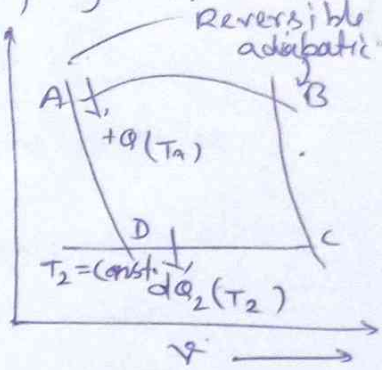
Inequality of Clausius

AB → either reversible or irreversible.
While all other process in cycle are reversible.

Let cycle → divided into # of elementry cycles.



for one of the cycles.

$$\eta = 1 - \frac{dQ_2}{dQ}$$

Now efficiency of general cycle ≤ efficiency of reversible cycle

$$1 - \frac{dQ_2}{dQ} \leq \left(1 - \frac{dQ_2}{dQ}\right)_{rev.}$$

$$\Rightarrow \frac{dQ_2}{dQ} \geq \left(\frac{dQ_2}{dQ}\right)_{rev.}$$

or

$$\frac{dQ}{dQ_2} \leq \left(\frac{dQ}{dQ_2}\right)_{rev.} \quad \text{——— (A)}$$

$$\left(\frac{dQ}{dQ_2}\right)_{rev.} = \frac{T}{T_2} \quad \text{——— (B)}$$

from (A) & (B)

$$\Rightarrow \frac{dQ}{dQ_2} \leq \frac{T}{T_2}$$

$$\Rightarrow \frac{dQ}{T} \leq \frac{dQ_2}{T_2} \quad \text{——— (C)}$$

for reversible process

$$ds = \frac{dQ_{rev.}}{T} = \frac{dQ_2}{T_2}$$

Hence, for AB process, $\frac{dQ}{T} \leq \frac{dQ_2}{T_2} = ds$ ——— (D)

from (C) & (D)

$$\Rightarrow \frac{dQ}{T} \leq ds$$

then for any cycle

$$\oint \frac{dQ}{T} \leq \oint ds$$

since entropy is point function

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

This equation is known as the inequality of clausius.

It provide criterion of the reversible cycle.

if

$$\oint \frac{dQ}{T} = 0 \qquad \text{reversible.}$$

$$\oint \frac{dQ}{T} \leq 0 \qquad \text{irreversible \& possible.}$$

if

$$\oint \frac{dQ}{T} > 0 \qquad \text{Cycle is impossible (voilate } 2^{nd} \text{ law)}$$

proof by example -
two heat engines with same source & sink take same heat Q_1, one is reversible & another irreversible.

irr. $\longrightarrow$ efficiency (η_1)

$\Rightarrow \quad \eta_1 < \eta_R$ — from reversible

$\Rightarrow \quad \dfrac{W_1}{Q_1} < \dfrac{W_R}{Q_1}$

$\Rightarrow \quad W_1 < W_R \Rightarrow Q_1 - Q_2 < Q_1 - Q_2'$

$\Rightarrow \quad Q_2' < Q_2$

For reversible engine.

$$\oint \frac{dQ}{T} = \frac{Q_1}{T_1} - \frac{Q_2'}{T_2} = 0$$

for irreversible.

$$\oint \frac{dQ}{T} = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} < 0$$

similarly one can prove for a cycle device working in more than two reserviors. $\Rightarrow$ so in general

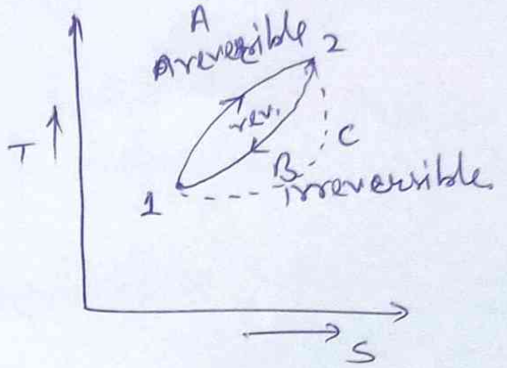
$$\oint \frac{dQ}{T} \leq 0$$

for any process

$$\frac{dQ}{T} \leq dS$$

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

Further clarification



$$\oint_R \frac{dQ}{T} = \int_{A'}^{2} \frac{dQ}{T} + \int_{2}^{1} \frac{dQ}{T} = 0$$

$$\Rightarrow \int_{A'}^{2} \frac{dQ}{T} = -\int_{2B}^{1} \frac{dQ}{T} \quad \text{———— (A)}$$

for A & C cycle.

$$\oint_{A,C} \frac{dQ}{T} < 0$$

$$\Rightarrow \int_{A'}^{1} \frac{dQ}{T} + \int_{2}^{1} \frac{dQ}{T} < 0$$

for (A)

$$\Rightarrow \int_{2_B}^{1} \frac{dQ}{T} + \int_{2_C}^{1} \frac{dQ}{T} < 0$$

$$\Rightarrow \int_{2\,B}^{1} \frac{dQ}{T} > \int_{2\,C}^{1} \frac{dQ}{T} \quad \text{——— (B)}$$

Since, B is reversible.

$$\int_{2\,B}^{1} \frac{dQ}{T} = \int_{2\,(B)}^{1} dS$$

and entropy is path function.

$$\int_{2\,(B)}^{1} dS = \int_{2\,(C)}^{1} dS$$

$$\Rightarrow \int_{2\,(C)}^{1} \frac{dQ}{T} < \int_{2\,(C)}^{1} dS$$

$$\Rightarrow dS > \frac{dQ}{T} \rightarrow \text{for irreversible}$$

for reversible

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

$$\Rightarrow S_2 - S_1 \geq \int_1^2 \frac{dQ}{T}$$

↳ equality → reversible
↳ inequality → irreversible

Summary : entropy

2nd law → entropy

adiabatic c ⟶ (some variable is constant)

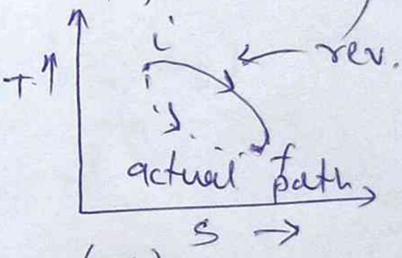
Clausius' theorem

heat generation in same random path = heat generation in equivalent (adiabatic + isothermal path).

$$\oint_R \frac{dq}{T} = 0 \longrightarrow \text{clausius' theorem.}$$

Entropy is point function (state variable)

$$\left(\frac{dq}{T}\right)_{rev.} \longrightarrow (\text{called entropy} = ds)$$



$$\int_{(R)}^{f} \frac{dq}{T} = S_f - S_i$$

$$S_f - S_i = \int_i^f \left(\left(\frac{dq}{T}\right)_{rev.}\right) = (\Delta S)_{irr.\ path.}$$

$$ds = \frac{dq_{rev.}}{T},$$

for reversible adiabatic.

$$dq_{rev.} = 0$$

$$\Rightarrow \quad ds = 0 \Rightarrow s = \text{Constant}$$

* reversible adiabatic process is also isoentropic.

Now. for isothermal

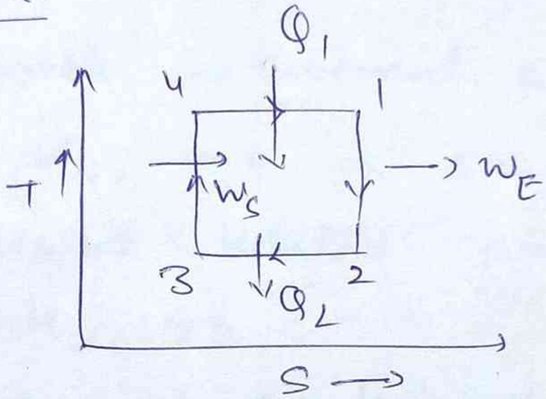
$$dQ_{rev.} = T\,ds$$

$$Q_{rev.} = T(S_f - S_i)$$

for genral process.

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

Carnot cycle.



$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1(S_1 - S_4) - T_2(S_2 - S_3)}{T_1(S_1 - S_4)}$$

Now $S_3 = S_4$ & $S_1 = S_2$

$$\eta = \frac{T_1(S_1 - S_4) - T_2(S_1 - S_4)}{T_1(S_1 - S_4)}$$

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

$$W_{net} = Q_1 - Q_2 = (T_1 - T_2)(S_1 - S_4).$$

Entropy principle

for any infinitesimal process.

$$dS \geq \frac{dQ}{T}$$

for isolated system.

$$dQ = 0$$

$$\Rightarrow \quad dS \geq 0$$

For reversible isothermal process.

$$dS_{iso} = 0 \Rightarrow S = \text{constant}.$$

For irreversible isolated process.

$$dS_{iso} > 0$$

thus entropy of an isolated system and never ~~decreases~~. decreases.

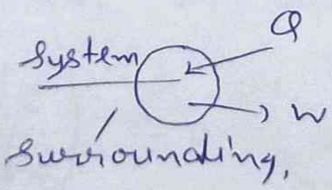
* Principle of increase of entropy or simply the entropy principle.

isolated system can always be formed.

(Sys. + surrounding) = isolated system.

e.g.

(sometime called subsystem.)



for all process

$$dS_{universe} \geq 0$$

$$dS_{sys.} + dS_{surrounding} \geq 0$$

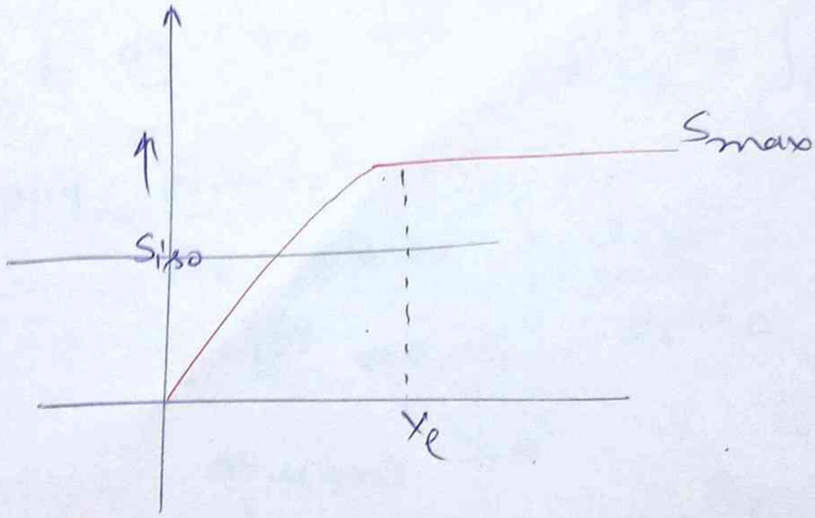
(2)

entropy may decrease locally, however, must increase elsewhere by a greater or same extent.

clausius summary of 1st & 2nd law.

(a) energy of universe is constant.

(b) entropy of " tends towards a maximum.



entropy of isolated system increase and become maximum at equlibrium.

$$\left(\frac{ds}{dx}\right) = 0 \quad \text{at equlibrium.}$$

Summary.

$$\frac{đQ}{T} = ds \rightarrow \text{Reversible}$$

In general.

$$\frac{đQ}{T} \le ds \quad \text{or} \quad ds \geq \frac{đQ}{T}$$

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

$\oint \frac{dQ}{T} < 0 \rightarrow$ Possible but irreversible.

$\oint \frac{dQ}{T} > 0 \rightarrow$ not possible.

$$(ds)_{irr.} = \int_1^2 \left(\frac{dQ}{T}\right)_{rev.}$$

Entropy principle

for isolated system

$$\frac{đQ}{T} = 0 \Rightarrow ds \geq 0$$

$$ds_{is(irr.)} \geq 0$$

$\downarrow$

Principle of increase of entropy.

or simply the entropy principle.

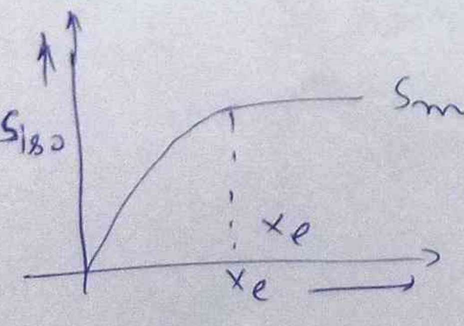
isolated system can always be formed.

* entropy may decrease locally.

but overall it will increase.

Entropy of isolated system increases and become maximum at equilibrium.

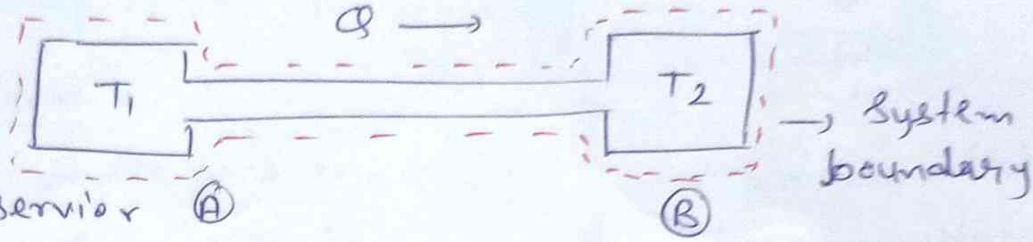
$$\left(\frac{ds}{dx}\right) = 0 \quad \text{at equilibrium.}$$



Application of entropy principle

higher the entropy increase → higher irreversible

1. Transfer of heat through a finite temp. difference



$T_1 > T_2$

For A. $\Delta S_A = -\frac{Q}{T_1}$ (−ve as heat flow out)

for B. $\Delta S_B = \frac{Q}{T_2}$

At steady state connecting wire, entropy does not change.

Hence. isolated system of A, B & wire.

$$\Delta S = \Delta S_A + \Delta S_B = \Delta S_{universe}.$$

$$\Rightarrow \Delta S_{uni.} = -\frac{Q}{T_1} + \frac{Q}{T_2} = \frac{(T_1 - T_2)Q}{T_1 T_2}$$

$\Delta S_{univ.} > 0$ or $T_1 > T_2$

hence, process is irreversible.

if $T_1 \approx T_2$ $\Delta S_{uni.} = 0 \rightarrow$ reversible.

Mixing of two fluids

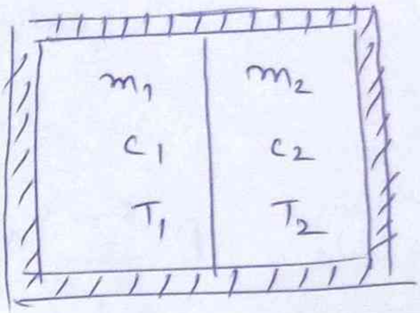
(5)

Subsystem 1.

mass $\rightarrow m_1$

Specific heat c_1

temp. $\rightarrow T_1$



Subsystem 2.

mass $\rightarrow m_2$

s.h. $\rightarrow c_2$

temp. $\rightarrow T_2$

& $T_1 > T_2$

inclosed by adiabatic boundary.

at $t = 0$ partition is removed.

at $t \rightarrow \infty$ (equilibrium)

$T_f \rightarrow$ Combined temp.

$T_2 < T_f < T_1$

Since system is isolated.

1st law.

$$\Delta U = 0 \Rightarrow m_1 c_1 (T_1 - T_f) = m_2 c_2 (T_f - T_1)$$

$$T_f = \frac{m_1 c_1 T_1 + m_2 c_2 T_1}{m_1 c_1 + m_2 c_2}$$

Now.

$$\Delta S_1 = \underbrace{\int_{T_1}^{T_f} \frac{dq_{rev.}}{T}}_{\text{why ??}} = \int_{T_1}^{T_c} \frac{m_1 c_1 \, dT}{T} = m_1 c_1 \ln\left(\frac{T_f}{T_1}\right)$$

for

$$\Delta S_2 = m_2 c_2 \ln\left(\frac{T_f}{T_2}\right)$$

$$\Delta S_{uni.} = m_1 c_1 \ln\left(\frac{T_f}{T_1}\right) + m_2 c_2 \ln\left(\frac{T_f}{T_2}\right)$$

⑥

Now for simiplicity

assume a case where.

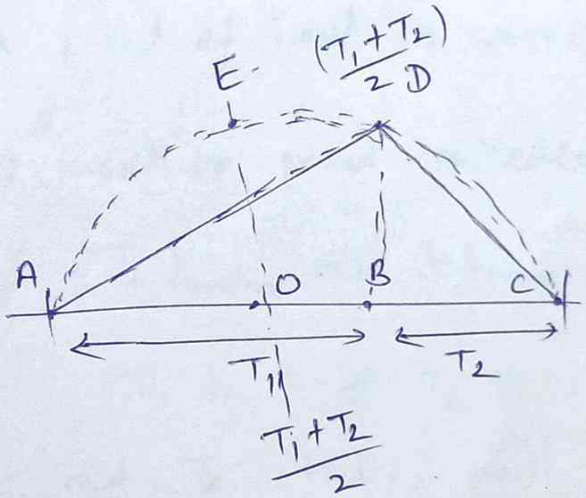
$$m_1 = m_2 = m, \quad c_1 = c_2 = c.$$

$$\Delta U_{unit} = mc \ln\left(\frac{T_f^2}{T_1 T_2}\right)$$

$$T_f = \frac{T_1 + T_2}{2}$$

$$\Delta S_{unit} = 2mc \ln\left[\frac{(T_1+T_2)/2}{\sqrt{T_1 T_2}}\right] > 0$$

prove.



$$BD^2 = AB.BC$$

$$BD = \sqrt{T_1 T_2}$$

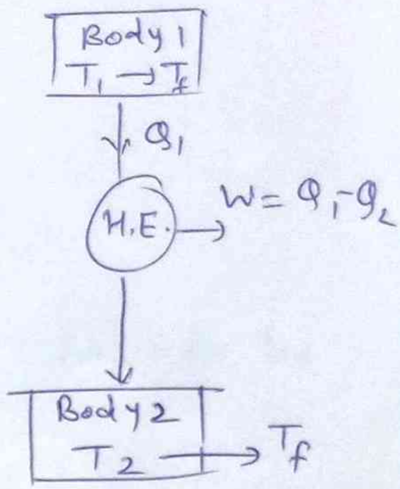
$$OE > BD.$$

$$\frac{T_1 + T_2}{2} > \sqrt{T_1 T_2}$$

maximum work obtainable from two finite bodies at temp. T_1 & T_2. (7)

Let us consider finite two identical body at T_1 & T_2 temp.

C_p as heat capacity



$\Rightarrow$ if thermal constant

no work.

$$\& \ T_f = \frac{T_1 + T_2}{2}$$

Now, suppose a H.E. in between these two bodies.

a part of heat is converted to work (W) by H.E.

& another part rejected (Q_2)

$$(T_f)_{min} \Rightarrow W_{max}.$$

$$T_1 \downarrow, \quad \& \ T_2 \uparrow$$

at T_f H.E. will stop delivering work,

total heat withdrawal.

$$Q_1 = C_p (T_1 - T_f)$$

for work

$$W = Q_1 - Q_2$$

&

$$Q_2 = C_p (T_f - T_2)$$

$$\Rightarrow \quad W = C_p \ (T_1 + T_2 - 2T_f)$$

Now

$$\Delta S = \int_{T_1}^{T_f} C_p \frac{dT}{T} = C_p \ln\left(\frac{T_f}{T}\right)$$

$$\Delta S_2 = C_p \ln\left(\frac{T_f}{T_2}\right)$$

(8)

$$\Delta S_{univ.} = \Delta S_1 + \Delta S_2 \geq 0$$

$$\Rightarrow \quad C_p \ln\left(\frac{T_f^2}{T_1 T_2}\right) \geq 0$$

$$\Rightarrow \quad \ln\left(\frac{T_f^2}{T_1 T_2}\right) \geq 0$$

for maximum work process has to be

$$\Delta S_{uni} = 0$$

$$\Rightarrow \quad \ln\left(\frac{T_f^2}{T_1 T_2}\right) = 0$$

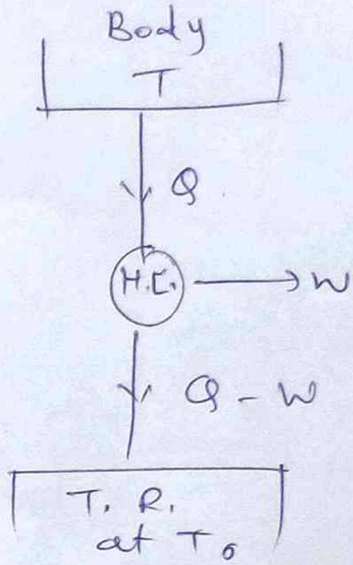
$$\Rightarrow \quad T_f^2 = T_1 T_2$$

$$W_{max} = C_p \left(T_1 + T_2 - 2\sqrt{T_1 T_2}\right)$$

$$\boxed{W_{max} = C_p \left(\sqrt{T_1} - \sqrt{T_2}\right)^2}$$

Max. work obtainable from a finite body of a T.R. at T_0

finite body heat capacity C_p, temp. T and thermal reservior at $T_0 < T$



when engine will stop ??.
(when body temp. $\Rightarrow T_0$)

$$\Delta S_{body} = \int_{T}^{T_0} C_p \frac{dT}{T}$$

$$= C_p \ln\left(\frac{T_0}{T}\right)$$

$$\boxed{\Delta S_{H.E.} = \oint dS = 0}$$

$$\Delta S_{TER} = \frac{Q - W}{T}$$

By ~~Boy~~ entropy principle.

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

$$\Rightarrow C_p \ln\left(\frac{T_0}{T}\right) + \frac{Q - W}{T_0} \geq 0$$

$$C_p \ln\left(\frac{T_0}{T}\right) \geq \frac{W - Q}{T_0}$$

$$\Rightarrow W \leq Q + T_0 C_p \ln\left(\frac{T_0}{T}\right)$$

$$\underline{W_{max}} = Q + T_0 C_p \ln\left(\frac{T_0}{T}\right)$$

$$= C_p(T - T_0) - T_0 C_p \ln\left(\frac{T}{T_0}\right)$$

$$= C_p\left[(T - T_0) - T_0 \ln\left(\frac{T}{T_0}\right)\right]$$