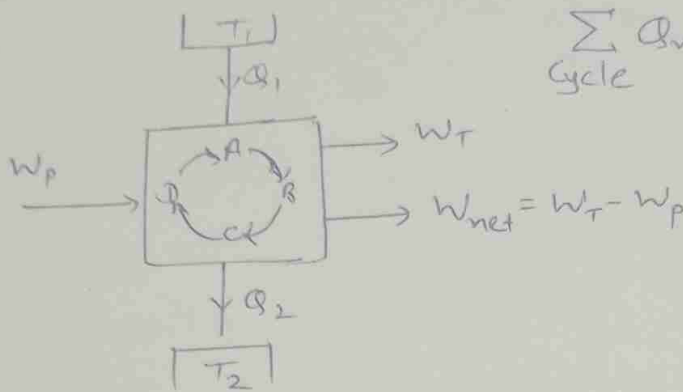


CARNOT CYCLE

slow & nondissipative (ideal process)

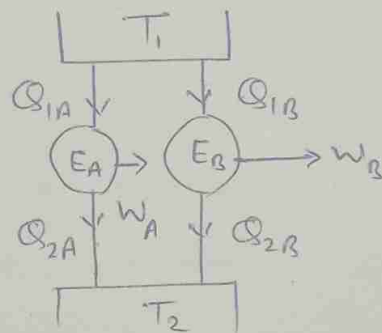


$$\sum_{\text{Cycle}} Q_{\text{net}} = \oplus \sum_{\text{Cycle}} W_{\text{net}}$$

CARNOT theorem:

none has higher efficiency than reversible engine.

Proof:

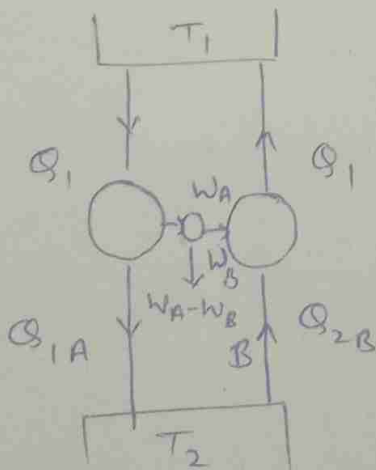


A → any Engine
B → reversible Engine.

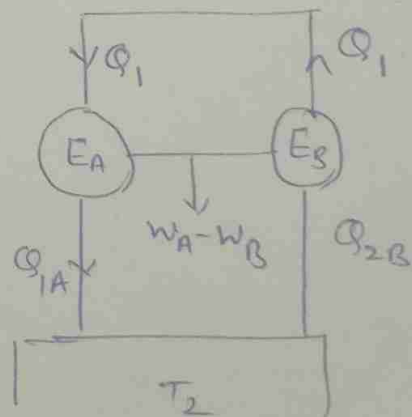
Assuming $\eta_A > \eta_B$ & $Q_{1A} = Q_{1B} = Q_1$

then $\frac{W_A}{Q_1} > \frac{W_B}{Q_1} \Rightarrow W_A > W_B$

Since B is reversible reverse all process in B.



=>



Absolute thermodynamic temp. scale

efficiency of heat engine cycle

$$\eta = \frac{w_{\text{net}}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

2nd law of thermodynamics.

heat flow from high temp. to low temp.

reversible cycle efficiency does not depend on substance, amount etc.

$$\eta = f(T_1, T_2)$$

$$1 - \frac{Q_2}{Q_1} = f(T_1, T_2) \Rightarrow \frac{Q_2}{Q_1} = F(T_1, T_2)$$

hence some functional relationship between.

$\frac{Q_2}{Q_1}$, T_1 & T_2 are assigned.

then that become temp. scale.

$$\Rightarrow \frac{Q_2}{Q_1} = \frac{Q_1/Q_2}{Q_2/Q_3} = \frac{F(T_1, T_3)}{F(T_2, T_3)} = F(T_1, T_2)$$

\Rightarrow functionality of T_3 cancel out.

$$\Rightarrow \frac{Q_2}{Q_1} = \frac{\Phi(T_1) \Psi(T_3)}{\Phi(T_2) \Psi(T_3)} = \frac{\Phi(T_1)}{\Phi(T_2)}$$

Simplest way.

$$\frac{Q_2}{Q_1} = \frac{\Phi(T_1)}{\Phi(T_2)} = \frac{T_1}{T_2}$$

Carnot engine between T, T_+
↓
triple point.

$$\frac{Q}{Q_+} = \frac{T}{T_+} \Rightarrow T = 273.16 \frac{Q}{Q_+}$$

↓
arbitrarily

kelvin scale, Q play the role of thermodynamic property.

hence efficiency of reversible heat engine.

$$\eta_{\text{rev.}} = \eta_{\text{max}} = 1 - \left(\frac{Q_2}{Q_1} \right)_{\text{max}} = 1 - \frac{T_2}{T_1}$$

as $\eta < 1$, $T_2 > \underline{0}$

$$(\text{COP})_{\text{ref}} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1 - Q_2}{Q_2}} = \frac{1}{\left(\frac{T_1}{T_2} \right) - 1} = \frac{T_2}{T_1 - T_2}$$

Similarly,

$$(\text{COP})_{\text{H.P.}} = \frac{T_2}{T_1 - T_2}$$

Just like, thermal emf in a thermocouple, absolute thermodynamic temp. scale has a definite zero point.

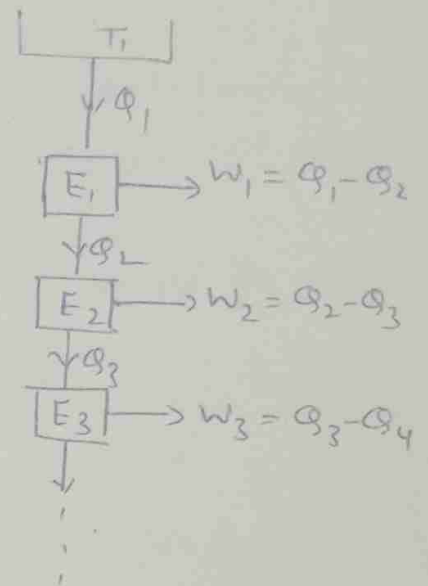
Assume.

A series of reversible engine extending from T_1 to lower temp.

$$\text{as, } \frac{T_1}{T_2} = \frac{Q_1}{Q_2}$$

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

$$\Rightarrow (T_1 - T_2) = (Q_1 - Q_2) \frac{T_2}{Q_2}$$



Similarly.

$$(T_2 - T_3) = (Q_2 - Q_3) \frac{T_3}{Q_3} = (Q_2 - Q_3) \frac{T_2}{Q_2}$$

$$(T_3 - T_4) = (Q_3 - Q_4) \frac{T_4}{Q_4}$$

Now assuming $T_1 - T_2 = T_2 - T_3 = T_3 - T_4 = \dots$

$$\Rightarrow W_1 = W_2 = W_3 = \dots$$

conversely, making equal work in a series of engine

$$\Rightarrow T_1 - T_2 = T_2 - T_3 = \dots$$

Suppose if we have 100 Carnot cycle between steam pt. & ice pt; we can measure hundred temp interval.

Such scale would be independent of substance.

What if keep on extending series of engine

rejected heat become zero.

or net work in all engine will be equal to Q_1
(Violate K-P).

heat rejected can not be zero.

but approaching to zero.

thus, appear that zero exist but cannot be reached, without violating 2nd law.

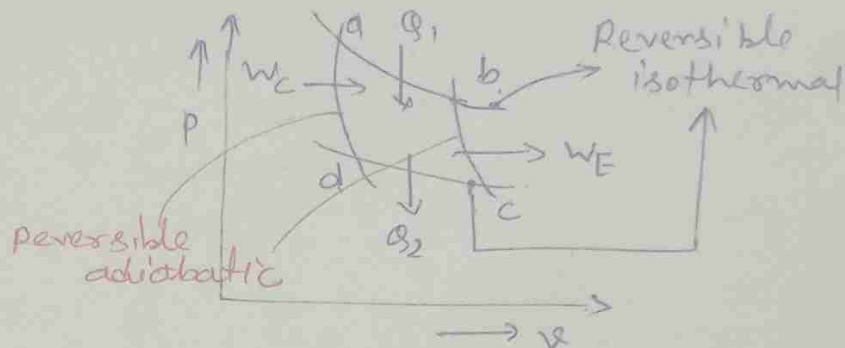
↓,
3rd law

It is impossible to reduced any system to absolute zero temp.

(even in the most idealized case in finite step)

Equality of ideal gas temp. and kelvin temp.

Assume : Carnot cycle ideal gas



$$\left. \begin{aligned} PV &= nRT_1 \\ PV &= nRT_2 \end{aligned} \right\} \text{--- isothermal curve} \\ \text{a to b} \\ \text{c to d.}$$

for any infinitesimal ideal gas process.

$$\delta Q = C_v dT + P dv$$

for isothermal process.

$$Q_1 = \int_{V_a}^{V_b} \frac{nRT_1}{V} dV = nRT_1 \ln\left(\frac{V_b}{V_a}\right)$$

Similarly c to d.

$$Q_2 = nRT_2 \ln\left(\frac{V_d}{V_c}\right)$$

So heat rejected.

$$Q_2 = |Q_2| = nRT_2 \ln\left(\frac{V_c}{V_d}\right)$$

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} = \frac{\ln(V_b/V_a)}{\ln(V_c/V_d)} \quad \text{--- (X)}$$

For b-c (adiabatic)

$$dQ = 0 = C_v dT + p dv$$

$$\Rightarrow -C_v dT = p dv = \frac{nRT}{V} dv$$

$$\Rightarrow -C_v \int_{T_1}^{T_2} \frac{dT}{T} = nR \int_{V_b}^{V_c} \frac{dv}{v} = nR \ln \frac{V_c}{V_b}$$

Similarly $\Rightarrow \frac{C_v}{nR} \int_{T_2}^{T_1} \frac{dT}{T} = \ln \left(\frac{V_c}{V_b} \right)$ — (A)

d to a

$$\frac{C_v}{nR} \int_{T_2}^{T_1} C_v \frac{dT}{T} = \ln \left(\frac{V_d}{V_a} \right)$$
 — (B)

(A) & (B)

$$\Rightarrow \ln \left(\frac{V_c}{V_b} \right) = \ln \left(\frac{V_d}{V_a} \right)$$

$$\Rightarrow \frac{V_c}{V_b} = \frac{V_d}{V_a}$$

$$\Rightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d}$$

④ reduce to

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

Thermodynamic temp. scale & ideal gas temp. scale are equivalent.

& hence gas thermometer.

Entropy

1st law

$$\sum_{\text{Cy}} Q = \oplus \sum_{\text{Cyc}} W \longrightarrow \text{existence of internal energy.}$$

2nd law

\longrightarrow Cycle

\hookrightarrow new property, entropy.

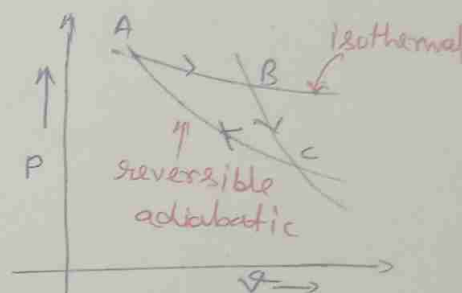
1st law
 \Downarrow
internal energy

2nd law
 \Downarrow
entropy

Rev.
Assume two adiabatic
AC & BC intersect at point "C"

\Downarrow
what wrong with
that??

Now, draw an rev. isotherm AB.



\Rightarrow then three reversible process AB, BC, CA constituent a reversible cycle.

Area under this cycle \Rightarrow net work output in a cycle by exchanging heat with a single.

Reversible in AB.
(Violate K-P).

\Rightarrow Assumption of the reversible adiabatic line intersection is wrong.

* thus through one point, only one reversible adiabatic.

Any reversible zigzag path may be substituted by a reversible adiabatic followed by a reversible isothermal and finally by adiabatic path.

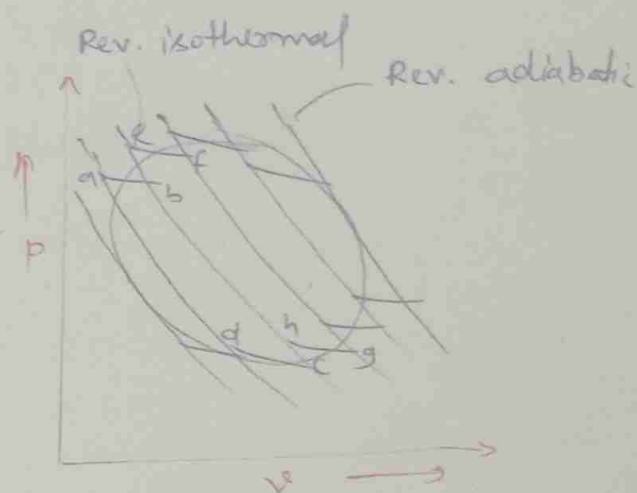
then heat transfer in these two path will be same.

* Now Let assume.

a smooth closed curve represent a reversible cycle.

* Now divide closed cycle using reversible adiabatic path.

* Each strip may be closed at top & bottom by Reversible isothermal curves.



So one can reach any point on the original cycle. using alternate isothermal & adiabatic path such that heat transfer will be same as original cycle.

If adiabatic path are very close to each-other than isotherm-adiabatic path will coincide with original closed cycle.

for each element abcd

dQ_1 absorbed reversibly at T_1
& dQ_2 rejected reversibly at T_2

$$\frac{dQ_1}{T_1} = \frac{dQ_2}{T_2}$$

If heat supplied is +ve. & heat reject is -ve.

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0$$

Similarly for

$$\frac{dQ_3}{T_3} + \frac{dQ_4}{T_4} = 0$$

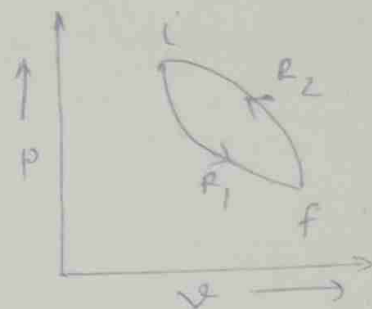
Similar equation can be written for
other cycle

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} + \dots = 0$$

$$\Rightarrow \oint_R \frac{dQ}{T} = 0$$

\hookrightarrow cycle integral of $\frac{dQ}{T}$ for reversible cycle is zero.

The property of entropy



System is taken from initial equilibrium state i to ~~equi~~ final equilibrium f state using reversible path R_1 .
& brought back by path R_2 (reversible)
then R_1 & R_2 together constitute a reversible cycle.

\Rightarrow Clausius' theorem

$$\oint_{R_1, R_2} \frac{dQ}{T} = 0$$

$$\Rightarrow \int_{R_1} \frac{dQ}{T} + \int_{R_2} \frac{dQ}{T} = 0$$
$$\int_{R_1, i}^f \frac{dQ}{T} = - \int_{R_2, f}^i \frac{dQ}{T}$$

\Rightarrow heat intersection is independent of path

$$\int \frac{dQ}{dT} \rightarrow \text{called entropy}$$

$$\int_i^f \frac{dQ}{T} = S_f - S_i$$

if two equilibrium state are infinitely near.

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

$$dQ_R/T = ds$$

ds is exact differential of a point function.

entropy (s) \rightarrow extensive, unit (J/K)

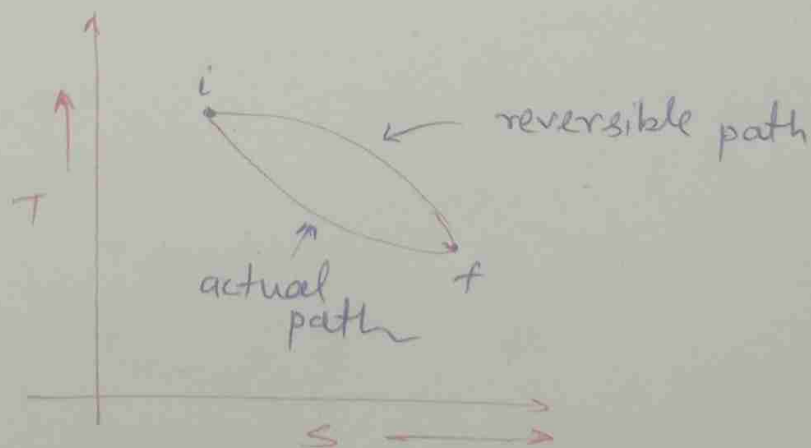
$$s = \frac{S}{m} \left(\frac{J}{kg \cdot K} \right)$$

what if equilibrium state i to f using irreversible path.

Since entropy is point function,
so it is independent of path.

So replace irreversible path with reversible
to calculate change in entropy.

$$s_f - s_i = \int_i^f \frac{dQ_{rev}}{T} = (\Delta s)_{irrev. path}$$



Temp. - Entropy plot

$$ds = \frac{dQ_{rev}}{T}$$

if $dQ_{rev} = 0 \Rightarrow$ process is reversible & adiabatic.

$$ds = 0$$

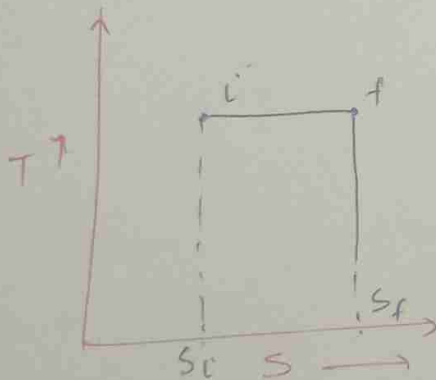
$$s = \text{constant}$$

A reversible adiabatic process is also isentropic process.

Now

$$dQ_{rev} = T ds$$

$$Q_{rev} = \int_i^f T ds$$

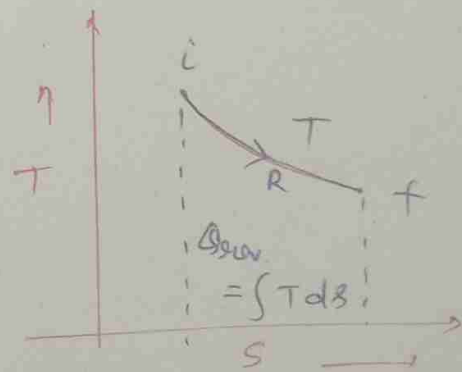


Reversible
isothermal
P

$$T = \text{constant}$$

$$Q_{rev} = T \int_i^f ds$$

$$= T(s_f - s_i)$$



for reversible adiabatic process.

$$ds = 0 \Rightarrow s = \text{constant.}$$

Carnot cycle

$$\eta_{\text{Carnot}} = \frac{Q_1 - Q_2}{Q_1}$$

$$= \frac{T_1(s_1 - s_4) - T_2(s_2 - s_3)}{T_1(s_1 - s_4)}$$

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

as. $(s_1 - s_4) \approx (s_2 - s_3)$

$$W_{\text{net}} = Q_1 - Q_2 = (T_1 - T_2)(s_1 - s_4)$$

