
How to achieve close to reversible process.

<u>Sadi Carnot</u>:

Carnot's engine

- Reversible isothermal process of Heat Addition (infinite small temperature difference dT) [infinite number of heat sources with small temperature difference] ∴ dT is small.
- Reversible adiabatic process of expansion no heat interaction (insulated) (P decrease, V increase)
- Reversible isothermal process of heat Rejection (according to 2nd law)
- Reversible adiabatic process of compression. (Pressure increase Volume reduce)

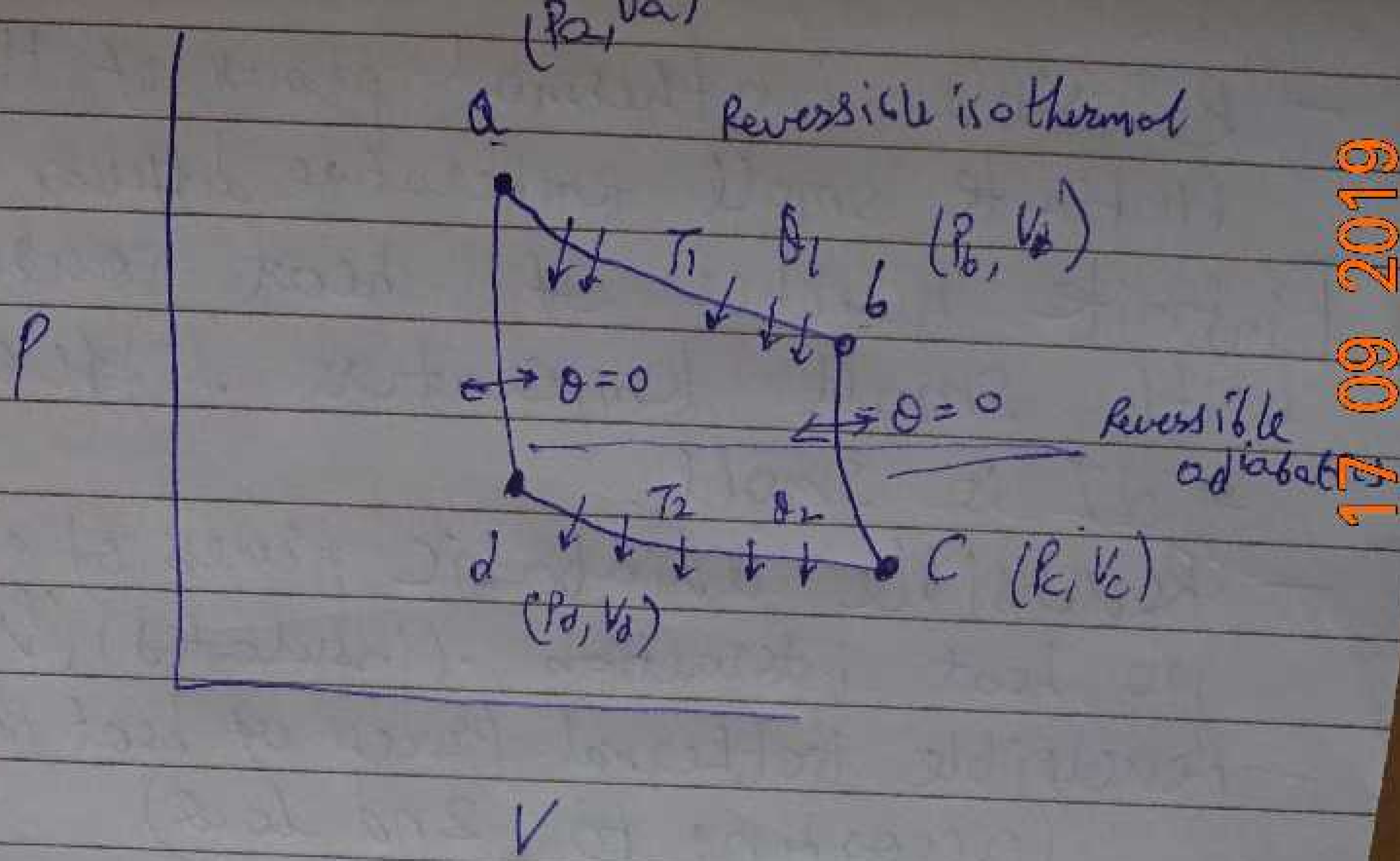
How it is concieved:



heat added and Piston moves to maintain const T
$Q = W$ $\Delta U = 0$ $\Delta T = 0$

Piston moves back to counter cooling

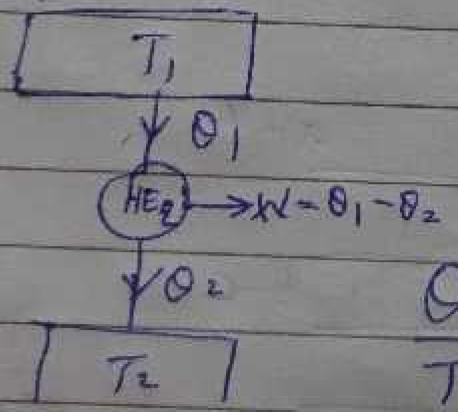
Show on a Graph.



$$\eta = 1 - \frac{\theta_2}{\theta_1} = 1 - \frac{T_2}{T_1}$$

Birth of entropy:

Reversible H.E



$$\frac{\theta_1}{\theta_2} = \frac{T_1}{T_2}$$

$$\frac{\theta_1}{T_1} - \frac{\theta_2}{T_2} = 0$$

$$\frac{\theta_1}{T_1} + \frac{(-\theta_2)}{T_2} = 0$$

θ_2 is heat rejection.

$$\sum_{cycle} \frac{Q}{T} = 0$$

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

(Only valid for Reversible)

Cyclic integral of a point function is zero.

$$\oint dS = 0$$

$$dS = \frac{dQ_R}{T}$$

Integrate

$$\Delta S = \int \frac{dQ_R}{T}$$

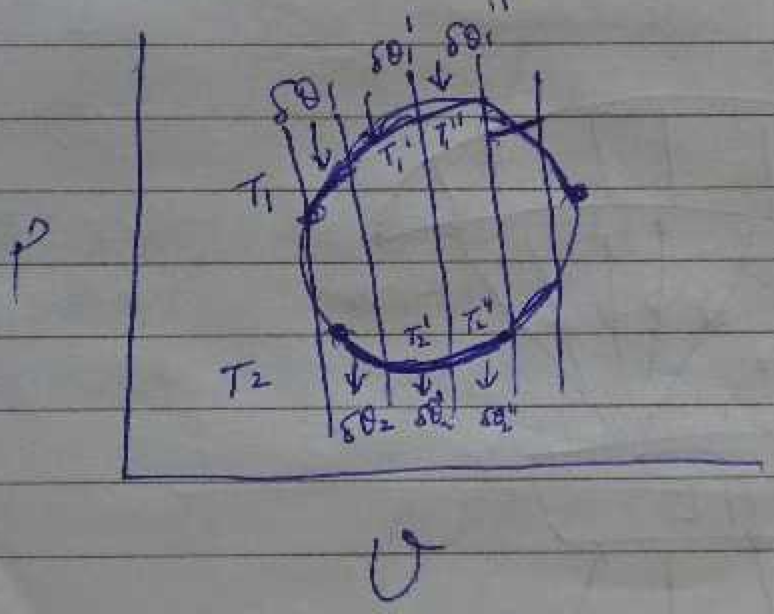
$$S_2 - S_1 = \int_1^2 \frac{dQ_R}{T}$$

S = <u>entropy</u>

Second law and its corrolories.

$$\oint \frac{\delta \theta_R}{T} = 0$$

$$\oint \left(\frac{\delta Q}{T}\right)_R = 0.$$



We can draw a large no. of adiabatic over any cycle. The isotherms can be next drawn.

So we see a large no. of carnot cycles of any cycle.

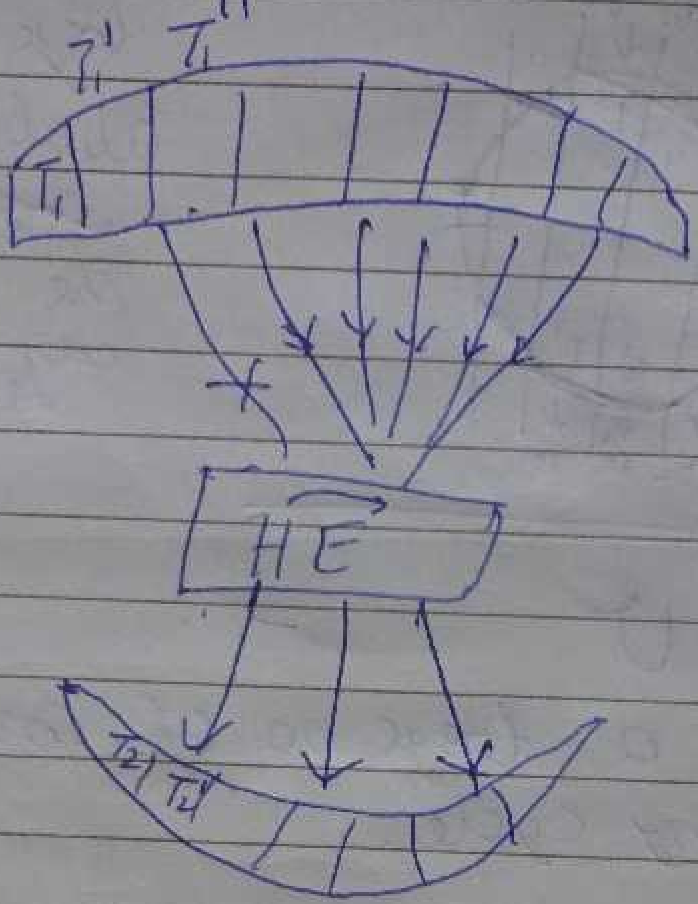
Infinite no of elemental carnot cycles.

$$\frac{\delta\theta_1}{T_1} = \frac{\delta\theta_2}{T_2} \qquad \Sigma \frac{\delta\theta_1}{T_1} = \Sigma \frac{\delta\theta_2}{T_2}$$

$$\frac{\delta\theta_1'}{T_1'} = \frac{\delta\theta_2'}{T_2'}$$

$$\frac{\delta\theta_1''}{T_1''} = \frac{\delta\theta_2''}{T_2''}$$

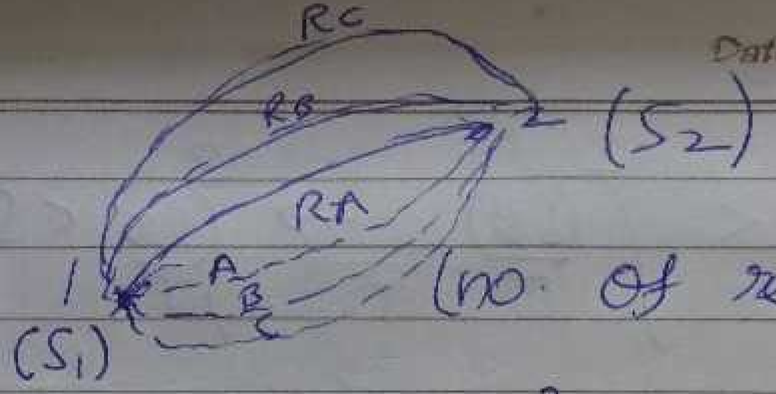
$$\oint \left(\frac{\delta \theta}{T}\right)_R = 0$$



$$\oint \left(\frac{d\theta}{T}\right)_R = 0 \qquad \oint dS = 0$$

$\oint \left(\frac{d\theta}{T}\right)_R = \Delta S$ // Check it will be $\int$ or $\oint$

$$\int_1^2 \left(\frac{d\theta}{T}\right)_R = S_2 - S_1$$



(no. of reversible process)

$$\int_{1\,R_A}^{2}\frac{\delta Q}{T} = \int_{1\,R_B}^{2}\frac{\delta Q}{T} = \int_{1\,R_C}^{2}\frac{\delta Q}{T}$$

R_A, R_B, R_C are all reversible processes.
A, B, C → irreversible.
What is $\oint \frac{\delta Q}{T}$ for irreversible process

$$\int \frac{\delta Q}{T} = ?$$

Clausius Gave the Answer.

Clausius Inequality:

$$\oint \frac{\delta Q}{T} < \oint \frac{(\delta Q)_R}{T} \rightarrow \boxed{\oint \frac{\delta Q}{T} < 0}$$

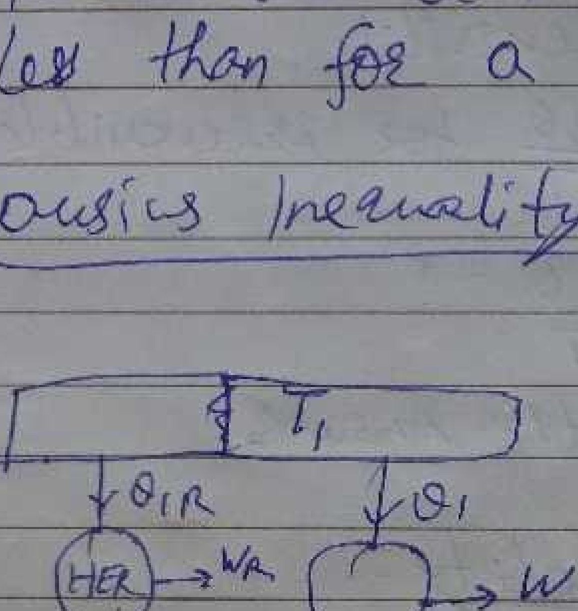
$${}_A\int_{1}^{2} \frac{\delta Q}{T} \neq {}_B\int \frac{\delta Q}{T} \neq {}_C\int \frac{\delta Q}{T}$$ not a Point fn.

$$\int \frac{\delta Q}{T} < \int \left(\frac{\delta Q}{T}\right)_R \Rightarrow \int \frac{\delta Q}{T} < \Delta S$$

$$\int_1^2 \frac{\delta Q}{T} < \int_1^2 \left(\frac{\delta Q}{T}\right)_R \rightarrow \int_1^2 \frac{\delta Q}{T} < S_2 - S_1$$

Even the maximum $\int_1^2 \frac{\delta Q}{T}$ for a irreversible or natural process is less than for a reversible process.

Clausius Inequality Proof



$W_R = Q_{1R} - Q_{2R}$

$W = Q_1 - Q_2$

$$\oint \frac{\delta Q}{T} < 0 \quad \text{as} \quad \oint \left(\frac{\delta Q}{T}\right)_R = 0$$

$$\eta = 1 - \frac{Q_2}{Q_1} \qquad \eta_R = 1 - \frac{Q_{2R}}{Q_{1R}}$$

We know $\eta < \eta_R$

$$\frac{\theta_1}{\theta_2} < \frac{\theta_{1R}}{\theta_{2R}}$$

$$\frac{\theta_1}{\theta_2} < \frac{T_1}{T_2}$$

hence $\frac{\theta_1}{T_1} - \frac{\theta_2}{T_2} < 0$

hence $\oint \frac{\delta\theta}{T} < 0$

$$\Delta S = \int \left(\frac{\delta\theta}{T}\right)_R$$

A reversible adiabatic process

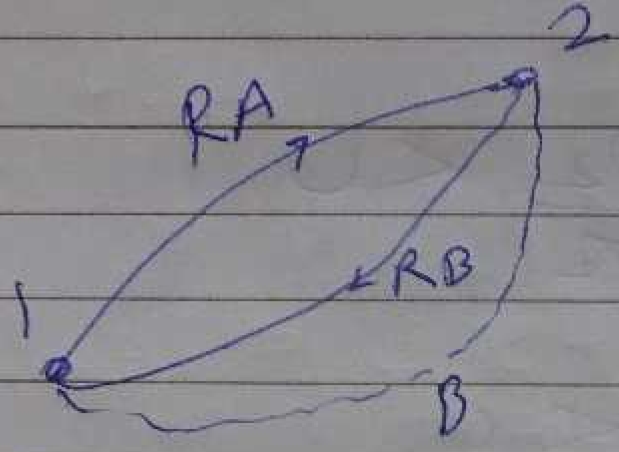
$$(\delta\theta)_R = 0$$

$\Delta S = \oint 0$ hence $S = \text{const}$.

A reversible adiabatic process
= isentropic process.

$\oint \frac{\delta Q}{T} < 0 \quad \left(\oint \frac{(\delta Q)_R}{T} \right)$

$\int \frac{\delta Q}{T} < \int \frac{\delta Q_R}{T}$ [To Prove]



For reversible cycle
$R_A - R_B$

$$_{R_A}\int_1^2 \frac{\delta Q}{T} + {}_{R_B}\int_2^1 \frac{\delta Q}{T} = 0$$

$$_{R_A}\int_1^2 \frac{\delta Q}{T} + {}_{B}\int_2^1 \frac{\delta Q}{T} < 0$$

hence

$$_{B}\int_2^1 \frac{\delta Q}{T} < {}_{R_B}\int_2^1 \frac{\delta Q}{T}$$

(~~[illegible]~~ (irreversible < Reversible) hence

$$\underset{\text{(irreversible)}}{\int \frac{\delta Q}{T}} < \Delta S.$$

IRreversible adiabatic process.

Example

1) Insulated Piston moving fast
2) Stir fluid in an insulated container.

$\delta Q = 0$ (but process is irreversible)

$$\Delta S > \int \frac{\delta Q}{T}$$

or $dS > \frac{dQ}{T}$

$$\boxed{\Delta S > 0 \quad \text{or} \quad dS > 0}$$

In a reversible adiabatic process heat transfer may have been required (like heat transfer without stirring) in (2) above.

$$\Delta S > 0$$

$$\boxed{\Delta S \geqq \int \frac{\delta Q}{T}}$$

$$\Delta S = \int \frac{\delta Q}{T} + X$$

$$\Delta S = \underset{\substack{\downarrow \\ \text{due to} \\ \text{heat transfer} \\ \text{(external irreversibility)}}}{\Delta S_e} + \underset{\substack{\downarrow \\ \text{due to internal} \\ \text{irreversibility}}}{\Delta S_I}$$

For a reversible process
$\Delta S_i = 0$

For an ~~adiabat~~ reversible diabatic process $\Delta S = \Delta S_e = \int \frac{\delta Q}{T}$

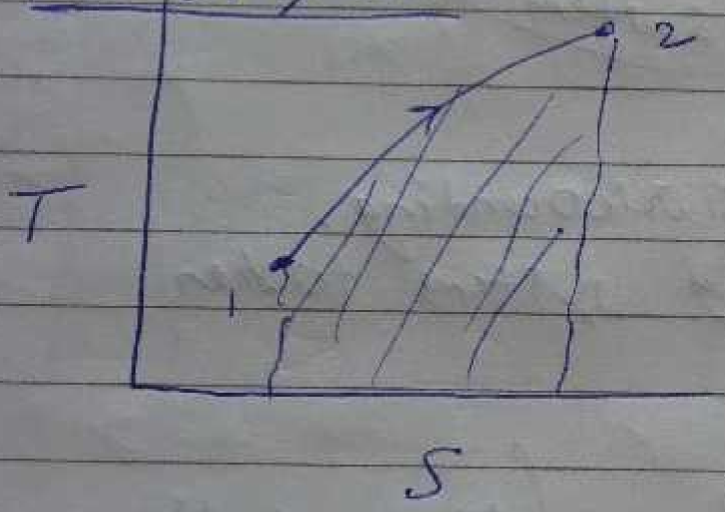
For on irreversible adiabatic process
$\Delta S_e = 0 \quad \Delta S_i > 0$

If process is reversible adiabatic then both terms will be zero and $\Delta S = 0$.

For irreversible Process $\Delta S_i > 0$

Isentropic Process : (Reversible Adiabatic)

TS diagram:



reversible

$$\frac{\delta Q}{T} = dS$$

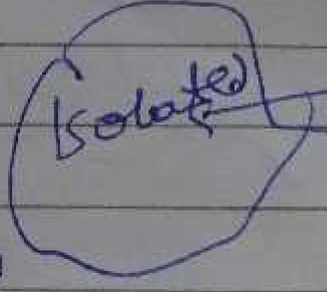
$$\delta Q = T\,dS$$

$$Q = \int T\,dS$$

Area under curve

Concept of an isolated system.

[May be reversible or irreversible]



$Q = 0$ (Adiabatic)

$W = 0$

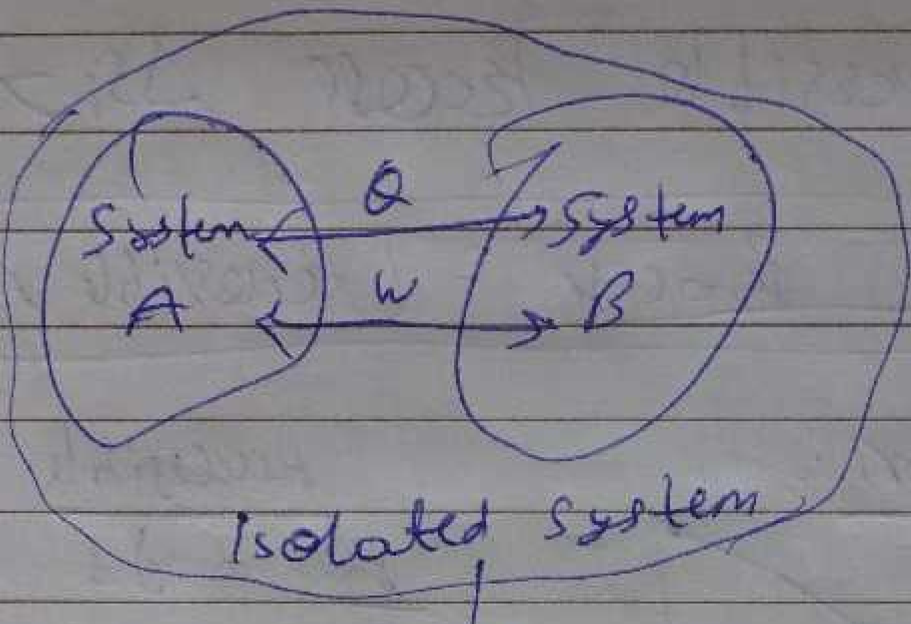
$\Delta S \geq \int \frac{\delta Q}{T}$

$(\Delta S = \Delta S_i)$

$$(\Delta S)_{\text{isolated}} \geq 0$$

$\Delta S = 0$ for reversible isolated system

Adjustment or internal process within the isolated system.
No interaction with surrounding.



↓

System + surrounding.
All interacting systems taken together

$(\Delta S)_{\text{isolated system}} \geq 0$ $\quad (\Delta S_{\text{system}} + \Delta S_{\text{surrounding}})$

$\Sigma (\Delta S)_{\text{All interacting system}} \geq 0$

$(\Delta S)_{\text{isolated system}} \geq 0$

$(\Delta S)_{\text{universe}} \geq 0$ Principle of increase in entropy.