

PH 207  
Heat & Thermodynamics

Quiz -1 - 10

Quiz -2 - 10

Mid-Sem - 30

End-Sem - 50

KTG



Microscopic  
understanding  
of heat

Transport phenomenon

Classical Model of  
Thermodynamic behaviour  
Establishes the concepts  
of thermodynamics

Thermodynamics

Macroscopic  
understanding  
of heat

Laws state  
functions

Energy

Processes for  
engineering applications

Potentials

Egbm. phenomenon

## Thermodynamics

Study of ~~matter~~ energy, their transformations & relation to matter

System -

Surroundings - Everything external to system

System + Surroundings = Universe

Isolated System - A system not influenced by surroundings

Closed System / Control Mass System - Fixed amount of mass  
No mass can cross boundary

Volume is not fixed

Energy can cross boundary

Open System / Controlled Volume System - Properly selected region of space

Usually encloses a device that  
involves mass flow

Both mass & energy can  
cross boundary



## Thermal Equilibrium

Macroscopic description of a gaseous mixture

Wire Under Tension (of constant mass but variable length)  $\Rightarrow T, L$

Surface Film  $\Rightarrow A, S$

System with constant mass & composition  $\Rightarrow$

Requires 2 independent co-ordinates

start from

Generalised force ( $P$ )

Generalised displacement ( $v$ )

Equilibrium state - Where  $x, y$  have definite values that remain constant so long as external conditions are unchanged.

~~Another~~ Adiabatic

An eqbm. system A

can ~~not~~ coexist

with any eqbm. state of system B

for all possible

values of  $(x, y), (x', y')$

of the 2 systems

provided the wall

is able to withstand

the stress due to

differences in 2

sets of values.

~~Another~~ Diathermic

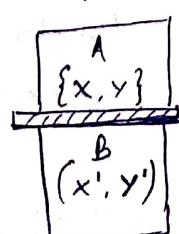
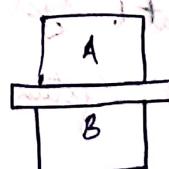
$\{x, y\} \& \{x', y'\}$

change spontaneously

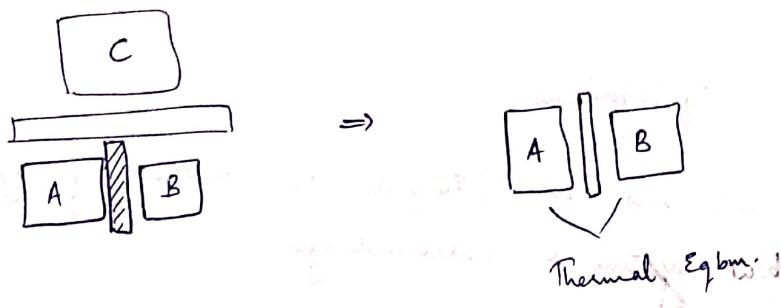
until an eqbm. state

of combined system

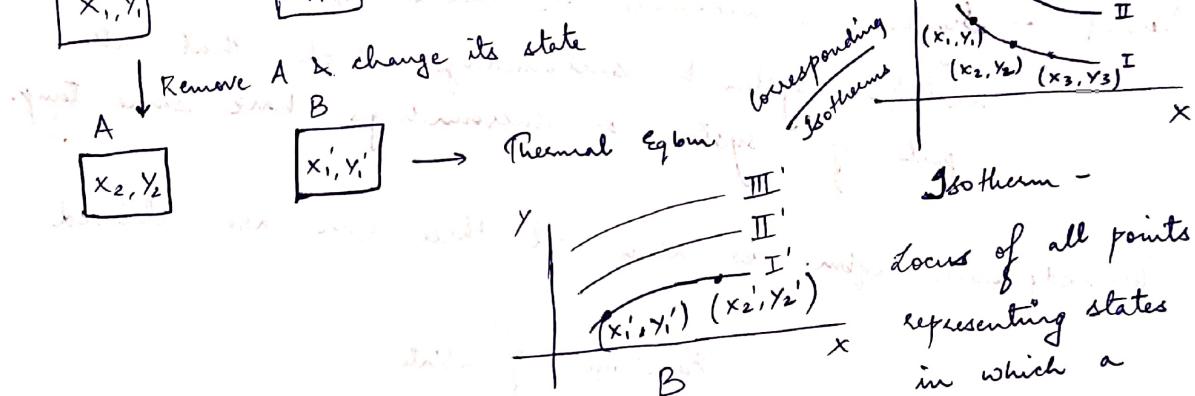
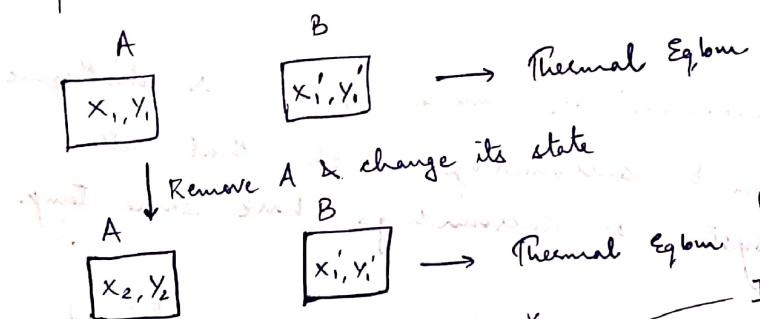
is attained.



2 systems separately or thermal eqm. with a 3rd system, are in thermal eqm. with each other.  
 (Zeroth Law of Thermodynamics)



Temperature



Temperature  $\Rightarrow$  Scalar quantity

Establishment of Temp. scale

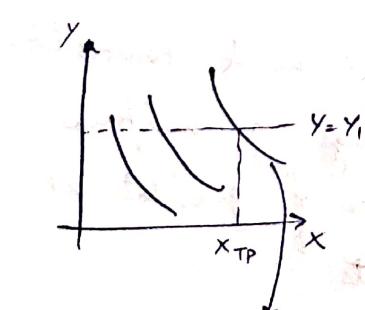
Isotherm -  
 locus of all points representing states in which a system is in thermal eqm. with one state of another system.

Thermometer  $\Rightarrow$  To establish an empirical T-scale

Select some system with co-ordinates

$x, y$  as a standard

Adopt a set of rules for assigning values.



$x \rightarrow$  Thermodynamic property

$\theta(x) \rightarrow$  Thermometric function that determines the T-scale

$$\theta(x) = a \times (\text{const. } y)$$

Isotherm at  
 $T = T_p$  of water

$T_p \Rightarrow$  Triple Point



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$$a = \frac{273.16 \text{ K}}{X_{TP}}$$

$$\theta(x) = 273.16 \frac{x}{X_{TP}}$$

$$\theta(P) = 273.16 \frac{P}{P_{TP}}$$

### Equilibrium

Mechanical - No unbalanced force/torque in interior of system or b/w system & surroundings

Chemical -

Thermal - System in mechanical & chemical eqm. & diathermic wall b/w system & surroundings such that all parts of system & surroundings have same temp.

Thermodynamic eqm. is when all three eqm are achieved.

### Equations of State

Constant mass of gas in a vessel measurable P, V, T.

Fix V, let T take on arbitrary values.

Any 2 out of 3 co-ordinates are independent.

Any 2 out of 3 co-ordinates are independent.

$$PV = nRT$$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Eq<sup>n</sup> of state - Eq<sup>n</sup> that connects thermodynamic co-ordinates x, y, z

Hydrostatic system - Isotropic system of constant m & composition that exerts on the surroundings a uniform hydrostatic pressure in absence of gravitational, electrical & magnetic effects.

Pure  
single chemical compound in form of gas/solid/liquid or ~~is~~ mixture of any 2

Homogeneous  
Mixture of different compounds  
 $\downarrow$   
mixture of gases/liquids/  
soln

Inhomogeneous  
Mixture of different gases in contact with mixture of different liquids.

### Differentials

$$x, y, z \rightarrow (\cancel{x}, \cancel{y}, \cancel{z} + dz)$$

If  $v \rightarrow v + dv$   $\frac{dv}{v} \ll 1$   
 $\frac{dv}{v} \gg 1$  space occupied by a few molecules

If  $p \rightarrow p + dp$   $\frac{dp}{p} \ll 1$   
 $\frac{dp}{p} \gg 1$  local fluctuations in  $p$  caused by momentary variations in microscopic form of molecular distribution

$$V = V(T, P)$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \rightarrow$  coefficient of volume expansion

Avg. coefficient of volume expansion =  $\frac{\text{change of volume per unit volume}}{\text{change in temp.}}$

$\beta > 0$  (mostly)

$$\beta = \beta(T, P)$$

Experimental  $\Rightarrow \beta$  is insensitive to variations in  $P$  & varies only slightly with  $T \Rightarrow$  in small ranges of  $T$ ,  $\beta$  is constant

Bulk Modulus =  $\frac{\text{change of Pressure}}{\text{change of Vol. per unit volume}}$

$$B = -V \left(\frac{\partial P}{\partial V}\right)_T \rightarrow$$
 Isothermal Bulk Modulus

$$\text{Isothermal compressibility } \kappa = \frac{-1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$P = P(T, V)$$

$$dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV$$

$$T = T(P, V)$$

$$dT = \left( \frac{\partial T}{\partial P} \right)_V dP + \left( \frac{\partial T}{\partial V} \right)_P dV$$

$dP, dT, dV \rightarrow$  Exact Differentials

If  $dz$  is an exact differential of  $x, y$  then

$$dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy$$

Theorem  $\Rightarrow$  Suppose there is a functional relationship among 3 coordinates  $x, y, z$  s.t.  $f(x, y, z) = 0$

$$\text{then } u = u(y, z)$$

$$dy = \left( \frac{\partial y}{\partial u} \right)_z du + \left( \frac{\partial y}{\partial z} \right)_u dz \quad du = \left( \frac{\partial u}{\partial y} \right)_z dy + \left( \frac{\partial u}{\partial z} \right)_y dz$$

$$\begin{aligned} du &= \left( \frac{\partial u}{\partial y} \right)_z \left[ \left( \frac{\partial y}{\partial u} \right)_z du + \left( \frac{\partial y}{\partial z} \right)_u dz \right] + \left( \frac{\partial u}{\partial z} \right)_y dz \\ &= \left( \frac{\partial u}{\partial y} \right)_z \left( \frac{\partial y}{\partial u} \right)_z du + \left[ \left( \frac{\partial u}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_u + \left( \frac{\partial u}{\partial z} \right)_y \right] dz \end{aligned}$$

choose  $dz = 0, du \neq 0$

$$\left( \frac{\partial u}{\partial y} \right)_z \left( \frac{\partial y}{\partial u} \right)_z = 1 \Rightarrow \left( \frac{\partial u}{\partial y} \right)_z = \frac{1}{\left( \frac{\partial y}{\partial u} \right)_z}$$

choose  $du = 0, dz \neq 0$

$$\left( \frac{\partial u}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_u + \left( \frac{\partial u}{\partial z} \right)_y = 0$$



$$\left(\frac{\partial u}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_u = - \left(\frac{\partial u}{\partial z}\right)_y$$

$$\left(\frac{\partial u}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_u \left(\frac{\partial z}{\partial x}\right)_y = -1$$

PVT system  $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = - \left(\frac{\partial P}{\partial T}\right)_V$

$$\left(\frac{\partial P}{\partial T}\right)_V = \beta/k$$

$$dP = \frac{\beta}{k} dT - \frac{1}{kV} dV$$

When  $V$  is const.

$$dP = \frac{\beta}{k} dT$$

$$T: T_i \rightarrow T_f \quad P: P_i \rightarrow P_f$$

$$P_f - P_i = \int_{T_i}^{T_f} \frac{\beta}{k} dT$$

If  $T_f - T_i \ll \frac{T_i}{T_f}$  then  $\beta, k \rightarrow \text{constant}$

$$P_f - P_i = \frac{\beta}{k} (T_f - T_i)$$

### Stretched Wire

Tension  $\tau$

Hooke's Law  $\Rightarrow \tau = -k(L - L_0)$

Length  $L$

(at const. temp.,

Temperature  $T$  within elastic limit

$$dL = \left(\frac{\partial L}{\partial \tau}\right)_T d\tau + \left(\frac{\partial L}{\partial T}\right)_\tau dT$$

Average linear expansion coefficient =  $\frac{\text{change of length / length}}{\text{change in } T \text{ with const. } \tau}$

$$\alpha = \frac{1}{L} \left(\frac{\partial L}{\partial T}\right)_\tau$$

For metals,  $\alpha > 0$  because  $T \uparrow, L \uparrow$

For rubber bands,  $\alpha < 0$  because  $\beta < 0$

$\alpha$  weakly depends on  $T$  &  $T$   
small  $T$  range,  $\alpha$  is const.

$$\text{Young's modulus} = \frac{\text{change of Tension / Area}}{\text{change of length / length}}$$

at const.  $T$

Isothermal Young's Modulus

$$Y = \frac{L}{A} \left( \frac{\partial \tau}{\partial L} \right)_T \quad Y > 0$$

For small Temp. range,

$$\left( \frac{\partial \tau}{\partial L} \right)_L = - \left( \frac{\partial \tau}{\partial T} \right)_T \left( \frac{\partial L}{\partial T} \right)_E$$

$$\left( \frac{\partial \tau}{\partial T} \right)_L = -\alpha A Y$$

Paramagnetic System

No permanent magnetisation

In an external field, it becomes slightly magnetised

Within paramagnet, microscopic currents are induced by magnetic field

Macroscopic effect of induced currents  $\Rightarrow$  magnetic dipole moment / magnetisation

$$H = \frac{B}{\mu_0} - M$$

Magnetic Field

magnetic induction  
magnetization

Thermodynamic co-ordinates

$$\text{Eqn of State} \Rightarrow M = C \frac{H}{T} \quad \text{Curie's Law}$$

$$\text{Susceptibility} \Rightarrow \left( \frac{\partial M}{\partial H} \right)_T = X = \frac{C}{T}$$

$$dM = \left( \frac{\partial M}{\partial H} \right)_T dH + \left( \frac{\partial M}{\partial T} \right)_H dT$$

When  $dT = 0, dH \neq 0$

$$dM = X dH$$

Thermodynamic co-ordinates

Additive & Extensive

Intensive

Independent of mass

Same value everywhere  
in system

Non-additive

Extensive

Depends on mass

Varies throughout system

Additive

System

Intensive

Extensive

Gas

P

V

Wire

T

L

Magnet

H

M

Product of conjugate pairs = Dimension of Work

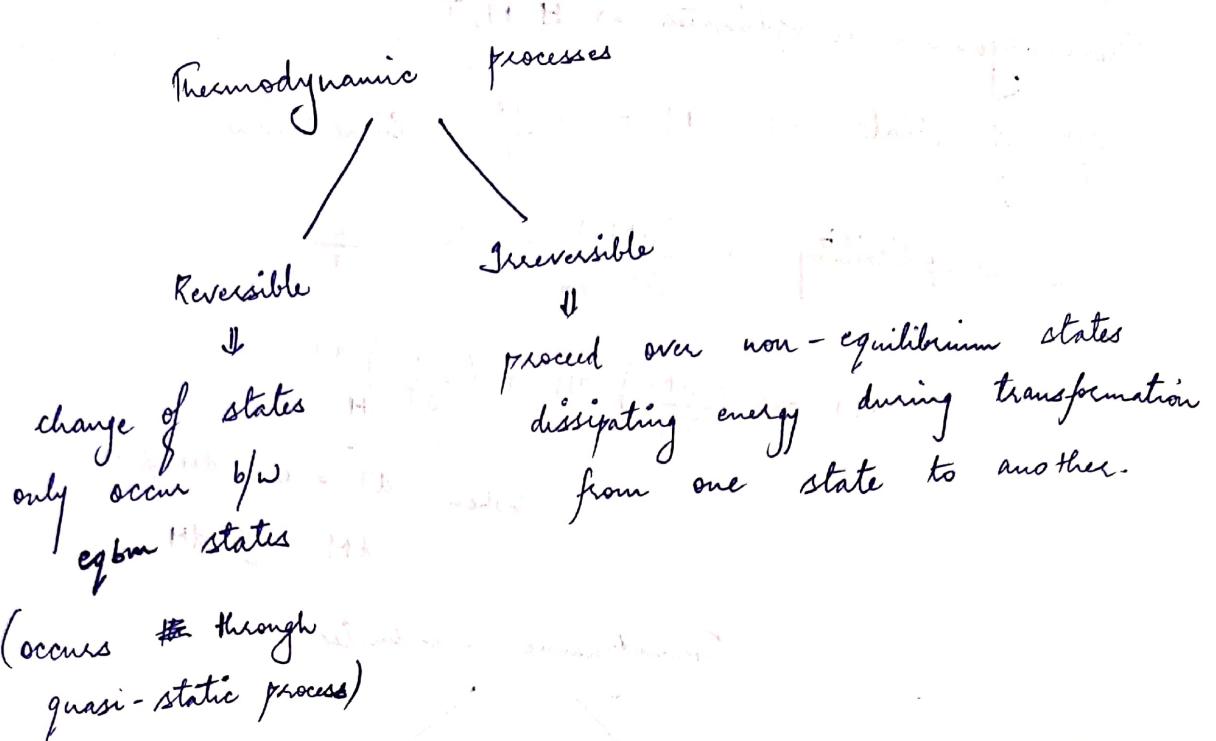
$$\text{Thermodynamic Work} \Rightarrow dW = - \int \vec{x} \cdot d\vec{y}$$

Thermodynamic force    Thermodynamic displacement

Convention  $\Rightarrow$

W.D. by the system,  $< 0 \Rightarrow$  energy is extracted

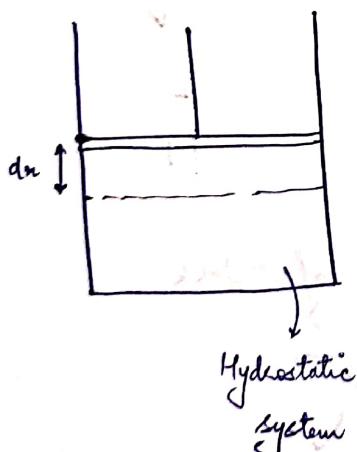
W.D. on the system,  $> 0 \Rightarrow$  energy is added



In a quasi-static process, infinitesimal changes in parameters are made sufficiently slowly compared to relaxation time

of system.

Work in changing volume  
in a hydrostatic system



Frictionless movable piston

Cross-section A.

Pressure exerted by system on piston =  $P$

Force on internal face of piston =  $PA$

Let force from surroundings on piston =  $F$

Let piston moves  $dn$  during compression

$$\begin{aligned} \text{W.D. by surroundings} &= dW = F \cdot dn \\ &= PA \cdot dn \end{aligned}$$

$$A \cdot dn = -dV \Rightarrow dW = -PdV \quad (dV < 0)$$

$$\text{Internal force} = PA \quad \text{displacement} = dx$$

$$dW = PA dx$$

$$Adx = dV$$

$$dW = P dV \quad (dV > 0)$$

Finite Quasi-static process  $\Rightarrow V_i \rightarrow V_f$

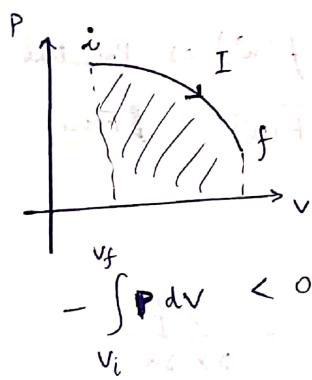
$$W = - \int_{V_i}^{V_f} P dV \quad P = P(T, V)$$

$$\begin{aligned} \text{Fix } T \\ P = P(V) \end{aligned}$$

$$V_f > V_i \quad W_{if} = - \int_{V_i}^{V_f} P dV$$

$$W_{fi} = -W_{if}$$

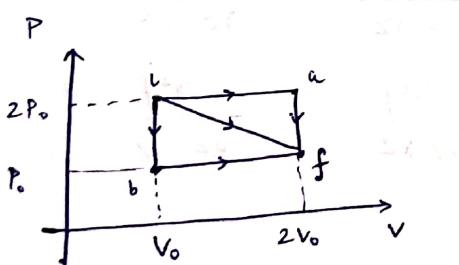
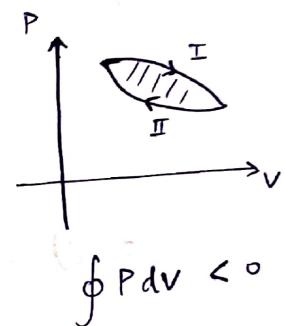
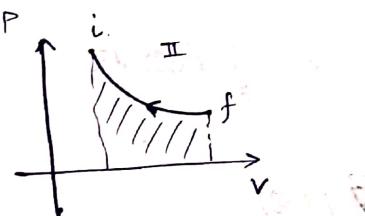
$$f \rightarrow i \quad W_{fi} = - \int_{V_f}^{V_i} P dV$$



$W.D.$  by system

$$-\int P dV < 0$$

$W.D.$  on system



$$\begin{aligned} i \rightarrow f \\ I: i \rightarrow a + a \rightarrow f \\ \text{isobaric} \quad \text{isochoric} \end{aligned}$$

$$W = -2P_0V_0 < 0$$

$$\begin{aligned} II: i \rightarrow b + b \rightarrow f \\ W = -P_0V_0 < 0 \end{aligned}$$

$$\begin{aligned} III: i \rightarrow f \\ W = \frac{-3}{2}P_0V_0 < 0 \end{aligned}$$

$$W = - \int_{V_0}^{2V_0} V dV = \frac{-3}{2}V_0^2 = \frac{-3}{2}P_0V_0 \quad (P = V)$$

$W \neq \text{state function}$

# Exact & Inexact Differentials

Eqn of state  $F(x, y, z) = 0$

$$z = f(x, y)$$

$$dz = \left. \frac{\partial f(x, y)}{\partial x} \right|_y dx + \left. \frac{\partial f(x, y)}{\partial y} \right|_x dy$$

exact  
differential

$$\Leftrightarrow df(\vec{x}) = \vec{\nabla} f(\vec{x}) \cdot d\vec{x}$$

$$\vec{x}(x, y)$$

change state of system  $\vec{x}_0 \rightarrow \vec{x}$



$$f(\vec{x}) - f(\vec{x}_0) = \int_C \nabla f(\vec{x}) \cdot d\vec{x}$$

$$= \int_C \vec{F}(\vec{x}) d\vec{x}$$

$f(\vec{x}) \Rightarrow$  Potential

$\vec{F}(\vec{x}) \Rightarrow$  Force

$$\vec{F}(\vec{x}) = \vec{\nabla} f(\vec{x})$$

For the differential to

$$\text{be exact, } \vec{\nabla} \times \vec{F} = 0 \Rightarrow$$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

$$\frac{\partial^2 f}{\partial x \partial z} = \frac{\partial^2 f}{\partial z \partial x}$$

$$\frac{\partial^2 f}{\partial y \partial z} = \frac{\partial^2 f}{\partial z \partial y}$$

Quasistatic isothermal expansion or compression of ideal gas

$$PV = nRT$$

$$W = - \int_{V_i}^{V_f} P dV$$

$$= -nRT \ln \frac{V_f}{V_i}$$

Q) quasi static isothermal increase of pressure in a solid

$$W = - \int_{P_i}^{P_f} P dV$$
$$= + \int_{V_i}^{V_f} k V P dP$$
$$\approx \frac{kV}{2} (P_f^2 - P_i^2)$$
$$dV = \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT$$
$$k = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$
$$dV = -kV dP$$

\*  $k$  &  $V$  are practically

constant at constant temp.

Q) compression of 2 mol of an ideal gas at 20°C from 4L to 1L.

$$W = -nRT \ln \left( \frac{V_f}{V_i} \right)$$
$$= -2 \times 8.31 \times 293 \ln \left( \frac{1}{4} \right) = 6735 \text{ J}$$

Q) Pressure on 2 gm of solid Cu is increased quasi-statically & isothermally at 20°C from 0 to 1000 atm.

$$W \approx \frac{kV}{2} (P_f^2 - P_i^2) = \frac{nk}{28} (P_f^2 - P_i^2)$$

$$\rho_{Cu} = 8.96 \times 10^3 \text{ kg/m}^3$$

$$k_{Cu} = 7.16 \times 10^{-12} \text{ Pa}^{-1}$$

$$W \approx 4.08 \text{ J}$$

w.d. in changing length of wire

$$\frac{L_i}{\tau} \rightarrow \frac{L_f}{\tau}$$

$$W = \int_{L_i}^{L_f} \tau dl$$

$$dW = \tau dl$$

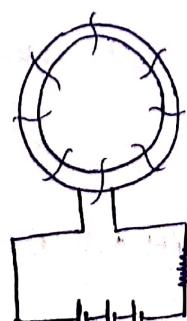
$$\tau = \tau(L, T)$$

$$dL > 0$$

$$dW > 0$$

w.d. in changing total magnetisation of paramagnetic field

Ans. Toroid  
Winding of  $N$   
closely spaced turns



Ring of paramagnetic material with area  $A$ , circumference  $L$

Maintain a constant current in the winding by a battery & charged charged by a variable resistor

Suppose magnetic induction in ring =  $B$   
Change current in time  $dt$  & induction changes from  $B \rightarrow B + dB$

$$\text{Induced emf } E = -NA \frac{dB}{dt}$$

Let a charge  $dz$  moves in circuit in a time interval  $dt$

w.d. by a battery to maintain current in circuit

$$dW = -E dz$$

$$= NA \frac{dB}{dt} dz$$

$$= NA \frac{dz}{dt} dB$$

$$= NAI dB$$

Magnetic field  $H$  due to current  $I$  inside toroidal winding

$$H = \frac{NI}{L} = \frac{NAI}{AL} = \frac{NAI}{V} \quad V \Rightarrow \text{Vol. of Paramagnetic material}$$

$$NAI = VH$$

$$dW = VH dB$$

If  $m$  is magnetization of paramagnetic material.

$$B = \mu_0 H + \frac{m}{V}$$

$$\therefore dW = VH d(\mu_0 H) + \mu_0 H dm$$

If no material was present within solenoidal winding,  $m = 0$   
 $\Rightarrow B = \mu_0 H$

$$\text{Then } dW = VH d(\mu_0 H); \text{ (vacuum)}$$

W.D. ~~to~~ to increase the magnetic field in a volume  $V$  of empty space by an amount  $d(\mu_0 H) \Rightarrow dW = \mu_0 d(\mu_0 H)$   
 $dW = \mu_0 H dm$

$\text{W.D.}$

$$W = \mu_0 \int_{\text{mi}}^{\text{mf}} H \cdot dm$$

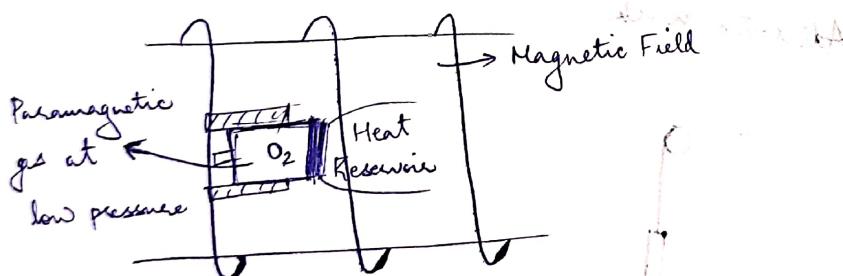
**Composite Systems**



2 eq's of states

3 independent coordinates

$$dW = -P dV - P' dV'$$

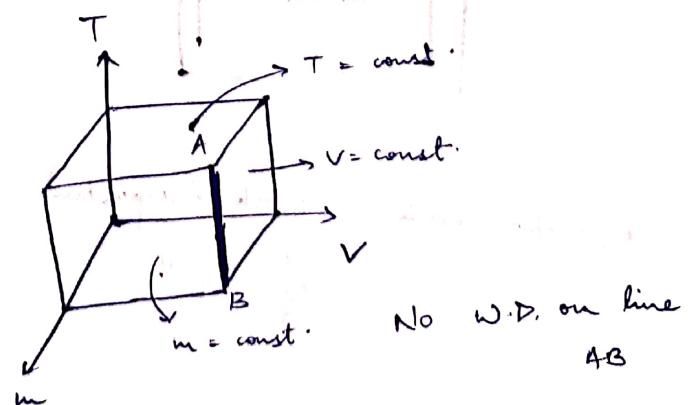
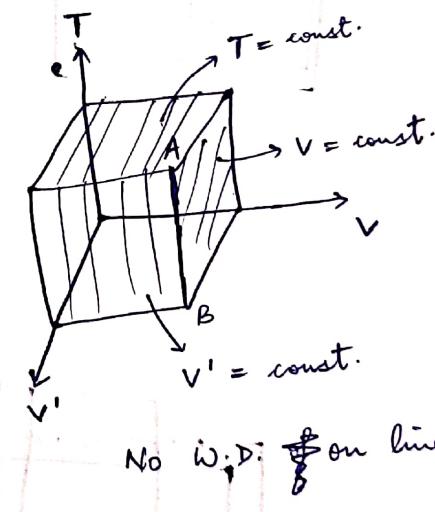


P, V, T, H, m

$$PV = nRT$$

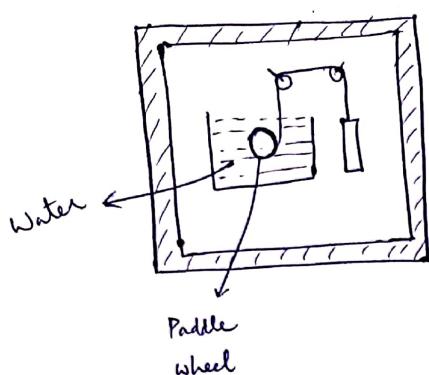
$$m = \frac{CH}{T}$$

$$dW = -P dV + \mu_0 H dm$$

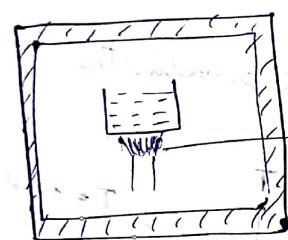
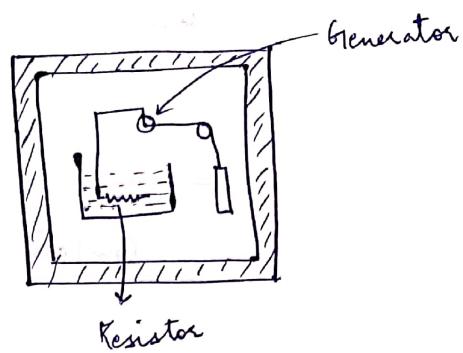


T = const.  $\Rightarrow dT = 0$

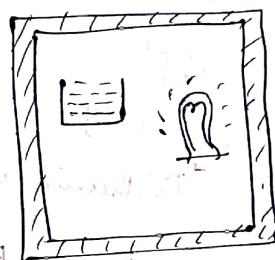
Heat



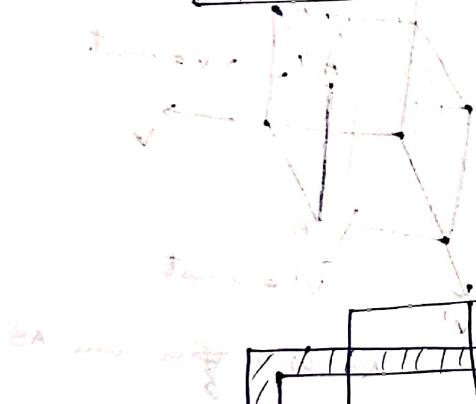
Temp. of  
water  
increases  
in both cases



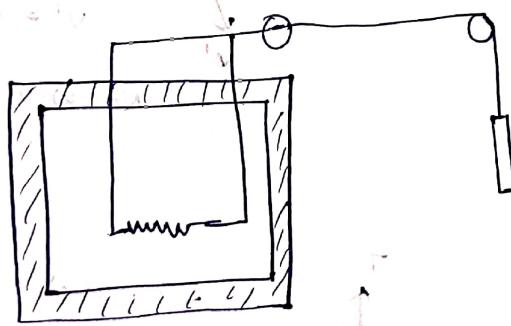
water becomes  
hot through heat  
transfer  
Temp. of  
water  
increases  
in both  
cases



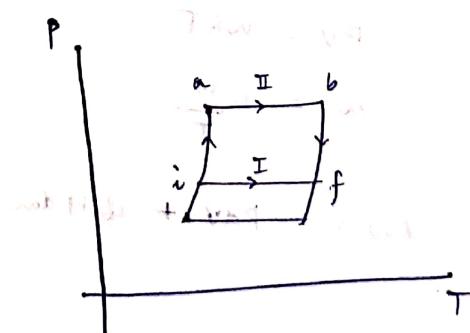
Temp. >> Twater



Adiabatic Work



Adiabatic work  $\Rightarrow$  Work independent  
of path



$$W_{i \rightarrow f} (\text{adiabatic}) = U_f - U_i$$



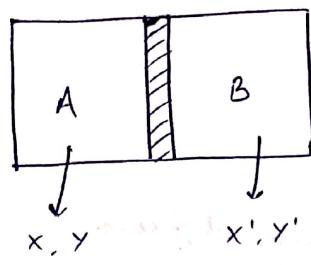
Change in  
internal energy

$i \rightarrow a \Rightarrow$  Compress adiabatically

$a \rightarrow b \Rightarrow$  Increase in T

$b \rightarrow f \Rightarrow$  Expand

$V \Rightarrow$  function of independent thermodynamic co-ordinates

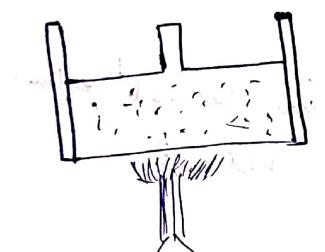


$dV \Rightarrow V$  is an exact differential

Hydrostatic system  $P, V, T$

$$dV(T, V) = \left(\frac{\partial V}{\partial T}\right)_V dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$dV(T, P) = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$



Gas in thermal contact with flame  
 $T_{\text{flame}} \gg T_{\text{gas}}$   
 Compression  $\Rightarrow$  Diathermic work

For non-adiabatic process,

$$W_{\text{non-adiabatic}} \neq V_f - V_i$$

(1)  $+ (2) \Rightarrow$  Energy transfer is by means other than work

or heat  
performed.

Heat  $\Rightarrow$  When a closed system whose surroundings are at a different  $T$  & on which diathermic work may be done undergoes a process, then the energy transferred by non-mechanical means, equal to difference b/w change in internal energy & diathermic work is called heat.

$$\vartheta = (V_f - V_i) - W \quad (\text{diathermic})$$

$$V_f - V_i = \vartheta + W$$

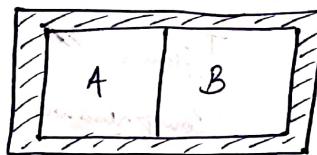
1<sup>st</sup> law of thermodynamics

$Q > 0 \Rightarrow$  Heat enters into system  
 $Q < 0 \Rightarrow$  Heat leaves the system

- (i) Existence of  $U$
- (ii) Conservation of Energy
- (iii) Heat as energy by virtue of a temp. difference

$Q$  is not a state function

Calculation of  $Q$  depends on path.  
 $dQ$  is not exact.



A in thermal eqm.  
with B

$$A : U_f - U_i = Q + W$$

$$B : U_f' - U_i' = Q' + W'$$

$$(U_f + U_f') - (U_i + U_i') = \underbrace{(Q + Q')}_{\text{Heat transferred to composite system}} + \underbrace{(W + W')}_{\text{W.D. on composite system}}$$

Change in  $U$  of composite function

$$Q + Q' = 0 \Rightarrow Q = -Q'$$

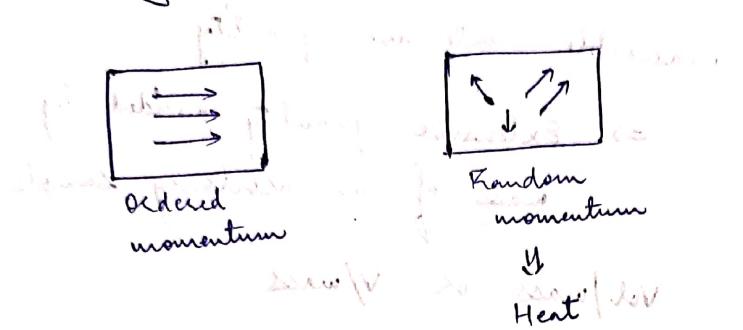
Within adiabatic boundary, heat lost by one equals heat gained by other

Work  $\Rightarrow$  Energy transfer via macroscopically observable degrees of freedom.

Heat  $\Rightarrow$  Direct energy transfer b/w microscopic degrees of freedom i.e. internal degrees of freedom.

Heating up  $\Rightarrow$  collision b/w gas molecules & piston.

Thermally isolated cylinder



$$dU = dQ + dW$$

↓  
Exact  
(Related to properties of system)

$U = \text{Total energy known from mechanics / electrodynamics}$   
 $(\text{no exchange with surroundings})$

Total Energy = energy of macroscopic mass motion  
+ Internal Energy

↓  
K.E. of motion of C.M. + P.E. due to external field      ↓  
K.E. of molecular motion + P.E. of molecular interaction

### 1<sup>st</sup> Law of Thermodynamics

System

Ideal gas

Stretched wire

Paramagnetic system

First Law

$$dU = dQ - PdV$$

$$dU = dQ + TdL$$

$$dU = dQ + HdM$$

$U$  is a function of any 2  
 $P, V, T$

$T, L, T$

$m, H, T$

$$\text{Heat capacity} \Rightarrow c = \frac{dQ}{dT}, \quad c = \frac{\Delta Q}{\Delta T}$$

↓  
Not a derivative

Standardisation of measurable extensive quantity  
 $\Rightarrow$  Extensive quantity divided by mass of an arbitrary sample  
 Vol/mass or v/mass

$$\text{No. of moles, } n = \frac{\text{Total mass}}{M}$$

If  $c$  is heat capacity of  $n$  moles,

$$\text{Molar heat capacity, } c = \frac{C}{n} = \frac{1}{n} \frac{dQ}{dT}$$

Hydrostatic system  $\Rightarrow C_p, C_v$

$$dQ = dW + PdV$$

$$\text{Let } V = V(T, V)$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_V dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$$

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT}$$

$$(i) dV = 0 \Rightarrow \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$



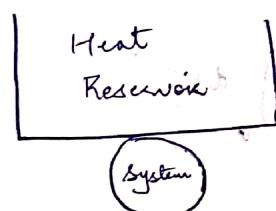
$$(iii) dP = 0 \quad \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[ \left(\frac{\partial V}{\partial T}\right)_P + P \right] \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P = C_V + \left[ \left(\frac{\partial V}{\partial T}\right)_P + P \right] V_B$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{V_B} - P$$

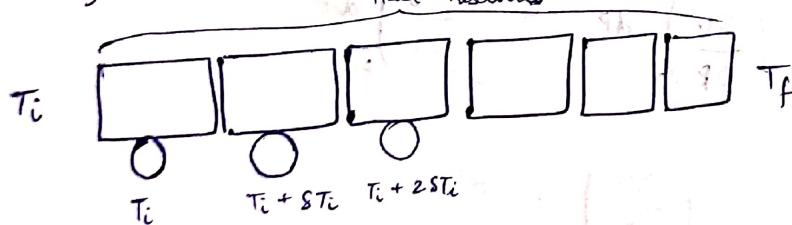
$$dU = C_V dT + \left[ \frac{C_P - C_V}{V_B} - P \right] dV$$

Quasistatic heat flow



$\Rightarrow$  Body of large mass such that it rejects or accepts heat of an infinite quantity without experiencing any appreciable change in its temp. or any other thermodynamic coordinates

Quasi-static heat flow  $\Rightarrow$  Isothermal process



Quasi-static isobaric process

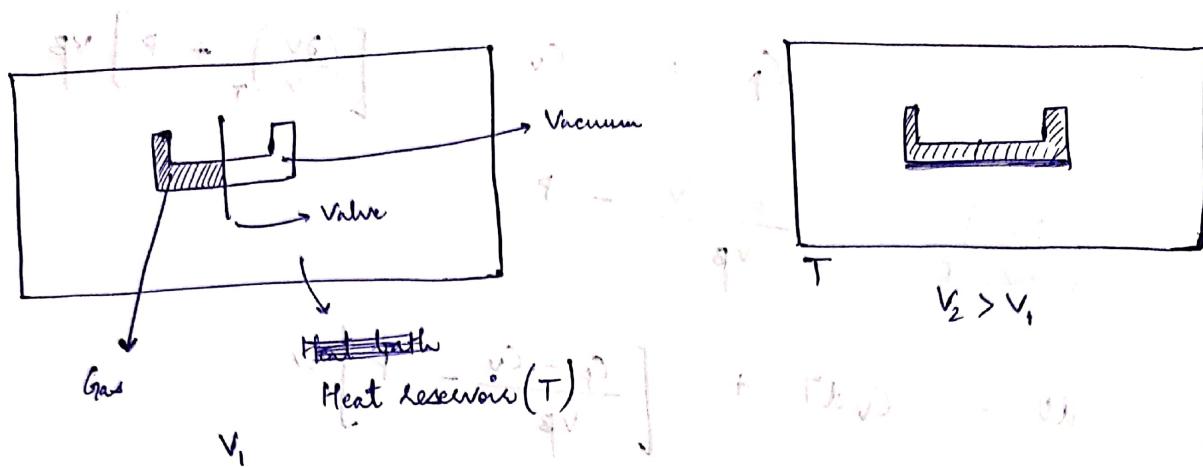
$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P, \quad Q_P = \int_{T_i}^{T_f} C_P dT \xrightarrow{\text{const.}}$$

$$Q_P = C_P (T_f - T_i)$$

~~Isobaric process~~  $C_V = \left(\frac{\partial Q}{\partial T}\right)_V$

$$Q_V = C_V (T_f - T_i)$$

$\frac{\partial U}{\partial T} + \frac{\partial U}{\partial V}$  Internal Energy of Gas



$$\text{Free Expansion} \Rightarrow \left. \begin{array}{l} \frac{\partial W}{\partial t} = 0 \\ \frac{\partial Q}{\partial t} = 0 \end{array} \right\} \Rightarrow dV = 0$$

$$dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP$$

$$\left( \frac{\partial V}{\partial T} \right)_P = 0$$

$$V = V(P, T)$$

$$dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP$$

$$\left( \frac{\partial V}{\partial P} \right)_T = 0$$

$$\Rightarrow V = V(T) \quad (\text{for free expansion})$$

Ideal Gas

$$PV = nRT$$

$$\left( \frac{\partial V}{\partial P} \right)_T = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{wRT}{V^2} = \frac{-P}{V} \neq 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \Rightarrow U = U(T)$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \Rightarrow C_V = \frac{dU}{dT}$$

$$dQ = C_V dT + P dV$$

$$PV = wRT$$

$$PdV + VdP = wRdT$$

$$dQ = (C_V + wR)dT - VdP$$

$$\frac{dQ}{dT} = C_V + wR - V \frac{dP}{dT}$$

$$\text{At const. } P, \frac{dQ}{dT} = C_P, \quad dP = 0$$

$$C_P = C_V + wR$$

$$dQ = C_P dT - VdP$$

$C_P > C_V$  always

$$C_V \text{ for ideal gas} \quad PV = \frac{2}{3} N \langle E_{kin} \rangle$$

Kinetic Energy  
No. of particles

$$\begin{aligned} \langle E_{kin} \rangle &= \frac{1}{2} m \langle v^2 \rangle \\ &= \frac{3}{2} kT \end{aligned}$$

$$\text{Ideal gas, P.E.} = 0 \quad \text{Avg. total energy} = \langle E_{kin} \rangle$$

Internal Energy = energy of particle reservoir

$$U = n \langle E_{kin} \rangle = \frac{3}{2} nRT$$

$$C_V = \frac{dU}{dT} = \frac{3}{2} nR$$



## Quasi-Adiabatic Process

$$dQ = C_v dT + P dV$$

$$dQ = C_p dT - V dP$$

Adiabatic process  $\Rightarrow dQ = 0$

$$V dP = C_p dT$$

$$P dV = -C_v dT$$

$$\frac{dP}{P} = \frac{-C_v}{C_p} \frac{dT}{dV} \Rightarrow \frac{dP}{P} = \frac{-C_p}{C_v} \frac{dV}{V}$$

$$= -\gamma \frac{dV}{V} \quad \gamma = \frac{C_p}{C_v}$$

$$\gamma = \gamma(T)$$

$$T : 300 - 3000 \text{ K}$$

$$\gamma : 1.4 - 1.29$$

$\gamma \neq \gamma(T)$  for finite T changes

$$P V^\gamma = C$$

## Ideal Gas in Adiabatic Process

$$dQ = C_v dT + P dV$$

$$C_v dT = -P dV$$

$$C_v dT = \frac{-nRT}{V} dV$$

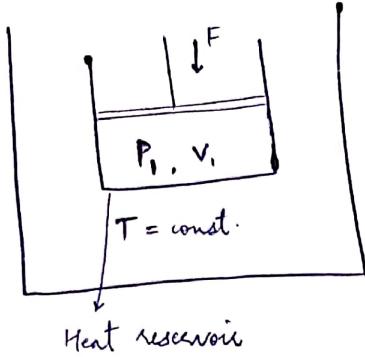
$$\frac{C_v}{nR} \int_{T_i}^{T_f} \frac{dT}{T} = - \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\frac{C_v}{nR} \ln \left( \frac{T_f}{T_i} \right) = - \ln \left( \frac{V_f}{V_i} \right)$$

$$C_v = 3/2 nR$$

$$\left( \frac{T_f}{T_i} \right)^{3/2} = \frac{V_i}{V_f}$$

## Isothermal expansion of gas



Remove  $F \Rightarrow$  gas expands to volume  $V_2$   
(rapidly)

Work done irrev. = 0

$$\text{W.D. rev.} = -NKT \ln(V_2/V_1)$$

$$dV = dW_{\text{rev.}} + dQ_{\text{rev.}}$$

$$= dW_{\text{irrev.}} + dQ_{\text{irrev.}}$$

$$dW_{\text{irrev.}} = -P dV$$

$$dQ_{\text{irrev.}} < dQ_{\text{rev.}}$$

$$dW_{\text{irrev.}} > dW_{\text{rev.}} = -P dV$$

$$dQ_{\text{irrev.}} < dQ_{\text{rev.}}$$

Reversible process produces maximum work  
A part of work is always converted into heat in case  
of irreversible process

$$\int dV = 0 \Rightarrow \text{Thermodynamic cycle}$$

$$\int dQ = \text{util. work} - \int dW$$

If utilisable work is done in this cycle, can  
all heat be converted to work?  $\Rightarrow$  2<sup>nd</sup> Law

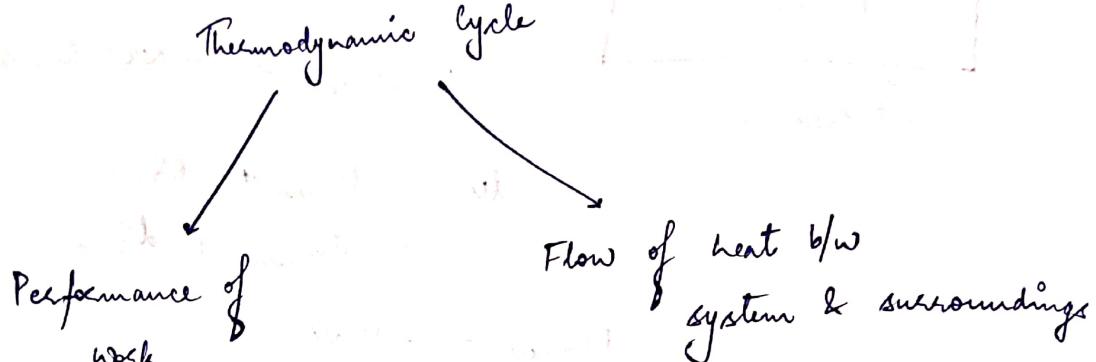
### Conversion b/w Work & Heat

Conversion of work to heat is 100%. & this process  
can happen for indefinite period of time.

Isothermal expansion of gas  $\Rightarrow dT = 0 \Rightarrow dV = 0$

$dQ \approx dW$

Heat is converted to work ~~but~~ but the state of system has changed.



In a complete cycle

let  $|Q_H| \rightarrow$  Heat exchanged b/w hot reservoir & system

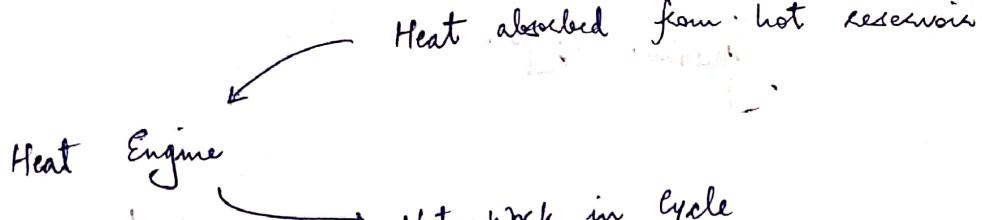
$|Q_L| \rightarrow$  Heat exchanged b/w cold reservoir & system

$|W| \rightarrow$  Work exchanged b/w system & surroundings

If  $|Q_H| > |Q_L|$  & if  $|W|$  is done by system during cycle

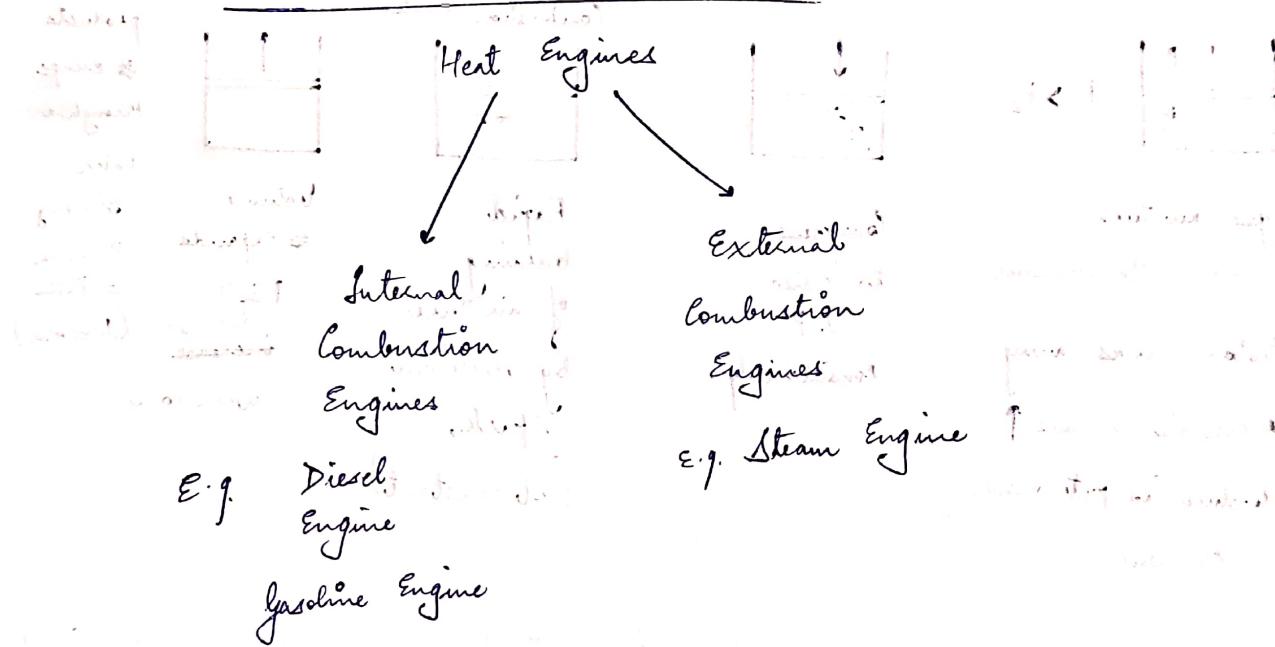
↓  
the machine that runs the cycle

↓  
Heat engine



$$\text{Thermal Efficiency } \eta = \frac{\text{Work Output}}{\text{Heat Input}} = \frac{|W|}{|Q_H|}$$

$$\text{cycle} \Rightarrow dV = 0 \quad |Q_H| - |Q_L| = W \quad \eta = 1 - \frac{|Q_L|}{|Q_H|}$$



Common characteristics  $\Rightarrow$  Gas / Mixture of gases

Raised to a high T & high P

Provides the force to perform work

Dissimilarity  $\Rightarrow$  Rapid burning of fuel + O<sub>2</sub> from air takes place in the chamber  $\rightarrow$  Raises T & P.  
(Internal combustion engine)

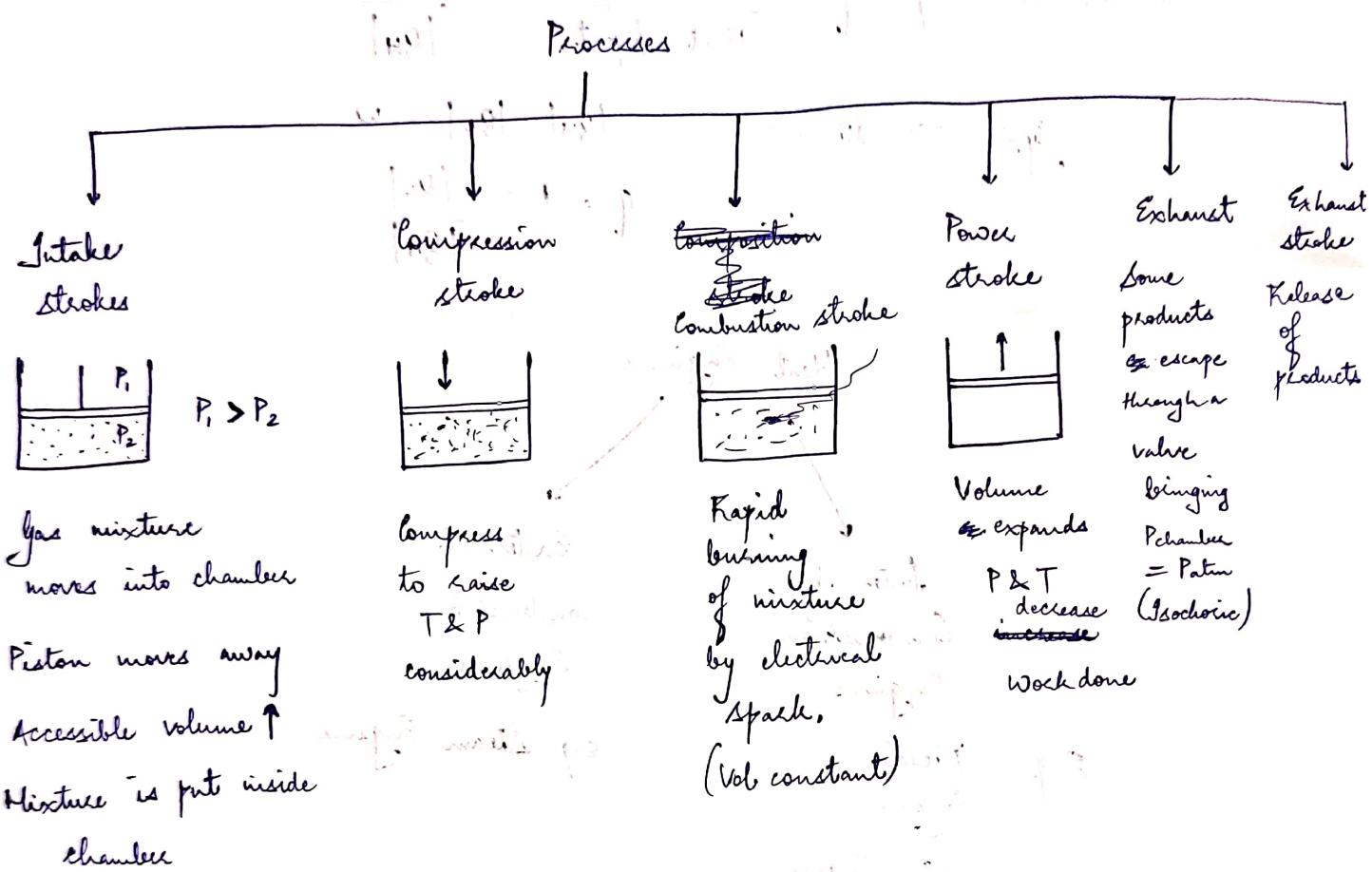
Raise in T & P is achieved by high T surroundings that transfer heat inside chamber

(External combustion engine)

# Gasoline Engine

6 processes

4 processes require vertical motion of piston  $\rightarrow$  strokes



Friction, turbulence, loss of heat by conduction, chemical reaction b/w gasoline vapors &  $O_2 \Rightarrow$  taken into account

Simplification  $\Rightarrow$  Idealisation

cycle  $\Rightarrow$  Otto cycle (Nicholas Otto 1876)

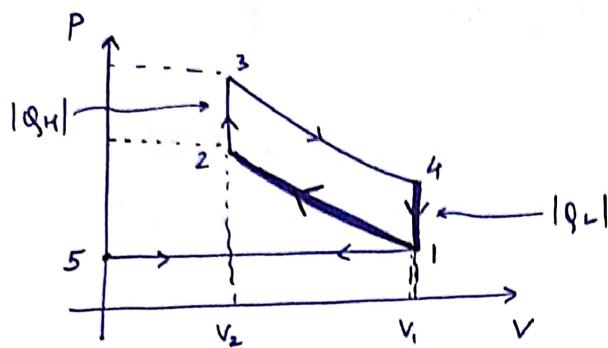
Idealisations - 1) Working substance in air behaving like ideal gas with constant c.

2) Processes are quasi-static

3) Neglect friction, turbulence, loss of heat through conduction chambers.

4) Reversible processes

Idealised air-standard Otto cycle of 6 simple processes of an ideal gas.



1)  $5 \rightarrow 1$  Quasi-static intake stroke

Isobaric at atm. pressure

Vol. :  $0 \rightarrow V_1$

Moles :  $0 \rightarrow n_1$

Eq<sup>n</sup> of state

$$P_0 V = n R T_1$$

2)  $1 \rightarrow 2$  Quasi-static adiabatic compression stroke

$$T: T_1 \rightarrow T_2$$

$$\text{Eq}^n \Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

3)  $2 \rightarrow 3$  Quasi-static isochoric increase of T & P of n moles of air, imagined to be brought out about by absorption  $|Q_H|$  from a series of high temp. reservoirs such that  $T: T_2 \rightarrow T_3$

4)  $3 \rightarrow 4$  Quasi-static adiabatic power stroke leading to drop in T:  $T_3 \rightarrow T_4$

$$T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$$

5)  $4 \rightarrow 1$  Quasi-static isochoric drop in T & P of n moles of air, brought about by expulsion of heat  $|Q_L|$  to a series of reservoirs.

$$T: T_4 \rightarrow T_1 \quad T_1: T \text{ of outside air}$$

6)  $1 \rightarrow 5$  Quasi-static exhaust stroke

Isochoric at atm. pressure,

$$V: V_1 \rightarrow 0, \quad n: n \rightarrow 0$$

$$T = T_1$$

$$2 \rightarrow 3 \quad |Q_H| = \int_{T_2}^{T_3} C_v dT = C_v(T_3 - T_2)$$

$$4 \rightarrow 1 \quad |Q_L| = - \int_{T_4}^{T_1} C_v dT = C_v(T_4 - T_1)$$

$$\eta = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

$$T_1 V_1^{Y-1} = T_2 V_2^{Y-1}$$

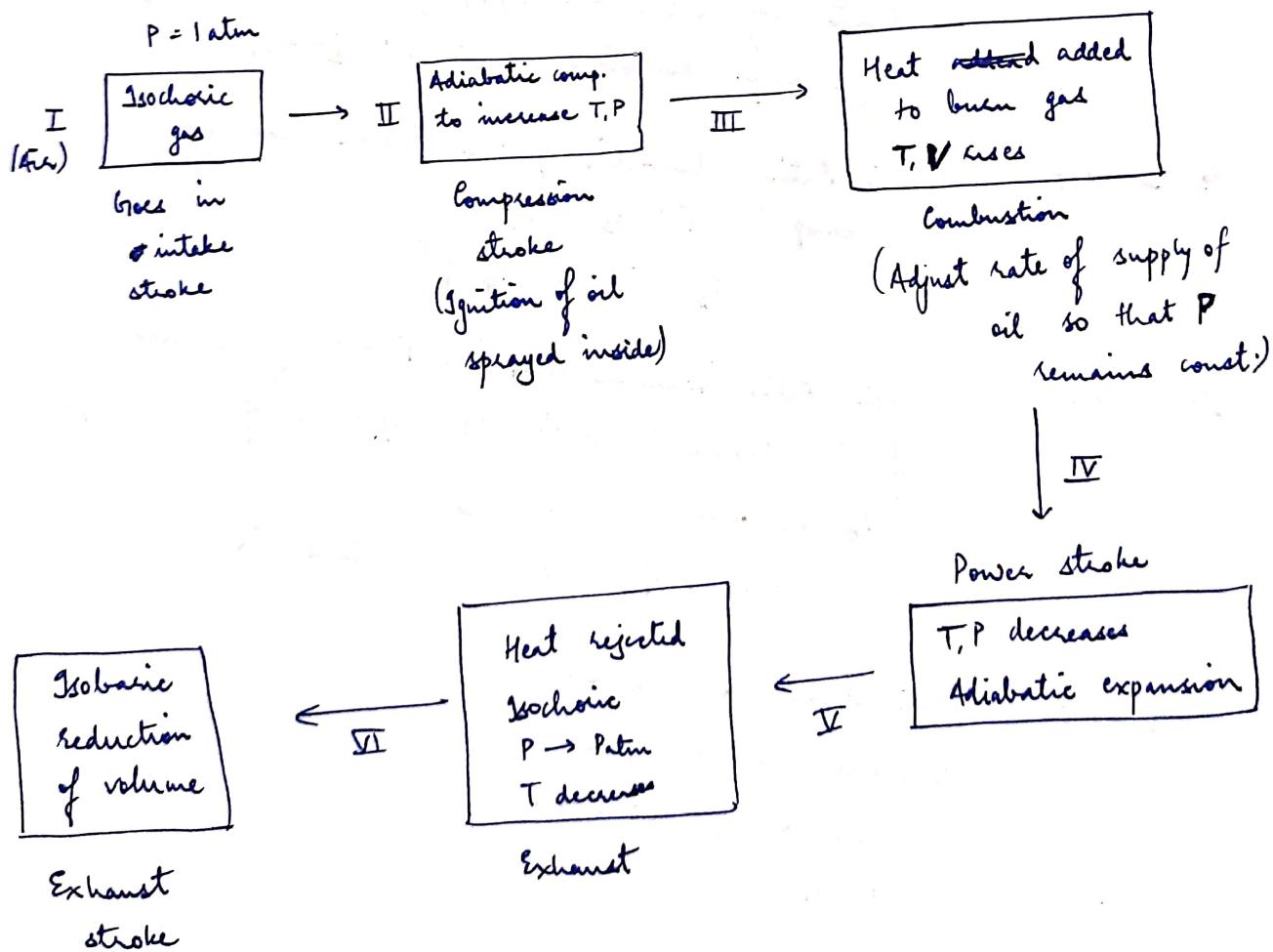
$$T_4 V_1^{Y-1} = T_3 V_2^{Y-1}$$

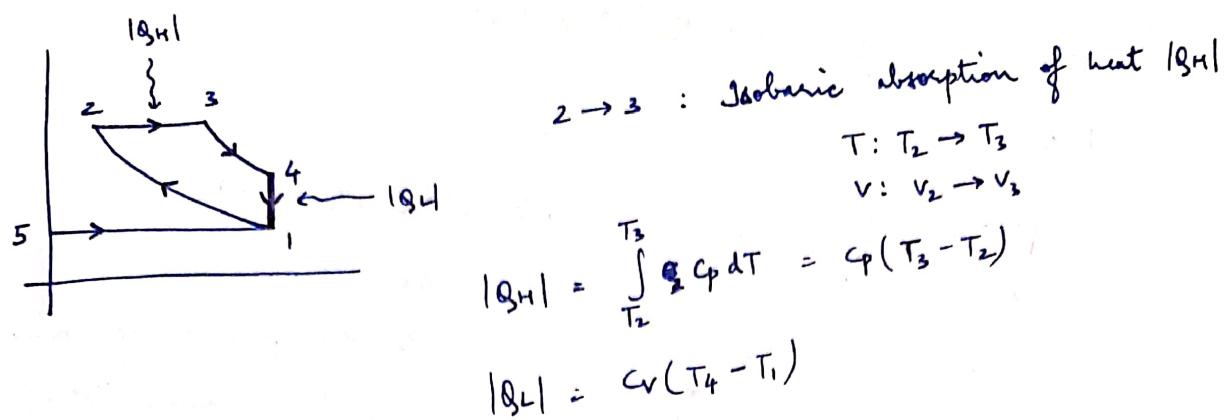
$$\eta = 1 - \frac{T_1}{T_2}$$

$$T_1 = 300 \text{ K} \quad \eta_{\text{theoretical}} = 0.48$$

$$T_2 = 580 \text{ K} \quad \eta_{\text{actual}} = 0.23$$

### Diesel Engine





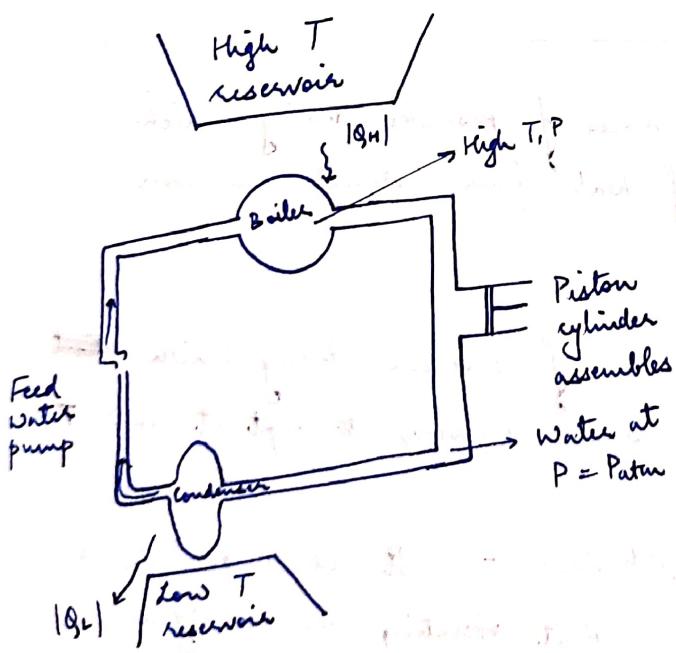
$$\eta = 1 - \frac{1}{\gamma} \frac{T_4 - T_1}{T_3 - T_2}$$

$$\eta = 1 - \frac{1}{\gamma} \left( \frac{\kappa_E^r - 1}{\kappa_E - 1} \right) \frac{T_1}{T_2}$$

$$\kappa_E = \frac{V_1}{V_3} \quad (\text{expansion ratio})$$

2 strokes are enough  $\Rightarrow$  every alternative stroke is a power stroke  $\Rightarrow$  Power is doubled in comparison with Otto cycle.

### Steam Engine



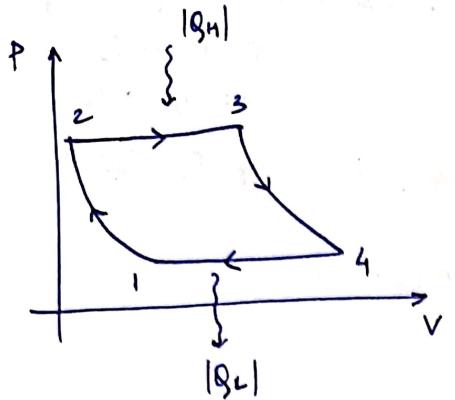
1) Water is heated to boiling point  
 $\downarrow$   
 vapourised, both at const. P

2) Steam is raised to  $T > T_{boiling\ point}$  (at const. P)

3) Steam flows to the cylinder where it expands adiabatically until P, T drops to that of condenser

4) In condenser, the steam condenses into water at same temp. & pressure as the beginning

Idealised  $\Rightarrow$  cycle  $\rightarrow$  Rankine cycle



1: Water at  $P = P_2, T = T_2$

1  $\rightarrow$  2: Adiabatic compression of water to the pressure of boiler ( $T \& V$  change little)

2  $\rightarrow$  3: a) Isobaric heating of water

so that  $T = T_{\text{boiling point}}$

b) Vaporization of water into ~~at~~ saturated steam

c) Superheating of steam so that  $T_{\text{steam}} > T_{\text{b.p.}}$

3  $\rightarrow$  4: Adiabatic expansion of ~~saturated steam~~ superheated steam into wet steam.

4  $\rightarrow$  1: Isobaric, isothermal expansion condensation of steam into water at  $T = T_2$

$|Q_L| \leftarrow$

$$|Q_L| \neq 0 \Rightarrow \eta \neq 1$$

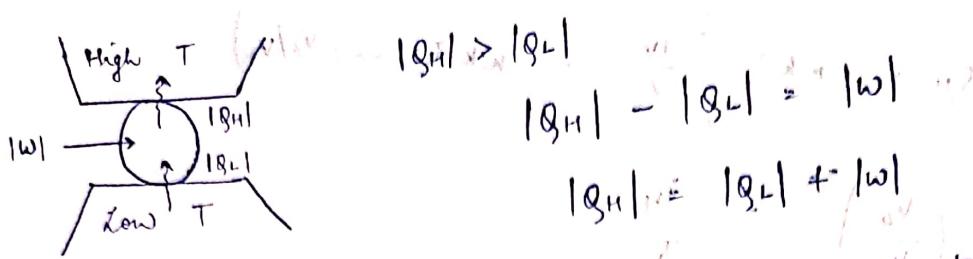
$$\eta = 1 - \frac{|Q_L|}{|Q_H|}$$

There are some processes or series of processes during which there is an absorption of heat from external reservoir kept at high T.

There are some process or series of processes during which heat is rejected to an external reservoir ~~is~~ kept at low T.

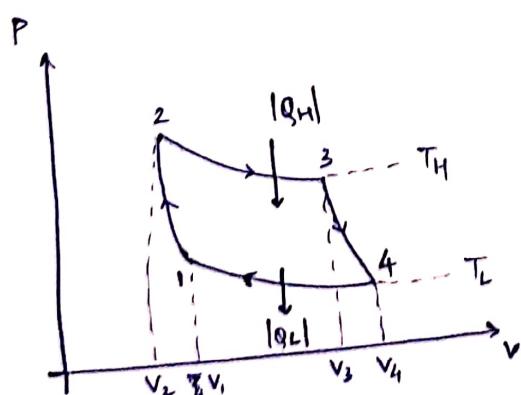
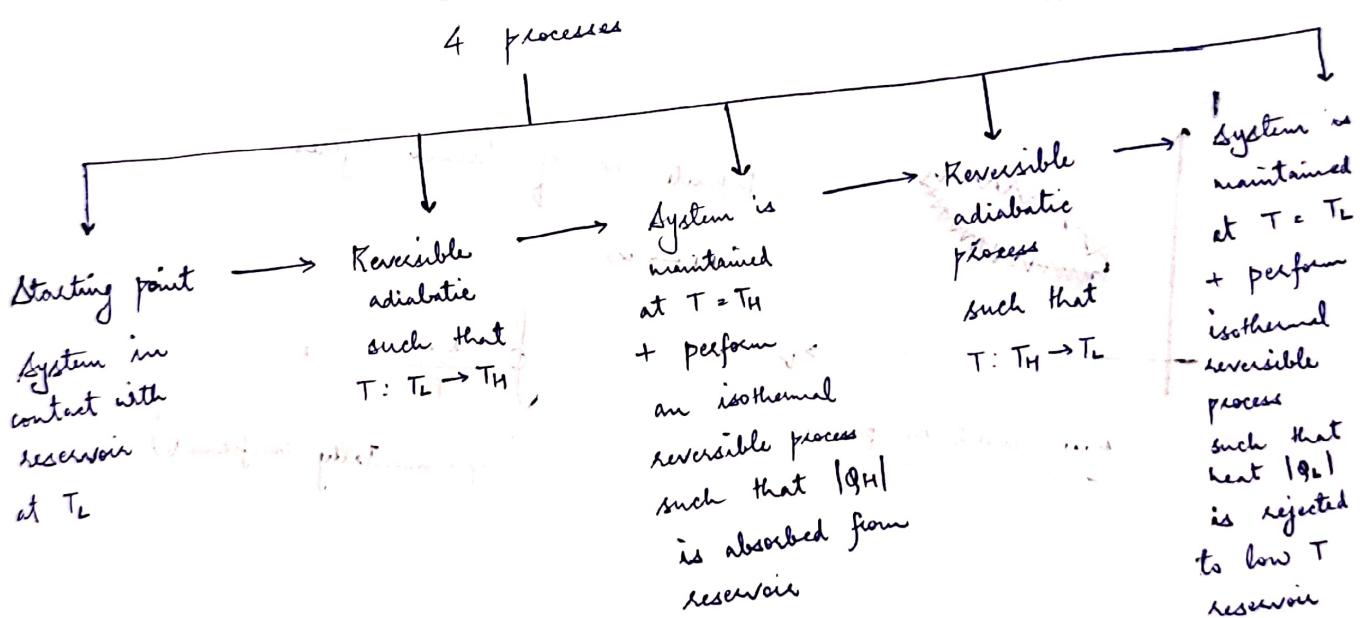
Kelvin-Planck Statement of 2nd Law - It is impossible to construct an engine that operating in a cycle will produce no effect other than extraction of heat from a reservoir & performance of equivalent amount of work.

# Refrigerators



Clausius statement of 2nd Law - it is impossible to construct a refrigerator that operating in a cycle will produce no effect other than transfer of heat from a low  $T$  reservoir to a high  $T$  one.

## Carnot Cycle



1 : 2 → Reversible adiabatic compression to take  $T$  from  $T_L \rightarrow T_H$

$$\left(\frac{V_2}{V_1}\right)^{3/2} = \left(\frac{T_L}{T_H}\right)$$

$$\Delta Q = 0$$

$$\Delta W_{1 \rightarrow 2} = Cv(T_H - T_L)$$

~~2 → 3 :~~

$$\Delta V_{2 \rightarrow 3} = 0$$

$$\Delta W_{2 \rightarrow 3} = -\Delta Q_{2 \rightarrow 3} = -Q_H$$

$$Q_H = n k T_H \int_{V_2}^{V_3} \frac{dv}{v} = n k T_H \ln \left( \frac{V_3}{V_2} \right)$$

~~3 → 4 :~~

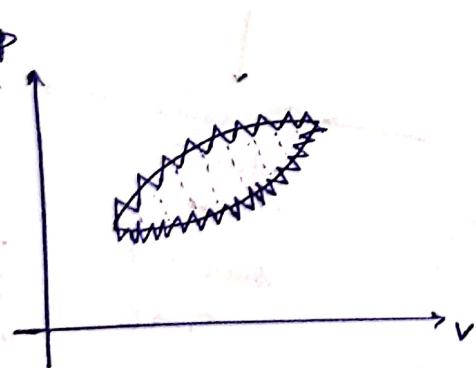
$$\left( \frac{V_4}{V_3} \right)^{3/2} = \frac{T_H}{T_L}$$

$$\Delta W_{3 \rightarrow 4} = \Delta V_{3 \rightarrow 4} = C_V (T_L - T_H)$$

$$4 \rightarrow 1 : \quad \Delta Q_{4 \rightarrow 1} = -\Delta W_{4 \rightarrow 1} = n k T_L \ln \left( V_1 / V_4 \right)$$

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \Rightarrow \text{Valid for all reversible cyclic processes}$$



Any arbitrary process

Infinite no. of Carnot cycles

$N \rightarrow \infty$

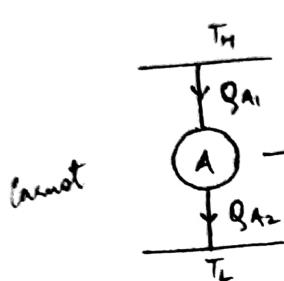
$$\int \frac{dq_{cv}}{T} = 0$$

(experimentally confirmed)

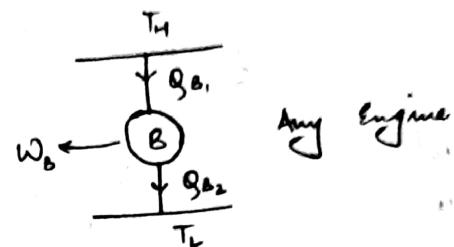
$$\eta = \frac{|W|}{|Q_H|} = \frac{nk(T_H - T_L) \ln(v_2/v_1)}{nkT_H \ln(v_2/v_1)} = 1 - \frac{T_L}{T_H}$$

$\eta < 1 \Rightarrow$  Validates Kelvin's statement

Carnot's Theorem  $\Rightarrow$  No engine operating w/o two reservoirs is more efficient than a Carnot engine operating b/w same two reservoirs.



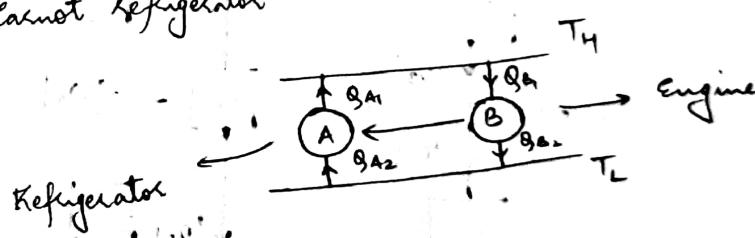
$$\eta_A = \frac{|W_A|}{|Q_{A1}|}$$



$$\eta_B = \frac{|W_B|}{|Q_{B1}|}$$

$$\text{Suppose } \eta_B > \eta_A \Rightarrow \frac{|W_B|}{|Q_{B1}|} > \frac{|W_A|}{|Q_{A1}|}$$

Let B drives A & backwards  
i.e. as a Carnot refrigerator



Let us arrange conditions such that  $|W_A| = |W_B|$   
 $\Rightarrow Q_{A1} > Q_{B1}$

Heat extracted from low T reservoir

$$\text{By A} \Rightarrow (|Q_{A1}| - |W_A|)$$

$$\text{By B} \Rightarrow (|Q_{B1}| - |W_B|)$$

$$\begin{aligned} \text{Net heat extracted from low T reservoir} &\approx (|Q_{A1}| - |W_A|) \\ &\quad - (|Q_{B1}| - |W_B|) \\ &\approx |Q_{A1}| - |Q_{B1}| \end{aligned}$$

Net heat delivered to high T reservoir

$$\Delta Q_H = |Q_{A1}| - |Q_{B1}|$$

$$\Delta Q_L = \Delta Q_H$$

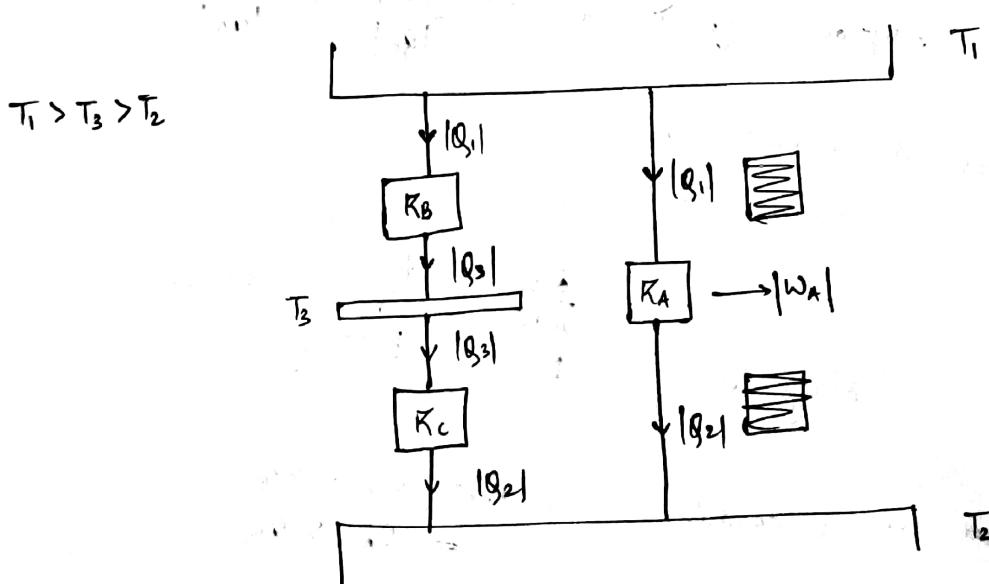
$\therefore$  2nd law violated

$$\therefore \eta_A > \eta_B$$

## Thermodynamic Temperature Scale

$$\eta = 1 - \frac{|Q_L|}{|Q_H|} \quad \frac{|Q_H|}{|Q_L|} = 1 - \phi(T_H, T_L)$$

$$\eta = \phi(T_H, T_L)$$



$$K_A \rightarrow \frac{|Q_1|}{|Q_2|} = f(T_1, T_2)$$

$$R_B + R_C = R_A$$

$$R_B \rightarrow \frac{|Q_1|}{|Q_3|} = f(T_1, T_3)$$

$$R_c \Rightarrow \frac{|Q_3|}{|Q_2|} = f(T_3, T_2) \Rightarrow \frac{|Q_2|}{|Q_3|} = f(T_2, T_3)$$

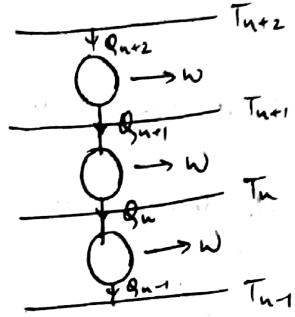
$$\therefore f(T_1, T_2) = \frac{f(T_1, T_3)}{f(T_2, T_3)}$$

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


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$n$  Carnot Engines

where heat rejected by previous is heat absorbed by current one & each one performs same work.



$$\frac{Q_n}{Q_{n+1}} = \frac{T_n}{T_{n+1}}$$

$$\frac{T_n}{Q_n} = \frac{T_{n+1}}{Q_{n+1}} = \alpha \Rightarrow \alpha \text{ is independent of } n.$$

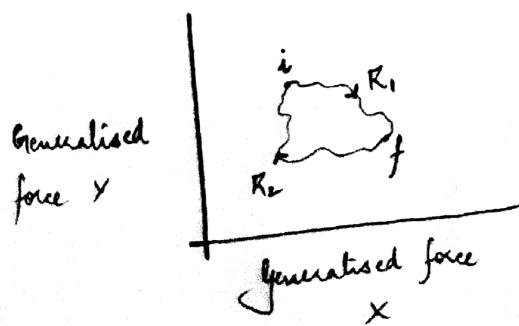
$$\frac{T_n}{T_{n+1}} - \frac{T_n}{Q_n} = \alpha (Q_{n+1} - Q_n) = \alpha w \rightarrow \text{independent of } n$$

$$\text{If } \alpha w = 1K \quad T_{n+1} - T_n = 1K$$

(Absolute Kelvin Scale)

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$$\oint \frac{dQ_{\text{rev}}}{T} = 0 \Rightarrow \text{Clausius Theorem}$$



$$\begin{aligned} \oint \frac{dQ_{\text{rev}}}{T} &= 0 \\ \int_{R_1+R_2}^i \frac{dQ_{\text{rev}}}{T} + \int_{\text{Ref}}^i \frac{dQ_{\text{rev}}}{T} &= 0 \\ \int_{R_1i}^i \frac{dQ_{\text{rev}}}{T} - \int_{R_2i}^i \frac{dQ_{\text{rev}}}{T} &= 0 \end{aligned}$$

$$\int_{T_1, i} \frac{dQ_{rev}}{T} = \int_{T_2, i} \frac{dQ_{rev}}{T}$$

$\Rightarrow \int \frac{dQ_{rev}}{T}$  → independent of any reversible path

$\frac{dQ_{rev}}{T}$  → exact differential

$\rightarrow dS \rightarrow$  exact differential

$$S_f - S_i = \int_i^f \frac{dQ_{rev}}{T} \quad \begin{matrix} S \rightarrow \text{state function} \\ (\text{Entropy}) \end{matrix}$$

$$dQ_{rev} = T dS$$

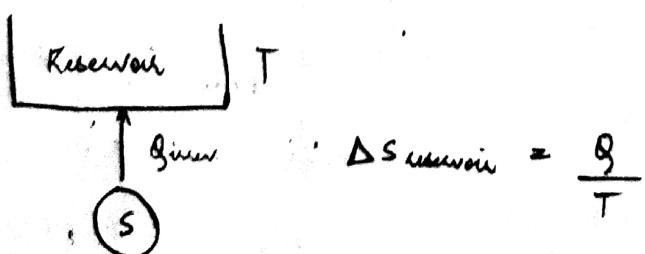
Total amount of heat transferred in a reversible process

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

### Entropy & Reversibility

$$\Delta S_{sys.} + \Delta S_{univ.} = \Delta S \text{ due to the process}$$

$$= \Delta S_{universe}$$



$$\Delta S_{reservoir} = \frac{Q}{T}$$

Consider  $\Delta S_{univ}$  due to reversible process  
 Process will be accompanied by heat flow b/w system & a set of reservoirs  
 $(T_i \leq T \leq T_f)$

Let, during any infinitesimal part of the process,  $dQ_{univ}$  is transferred b/w system & one of the reservoirs at  $T$ .

If  $dQ_{univ}$  is absorbed by system

$$dS_{system} = \frac{dQ_{univ}}{T}, \quad dS_{reservoir} = -\frac{dQ_{univ}}{T}$$

$$dS_{univ} = 0$$

For a finite process,  $\Delta S_{univ} = 0$

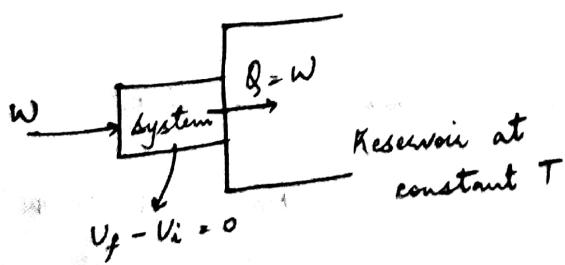
### Inevitability

$$\Delta S_{system} = \int_{R_i}^f \frac{dQ}{T}$$

a) Processes involving external mechanical irreversibility

e.g. Friction from 2 solids in contact with a reservoir

↳ Isothermal dissipation of work through a system into internal energy of reservoir



state doesn't change

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

$$\Delta S_{reservoir} = \frac{Q}{T}$$

$$\Delta S_{univ} = \frac{Q}{T} > 0$$

e.g. Friction from rubbing thermally insulated liquids  
 ↳ Adiabatic dissipation of work into internal energy of a system open to atmosphere

$$\Delta S_{\text{surroundings}} = 0$$

$$W \rightarrow U_{\text{system}} \rightarrow \text{Temp. rises from } T_i \text{ to } T_f$$

Irreversible process is replaced by a reversible isobaric flow of heat from a series of reservoirs ranging from  $T_i \rightarrow T_f$

$$\Delta S_{\text{system}} = \int_{\text{Rev } T_i}^{T_f} \frac{dQ}{T}$$

$$dQ = C_p dT$$

$$\Delta S_{\text{system}} = \int_{T_i}^{T_f} \frac{C_p dT}{T}$$

$$\therefore C_p + C_p(T)$$

$$\Delta S_{\text{system}} = \int C_p \ln \left( \frac{T_f}{T_i} \right) > 0$$

$$\Delta S_{\text{universe}} > 0$$

b) Process involving internal mechanical ~~work~~ irreversibility.

Transformation of  $U_{\text{system}}$  → Mechanical energy & then back to  $U$ .

(system is enclosed by adiabatic wall)

Free expansion of gas

$$\Delta S_{\text{surroundings}} = 0$$

Reversible process

$V_i \rightarrow V_f$  at  $T$

$$\Delta S_{\text{system}} = \int_{V_i}^{V_f} \frac{dq}{T}$$

Reversible process

Isothermal expansion

$$dV = 0 \Rightarrow dS_{\text{env}} = \frac{pdV}{T}$$

$$\Rightarrow \frac{dS_{\text{env}}}{T} = nR \frac{dV}{V}$$

$$\Delta S_{\text{system}} = nR \ln\left(\frac{V_f}{V_i}\right) > 0$$

$$\Delta S_{\text{universe}} > 0$$

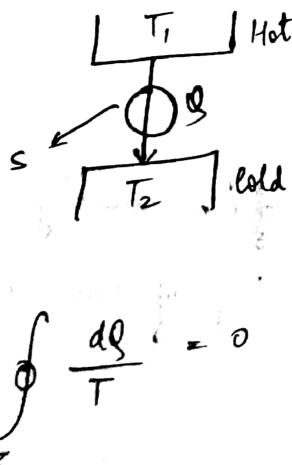
c) Process involving external thermal irreversibility

Process involving heat transfer by virtue of finite  $T$  difference

Conduction of heat from system to cooler surroundings

Conduction of heat through a system from hot to

cold reservoir

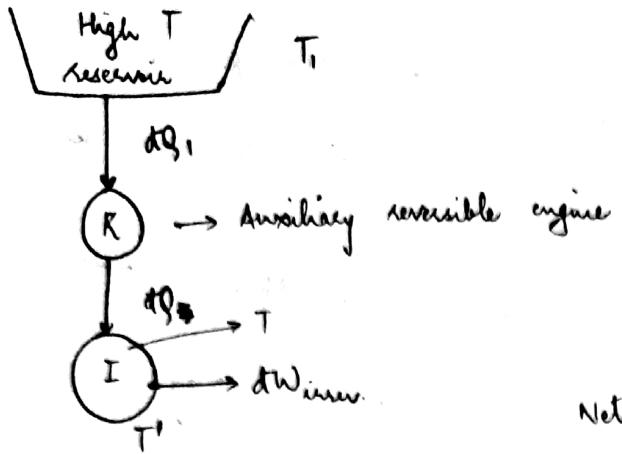


$$\Delta S_{\text{system}} = -\frac{Q}{T_1}$$

$$\Delta S_{\text{univ.}} = Q/T_2$$

$$\Delta S_{\text{universe}} = Q \left( \frac{1}{T_2} - \frac{1}{T_1} \right) > 0$$

$\int_{V_i}^{V_f} \frac{dq}{T} = 0 \rightarrow \text{Clausius Theorem}$   
(Reversible part of 2nd law)



$R + I \rightarrow$  irreversible cycle

$$R: dW_R = dQ_1 - dQ_R$$

$$I: dW_I = dQ_I$$

Net work in  $R + I$

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

$$\oint dQ_1 < 0$$

$$\frac{dQ_1}{T} = -\frac{dQ}{T}$$

$$\int_R^I -\frac{dQ}{T} = \frac{1}{T_1} \int_K^Q dQ_1$$

$$\Rightarrow T_1 \int_I^R \frac{dQ}{T} = \int_K^Q dQ_1 < 0$$

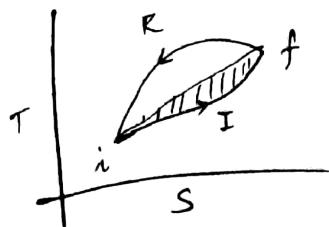
2<sup>nd</sup> law

$$\int \frac{dQ}{T} \leq 0 \quad dQ > 0 \quad T' \leq T$$

Reversible  $\Rightarrow T =$  temp. of reservoir or surrounding

Irreversible  $\Rightarrow T =$  Temp. of auxiliary of reservoir

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



$$\int f ds = 0$$

$$\int_{Ii}^f ds + \int_{Rf}^i ds = 0 \quad \text{--- (1)}$$

$$\int_I^f \frac{dQ}{T} = \int_{Ii}^f \frac{dQ}{T} + \int_{Rf}^i \frac{dQ}{T} \quad \text{--- (2)}$$

$$(1) - (2) \Rightarrow$$

$$\int_{Ii}^f ds - \int_{Ii}^f \frac{dQ}{T} > 0$$

$$\int_{Ii}^f ds > \int_{Ii}^f \frac{dQ}{T}$$

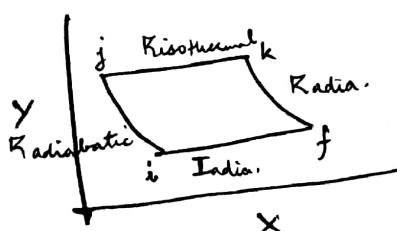
$$ds \geq \frac{dQ}{T}$$

$$ds_{\text{irr}} > \frac{dQ_{\text{irr}}}{T}$$

### Principle of Increase of Entropy

$$I : \Delta S_{\text{universe}} > 0$$

Adiabatic I process b/w two  $\neq$  eqbm. states



$$I \Rightarrow I_{\text{adiab.}} = \Delta S = s_f - s_i$$

$$II \Rightarrow f \rightarrow k \quad T_{\text{sys.}} = T_{\text{reservoir}} = T' \\ s_f = s_k$$

$$\Delta S = s_k - s_i$$

$$III \Rightarrow \text{Isothermal} =$$

$$k \rightarrow j \quad s_j = s_i$$

$$\Delta S = s_k - s_j$$

$$Q_R = T'(s_j - s_k) \leq 0$$

$$T'(s_k - s_j) \geq 0$$

$$s_k - s_j = \Delta S \geq 0$$