

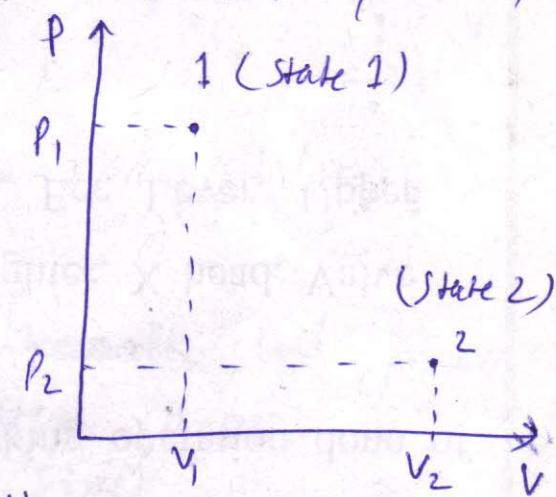
Thermodynamic State, Path, Process & Cycle:

The physical condition of a thermodynamic system at any time is known as thermodynamic state of system, if it is described by a set of thermodynamic properties.

Ex: 5 kg of gas is kept at a pressure of 5 MPa & temp. of 350 K.

The state of the system is described by thermodyn. co-ordinates on property diagram.

Any operation; in which at least one of the properties of system changes is known as change of state,



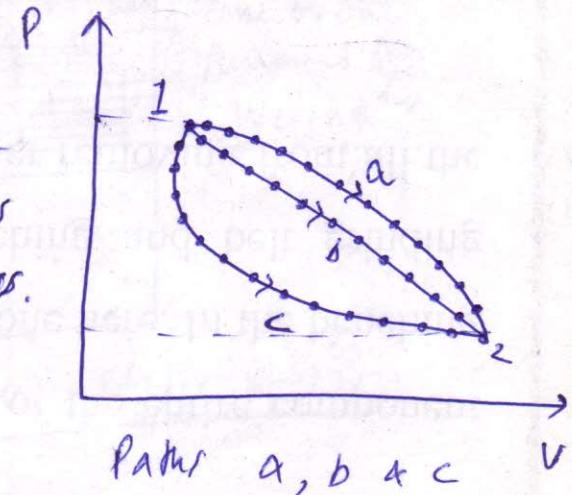
The locus of the infinite intermediate states, during a change of state is known as thermodyn. path.

If during a change of state; the path is completely specified; it is known as a thermodynamic process.

Ex: Process 1 a 2

.. 1 b 2

.. 1 c 2

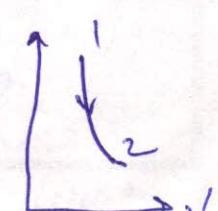
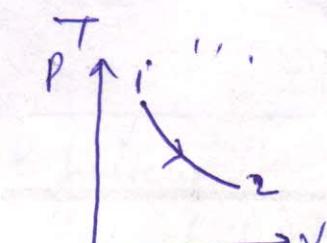
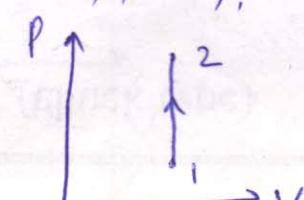
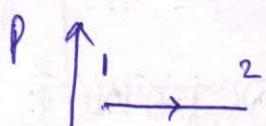


An isobaric process is a const. P process,

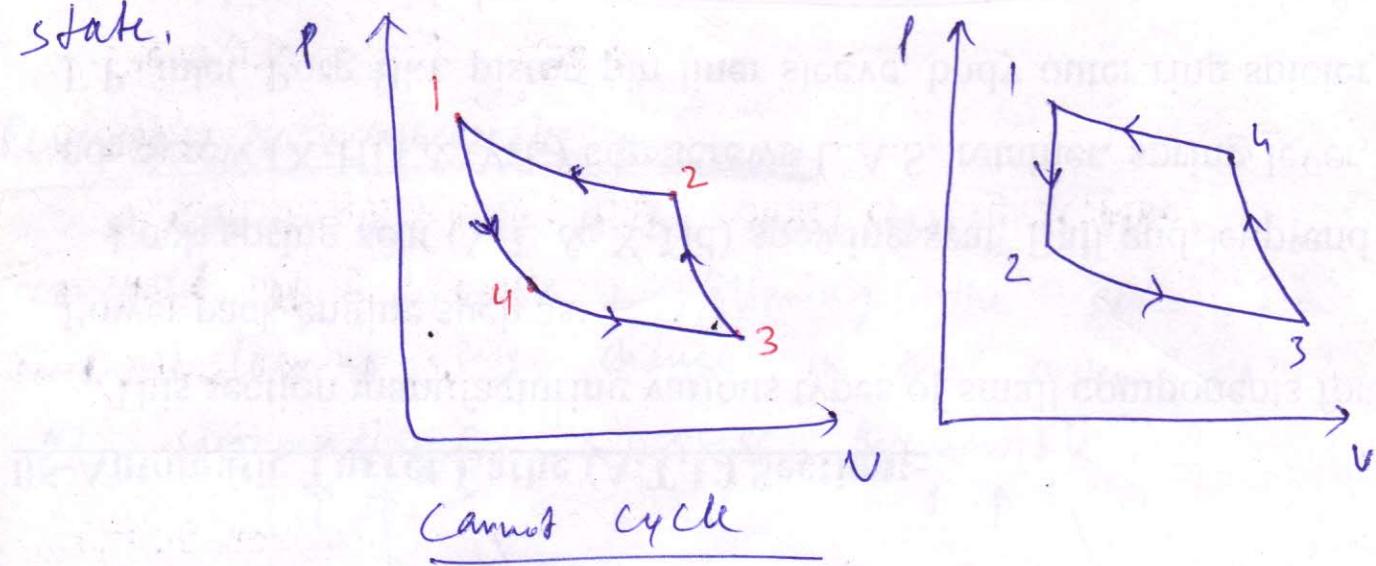
.. Isobaric V ..

.. Adiabatic .. is Heat .. (No heat flow)

.. Isotermal



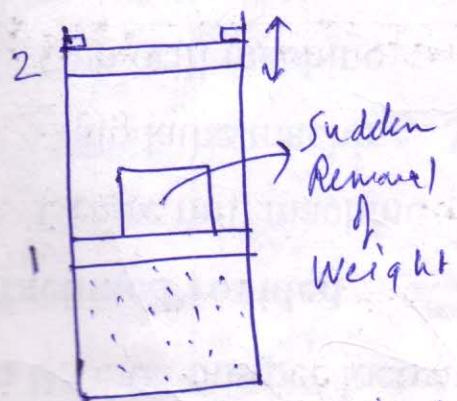
A thermodynamic cycle is a series of thermodynamic processes such that the final state is coinciding with the initial state.



QUASI-STATIC PROCESS

is known as a

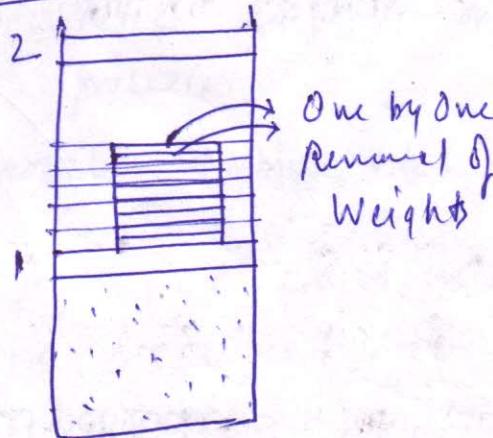
QUASI: Almost



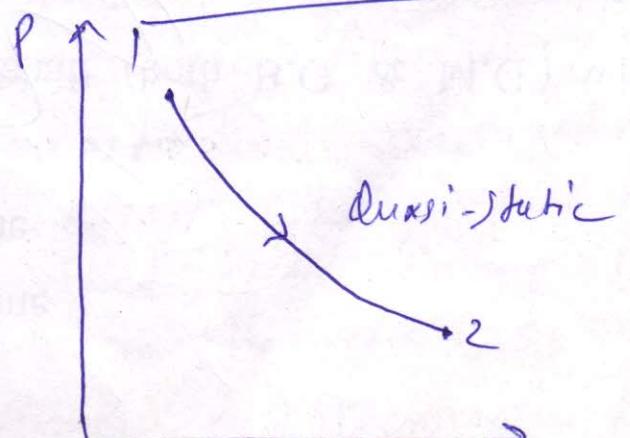
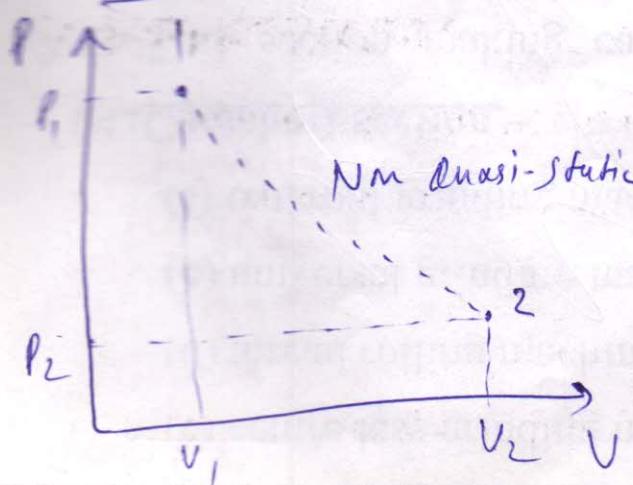
Nm Quasi-Static Process

An infinitesimally slow process
Quasi-static Process,

Static: Fixed



Quasi-Static Process

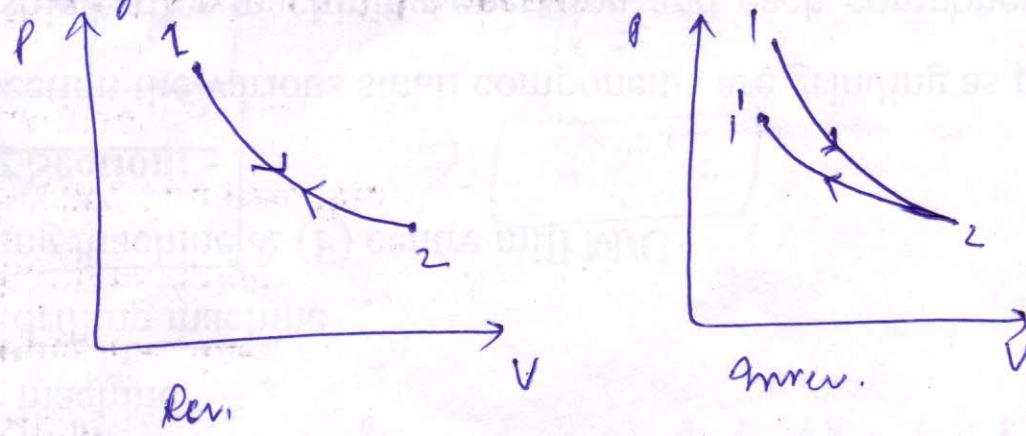


Experiments (All intermediate states are clear)

A quasi-static process is represented by a continuous line on property diagrams & non-quasi-static by a dashed line.

Reversible & Irreversible processes

A process is said to be reversible; if it can be reversed in direction; following the same path; without leaving any change in the system as well as surroundings, otherwise irreversible.



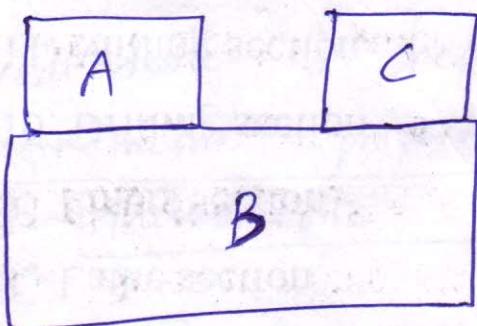
- Ex: • A frictionless quasi-static expansion or compression of a gas is a rev. proc.,
• Ideal flow through a nozzle, turbine etc. Irrev.

CONCEPT OF CONTINUUM: For continuum condition, the matter is assumed to be continuously distributed throughout the system, without any voids or gaps in between. For Classical Thermodynamics or Macroscopic Approach, the continuum condition must be satisfied.

But in some cases like: Space research, the matter (gas) is rarified, so continuum is not satisfied, as voids exists in between, so there, we use Statistical Thermodynamics or Microscopic Approach.

Zeroth Law of Thermodynamics : If a body

A is in thermal equilibrium with body B & body B is in thermal equilibrium with body C ; then Body A & Body C will be in thermal equilibrium, without even in direct contact.



$$\begin{aligned} T_A &= T_B \\ T_B &= T_C \\ \Rightarrow T_A &= T_C \end{aligned}$$

Zeroth law is the basis of Thermometry

i.e. the science of temp. measurement.

• R.H. Fowler gave Zeroth law in 1931. (VERY NEW)

Temperature Measurement (Thermometry)

Temperature difference is the driving potential; which causes the heat transfer.

• $q_f(T)$ is also said as the degree of hotness or coldness of any body.

Temperature is the measure of the mean K.E. of the molecules of any ~~object~~ system,

Unlike other properties like Mass, Volume, length etc. of the system ; temperature is not directly seen or measured. But temperature is measured in the form of some physical characteristic of the

Material; which varies with temperature in a predictable & repeatable way. Now the change in this property is taken as an indication of the change in temperature.

The device, which is used to measure temp., is known as a thermometer; the physical property; which changes with r.t. temp. in a predictable & repeatable way, is known as thermometric property & the material is known as thermometric material.

Ex: ① In Mercury in Glass Thermometer; Hg is thermo. material; expansion in the length of Hg column is^{used as} the thermometric property.

② In case of Thermistor (Resistance Thermometer); A metal like Pt etc. is thermo. material & resistance acts as a thermometric property.

$$R_t = R_0 (1 + \alpha \cdot t)$$

R_0 = Resist. at 0°C ; α = const (dependent on Metal)

$$R_t = " " " t^\circ\text{C}$$

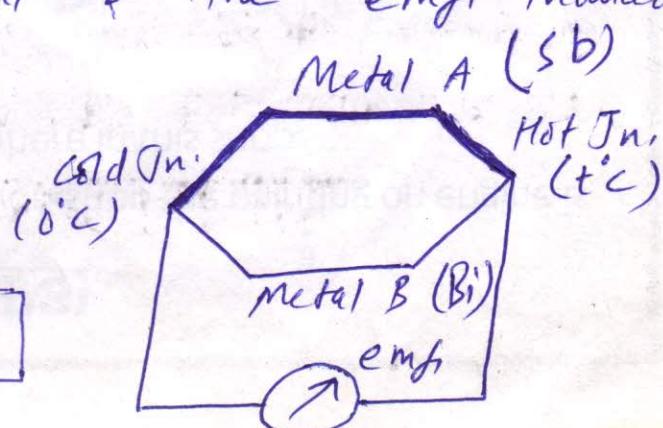
③ In case of a thermocouple; Bimetallic joint acts as thermometric material & the emf induced is the the property.

$$\text{emf} \propto t$$

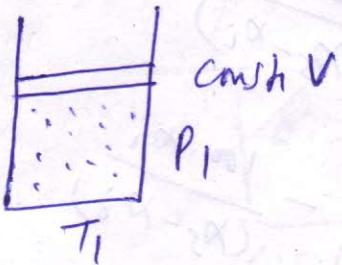
$$\text{when } t = 0^\circ\text{C}$$

$$\text{emf} = 0$$

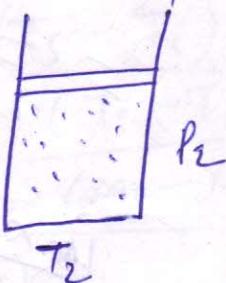
Pt-Rh



④ In case of const Vol. ideal Gas Thermometer;
ideal Gas is the thermo. material & pressure acts
as thermometric property.



$$P_1 \propto T_1$$



$$P_2 \propto T_2$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Reference Points & Temperature Scales:

- The thermometric property must vary uniformly w.r.t temp.; within the measurable temp. range.

Suppose the temp. varies linearly w.r.t. thermometric property, i.e.

$$T \propto x$$

or $T = a \cdot x + b$

--- $x = \text{th. property}$
 $a+b = \text{constant}$

Now some reference points are required for the calibration of this temp. scale.

Before 1954: 2 std. reference points;

① F.P. or I.P. of water (0°C)

② S.P. or B.P. of .. (100°C)

* Reference points correspond to easily reproducible state.

Now from ① : for F.P. $T_{F.P.} = a \cdot x_{F.P.} + b$

$$\text{or } T_i = a \cdot x_i + b$$

for B.P. $T_s = a \cdot x_s + b$

After 1954

Only single Reference Point i.e.

Triple point of water (273.16 K) is used for calibration of the thermometer.

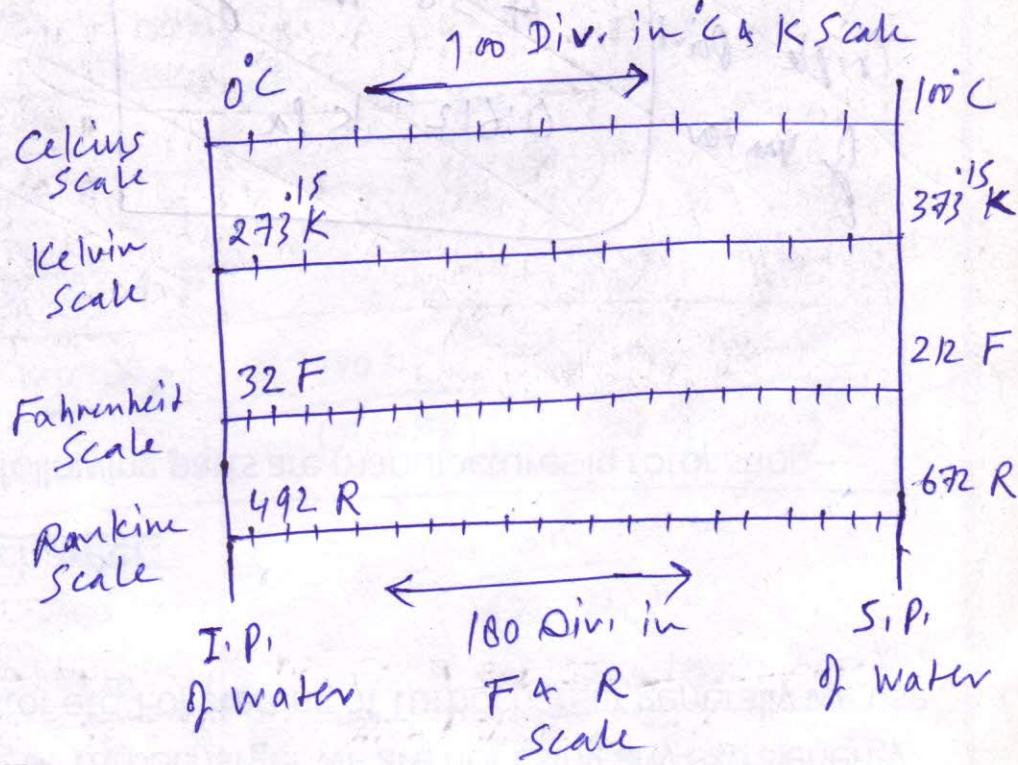
Triple Point: At which all the 3 phases, viz. 1 solid, liquid & gas co-exist in equilibrium
e.g. for water (0.01°C or 273.16 K)

$$\Rightarrow T_{tp} = \alpha \cdot x_{tp} \Rightarrow \alpha = \frac{T_{tp}}{x_{tp}}$$

$$\text{Now } T = \alpha \cdot x$$

$$T = \frac{T_{tp} \cdot x}{x_{tp}}$$

Temperature Scales



From the eqn

$$\frac{T - T_i}{T_s - T_i} = c$$

$$\frac{c - 0}{100 - 0} = \frac{K - 273.15}{373.15 - 273.15} = \frac{F - 32}{212 - 32} = \frac{R - 492}{672 - 492}$$

$$\left[\frac{c}{s} = \frac{K - 273.15}{s} = \frac{F - 32}{9} = \frac{R - 492}{9} \right] \checkmark$$

Note: All the thermometers will give the same reading at the calibration points i.e. reference points ($T_{\text{F.P.}}$ & $S_{\text{P.}}$ of water); but it is not necessary that they will give the same reading in between these reference points; that's why temp. scales are said to be ARBITRARY in nature.

Prob! A new temp. scale in $^{\circ}\text{N}$ is defined with F.P. at 100°N & B.P. at 400°N ; Establish a correlation between $^{\circ}\text{C}$ & $^{\circ}\text{N}$.

$$\text{Soln} \quad ^{\circ}\text{C} : \quad 100 = a \cdot x_s + b \quad ; \quad 0 = a \cdot x_i + b \\ \Rightarrow b = -a \cdot x_i$$

$$100 = a \cdot x_s - a \cdot x_i$$

$$a = \frac{100}{(x_s - x_i)} \quad ; \quad b = -\frac{100 \cdot x_i}{(x_s - x_i)}$$

$$^{\circ}\text{N} \quad 400 = a \cdot x_s + b \quad ; \quad 100 = a \cdot x_i + b$$

$$T_c = \frac{100 \cdot x_s}{(x_s - x_i)} - \frac{100 \cdot x_i}{(x_s - x_i)} = \frac{100(x - x_i)}{(x_s - x_i)} \quad (1)$$

$$a(x_s - x_i) = 300 \quad \Rightarrow \quad a = \frac{300}{(x_s - x_i)}$$

$$b = 100 - \frac{300 \cdot x_i}{(x_s - x_i)} = \frac{100x_s - 100x_i - 300x_i}{(x_s - x_i)}$$

$$b = \frac{100x_s - 400x_i}{(x_s - x_i)}$$

$$T_N = \frac{300 \cdot x}{(x_s - x_i)} + \frac{100x_s - 400x_i}{(x_s - x_i)}$$

$$T_N = \frac{300(x - x_i)}{(x_s - x_i)} + 100$$

from eq. (1) $\quad T_N = 3T_c + 100$

Ans

or direct Approach

$$\frac{T_c - 0}{100 - 0} = \frac{T_N - 100}{400 - 100}$$

$$\frac{T_c}{100} = \frac{T_N - 100}{300}$$

$$T_N = 3T_c + 100$$

Ans

Q: On a thermocouple; the emf induced for $t^{\circ}\text{C}$ temp. is given as $E = 0.0031t - 5 \times 10^{-7}t^2 + 0.15 \times 10^{-3}$ Volts. Thermometer is having reference junction at I.P. & is calibrated at I.P. & S.P. What temp. shall be shown by thermocouple for a substance at 30°C .

Soln.

$$E_i = 0.15 \times 10^{-3} \text{ Volts}$$

$$E_s = 0.0031 \times 100 - 5 \times 10^{-7} \times 10^4 + 0.15 \times 10^{-3} = 0.3005 - 0.005 = 0.2955 \text{ V}$$

$$= (0.0265 \text{ Volts}) \quad 0.3 - 0.15 \times 10^{-3}$$

$$\frac{T - T_i}{T_s - T_i} = \frac{x - x_i}{x_s - x_i} = \frac{E - E_i}{E_s - E_i} \quad (\text{Here } x = E)$$

$$E = E(30^{\circ}\text{C}) = 0.0031 \times 30 - 5 \times 10^{-7} \times 900 + 0.15 \times 10^{-3}$$

$$= 9.14 \times 10^{-3} \text{ Volts.} \quad = 0.09 - 4.5 \times 10^{-4} + 0.15 \times 10^{-3}$$

$$\frac{T - 0}{100 - 0} = \frac{9.14 \times 10^{-3} - 0.15 \times 10^{-3}}{0.0265 - 0.15 \times 10^{-3}} = 9.0 \times 10^{-3} - 0.45 \times 10^{-3} + 0.15 \times 10^{-3}$$

$$T = 33.23^{\circ}\text{C}$$

$$\frac{T}{100} = \frac{9.0 \times 10^{-3} - 0.15 \times 10^{-3}}{0.2955 - 0.15 \times 10^{-3}} = \frac{8.85 \times 10^{-3}}{0.2955 - 0.15 \times 10^{-3}}$$

Q1 An am unknown temp. scale ; F.P. of water is $0^\circ X$ & B.P. is $1000^\circ X$. Obtain a conversion relation b/w degree X & ${}^{\circ}\text{C}$. Also determine Abs. zero in ${}^{\circ}X$.

Sol: We know, for all scales: $\frac{T - T_i}{T_s - T_i} = c$

$$\Rightarrow \frac{c - 0}{100 - 0} = \frac{x - 0}{1000 - 0}$$

$$x = 10c$$

$$\boxed{\text{Absolute zero in } X = 10 \times (-273.15) = -2731.5 {}^{\circ}X}$$

ENERGY & ENERGY INTERACTIONS

Energy is defined as the capacity to produce a change from existing conditions or capacity to do work. When energy is added to or subtracted from a system, a change in one or more properties of the system takes place.

Energy may exist in two forms :

- ① Stored Energy (Contained within system boundary ; e.g. : K.E., P.E., Int. Energy etc.)
- ② Energy in Transit (which crosses the system boundary e.g. Heat, Work, Electricity etc.)

ENERGY of a System

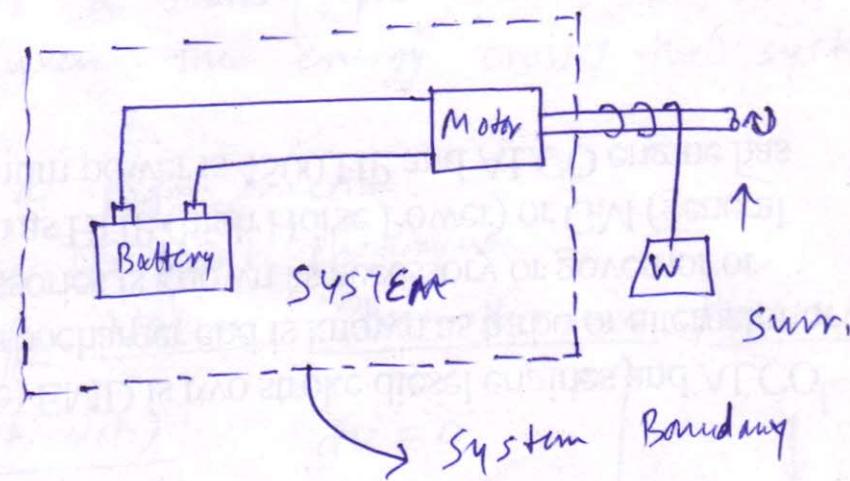
Microscopic (Qnt En., Sens. En., Chem., Nucl. etc.)

Macroscopic (KE, PE etc.)

Any system can have the following energy interactions:

- (a) Work anti. } Closed system
- (b) Heat anti. } Open System
- (c) Mass anti.

(a) Work interaction: Work is the energy transfer associated with force accompanied by some displacements in thermo.; work is said to be done by a system; if the sole effect on the surroundings can be reduced to raising of weights; though weights may not actually be raised.



in thermo.; two types of work are taken into consideration
 ① Displacement Work (P.dV Work) or Boundary Work

② shaft work

① Displacement Work (P.dV Work):

work done for the infinitesimal displacement $a \rightarrow b$:

$$\delta W = F \cdot dx$$

$$= (P \times A) \cdot dx$$

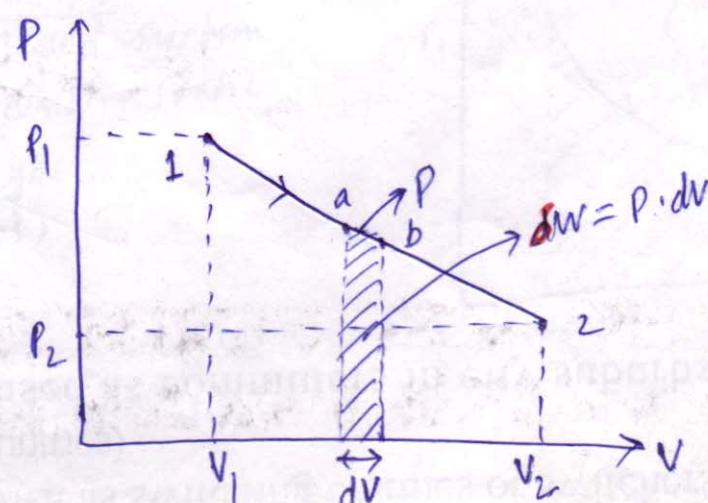
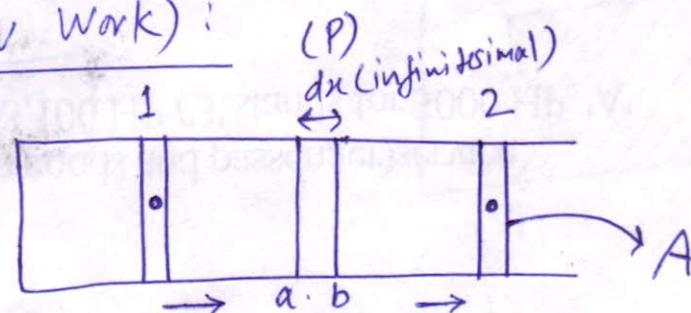
$$= P \times (A \cdot dx)$$

$$\delta W = P \times dV$$

Total Work

$$W = \int_a^b \delta W$$

$$[W = \int_{V_1}^{V_2} P \cdot dV]$$



- [for closed system, Quasi-static process]

So work done by/on a closed system during a Quasi-static (Reversible) process is equal to the area under the P-V diagram, when projected on volume axis.

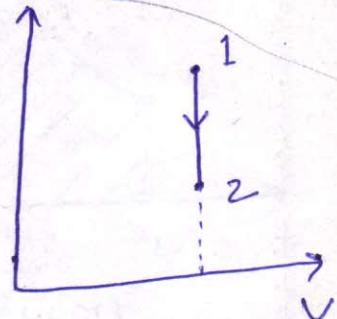
Important Points regarding Work:

- ① Work done is an exact differential. ($\int_1^2 dw \neq w_2 - w_1$)
- ② Work interaction is a boundary phenomenon, i.e., work takes place, only when the energy crosses the system boundary.
- ③ Work done is a path function.
- ④ Work done ... Transient phenomena.

Work interaction for Various Thermodynamic Processes:

① Isochoric Process (Const. Vol.):

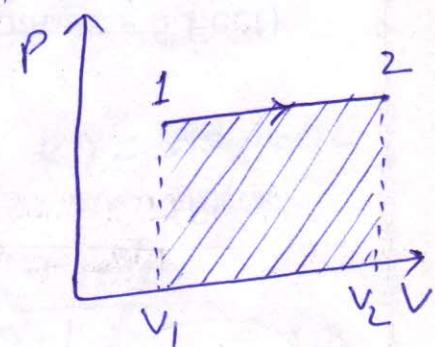
$$dV = 0$$



② Isobaric or Isopiestic Process (Const. Pressure):

$$W = \int_1^2 P \cdot dV = P \cdot [V]_{V_1}^{V_2}$$

$W_{1-2} = P \cdot [V_2 - V_1]$



③ Isothermal Process (Const. Temp.):

$$W = \int_1^2 P \cdot dV \quad * \text{Closed System}$$

$* \text{Quasi-static}$

We know; for an ideal gas:

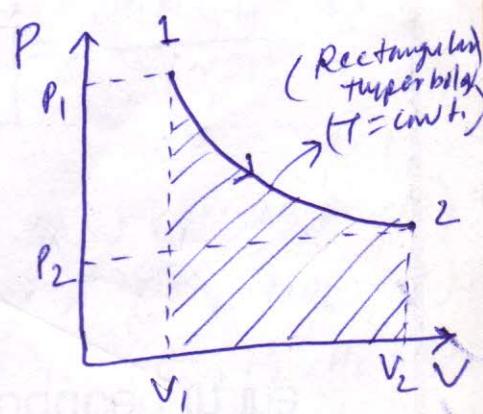
$$P \cdot V = m \cdot R \cdot T = C \quad (\text{const.})$$

$$P = \frac{C}{V}$$

$$\Rightarrow W = \int_1^2 \frac{C}{V} \cdot dV = C [\ln V]_{V_1}^{V_2}$$

$$= C [\ln V_2 - \ln V_1] = C \ln \left(\frac{V_2}{V_1} \right)$$

$W = C \ln \left(\frac{V_2}{V_1} \right)$



Now, as $[P_1V_1 = P_2V_2 = mRT_1 = mRT_2 = C]$

$$\text{as; } P_1V_1 = P_2V_2 \Rightarrow \left[\frac{V_2}{V_1} = \frac{P_1}{P_2} \right]$$

$$W = C \ln \left(\frac{V_2}{V_1} \right) = C \ln \left(\frac{P_1}{P_2} \right)$$

④ Adiabatic Process (NO heat Flow):

* Closed System
* Quasi-static

$$W = \int_1^2 P dV$$

For adiabatic process: $P_1V_1^\gamma = C$

$$W = \int_1^2 \frac{C}{V^\gamma} dV = C \int_{V_1}^{V_2} \frac{dV}{V^\gamma}$$

$$= C \cdot \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2}$$

$$= C \cdot \left[\frac{V_2^{-\gamma+1} - V_1^{-\gamma+1}}{1-\gamma} \right] = \frac{C \cdot V_2^{-\gamma+1} - C \cdot V_1^{-\gamma+1}}{1-\gamma}$$

Now; as $[P_1V_1^\gamma = P_2V_2^\gamma = C]$ $\because \gamma = \text{Adiabatic index}$

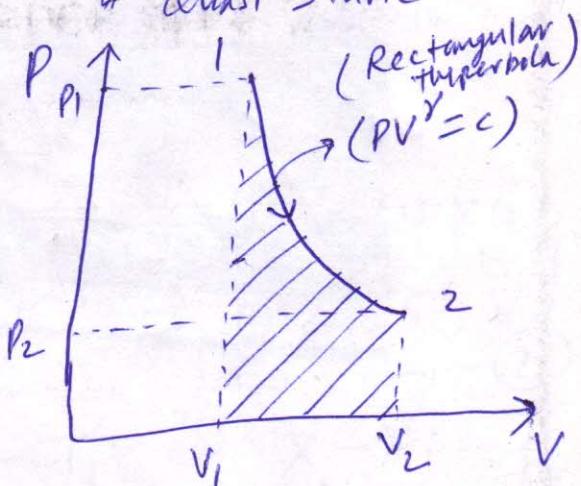
$$W = \frac{P_2V_2^\gamma \cdot V_2^{-\gamma+1} - P_1V_1^\gamma \cdot V_1^{-\gamma+1}}{1-\gamma} = \frac{P_1V_1 - P_2V_2}{\gamma-1}$$

$$W_{\text{Adiab.}} = \frac{P_1V_1 - P_2V_2}{\gamma-1} = \frac{mR(T_1 - T_2)}{(\gamma-1)}$$

$\gamma = 1.67$ for Monoatomic Gases (He, Ne, Ar etc.)

$\gamma = 1.33$ " Polyatomic " (CO₂, NO₂ etc.)

$\gamma = 1.4$ " Diatomic " (O₂, N₂, H₂ etc.)



⑤ Polytropic Process: $[P \cdot V^n = C]$ -- $(-\infty < n < \infty)$

Generally (from Appln. pt. of view): $1 < n < \gamma$

$$W = \int_{V_1}^{V_2} P \cdot dV = \int_{V_1}^{V_2} \frac{C}{V^n} \cdot dV$$

$$W = \frac{P_1 V_1 - P_2 V_2}{n-1} \quad (n \neq 1)$$

(similar to Adiabatic work derivation)

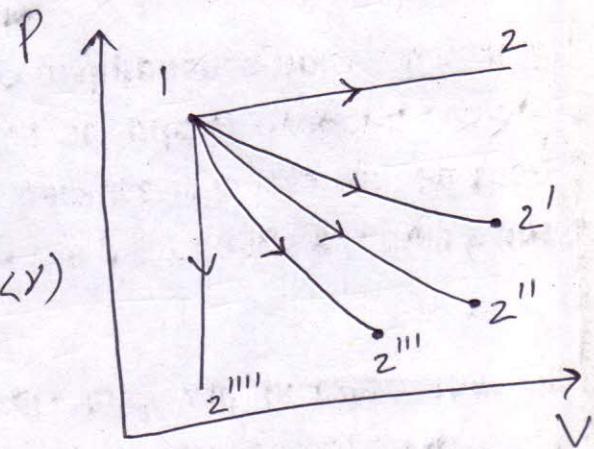
$1-2 \Rightarrow$ Isobaric Process

$1-2' \Rightarrow$ Isothermal " $(n=1)$

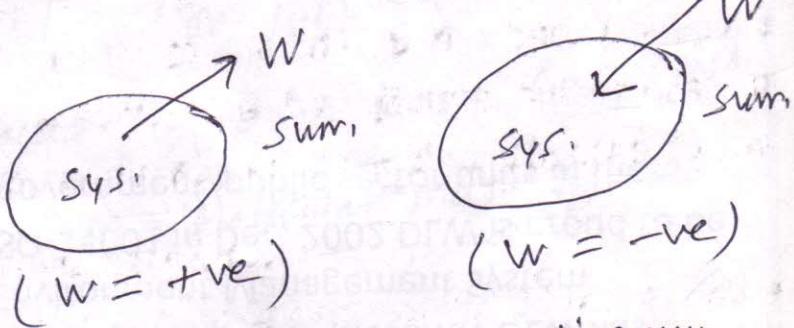
$1-2'' \Rightarrow$ Adiabatic " $(n=\gamma)$

$1-2''' \Rightarrow$ Polytropic " $(n=n, 1 < n < \gamma)$

$1-2'''' \Rightarrow$ Isochoric " $(n=\infty)$



NOTE: • Work done by the system is taken +ve
• vice-versa.



- All left to Right processes on P-V diagram represent work done by the system & vice-versa
- All clockwise (CW) cycles on P-V diagram represent work producing devices & vice-versa
- Area enclosed by the cycle on P-V diagram represents net work interaction during the cycle.

Ideal Gas Behavior:

Favorable conditions: low P; High T, compared to critical T & P.

Assumptions for I.G.B.:

Intermolecular forces are negligible.

(1) Intermolecular forces are negligible,
(2) the volume occupied by gas molecules is negligible,
compared to the container volume.

- All the substances that occur as gases naturally, will be taken as ideal Gases.
e.g.: N₂, O₂, CO₂, H₂, Air etc.
- Water vapour will always be treated as ideal gas, unless mentioned.
- Steam will never be treated as ideal gas, unless mentioned.

Ideal Gas Eqn.:

$$P \cdot V = m \cdot R \cdot T \quad [P \cdot V = m \cdot R \cdot T]$$

where $V = \text{vol.}$; $m = \text{Mass (kg)}$; $R = \text{char. Gas const.}$

$$P \cdot V = \frac{m}{M} \cdot (M \cdot R) \cdot T$$

$$P \cdot V = n \cdot \bar{R} \cdot T \quad [P \cdot V = n \cdot \bar{R} \cdot T]$$

Here $n = \text{No. of moles}$; $\bar{R} = \text{Univ. Gas const.}$
 $M = \text{Molecular Mass of gas}$

$$\boxed{\bar{R} = M \cdot R}$$

$$[\bar{R} = 8.314 \text{ kJ / k-mole - K}]$$

$$[R_{\text{air}} = 0.287 \text{ kJ / kg - K}]$$

$$[R_{\text{O}_2} = 0.262 \text{ " }]$$

Q: Prove that Adiabatic curve is steeper than Isothermal curve?

Sol) Isotherm: $P \cdot V = C$

$$P \cdot dV + V \cdot dP = 0 \Rightarrow \boxed{\frac{dP}{dV} = -\left(\frac{P}{V}\right)} \quad \text{---(1)}$$

Adiabatic: $P \cdot V^\gamma = C$

$$P \cdot \gamma \cdot V^{\gamma-1} \cdot dV + V^\gamma \cdot dP = 0 \Rightarrow \boxed{\frac{dP}{dV} = -\gamma \cdot \left(\frac{P}{V}\right)} \quad \text{---(2)}$$

from (1) & (2)

$$\boxed{\left(\frac{dP}{dV}\right)_{\text{Adiab.}} = \gamma \cdot \left(\frac{dP}{dV}\right)_{\text{Isoth.}}} \quad \underline{\text{Proved}}$$

(b) Heat Interaction: $Q \propto m$; $Q \propto dT$

$$Q \propto m \cdot dT$$

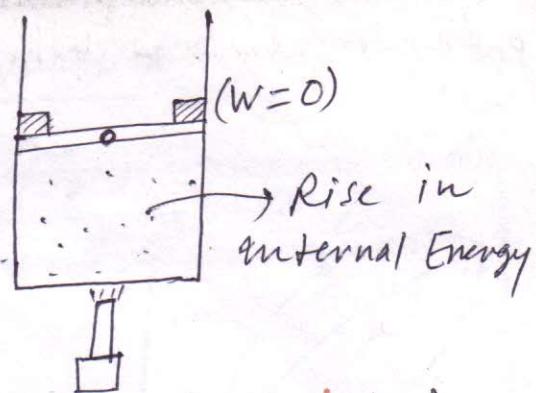
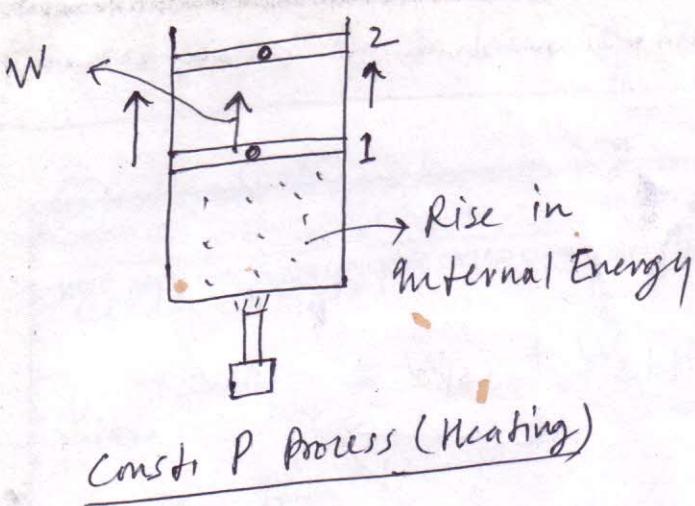
$$\boxed{Q = m \cdot c \cdot dT}$$

Start [c = sp. heat of the substance (kJ/kg-K)]
 Heat is the mode of energy transfer, which takes place, by virtue of temp. difference.

Sp. Heat is the heat required to rise the temp. of unit mass of a substance by unity (1°C).

For solids & liquids (incompressible): Sp. heat (C)

For Gases (compressible fluids): Sp. heat $\begin{cases} C_P \\ C_V \end{cases}$



We can notice that C_P involves both; rise in internal energy & boundary work & C_V involves only rise in internal energy ($W=0$), that's why:

$$C_P > C_V$$

$\propto C_P - C_V = R$ (Characteristic Gas Const.)

$\propto \frac{C_P}{C_V} = \gamma$ (Adiabatic Index)

$\gamma \downarrow$ with $T \uparrow$

I law of Thermodynamics: q_f is just the sum of conservation of Energy.

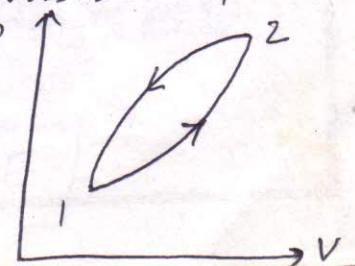
For a closed system, undergoing a thermodynamic cycle; net heat interaction is equal to the net work interaction.

$$(\sum Q)_{\text{cycle}} = (\sum W)_{\text{cycle}} - \text{(I law for a th. cycle)}$$

→ For both reversible as well as irreversible cycles,

$$Q_{1-2} + Q_{2-1} = W_{1-2} + W_{2-1}$$

$$\oint \delta Q = \oint \delta W$$



Consequences of I law of Thermodynamics

(a) heat transfer is a path function.

cycle $1 \alpha 2 b 1$:

$$Q_{1\alpha 2} + Q_{2b1} = W_{1\alpha 2} + W_{2b1}$$

cycle $1 \alpha 2 c 1$:

$$Q_{1\alpha 2} + Q_{2c1} = W_{1\alpha 2} + W_{2c1}$$

$$[Q_{2b1} - Q_{2c1} = W_{2b1} - W_{2c1}] - A$$

& we know: $W_{2b1} \neq W_{2c1}$ - (w is a path fn.)

$$\Rightarrow Q_{2b1} - Q_{2c1} \neq 0$$

$Q_{2b1} \neq Q_{2c1}$

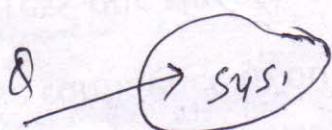
heat transfer is also a
path function.

Similar to work!

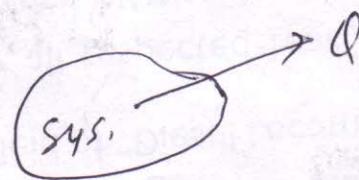
heat transfer is also a boundary phenomenon.

" " " " " an inexact differential

heat supplied to the system $\Rightarrow +ve$
heat rejected from " " $\Rightarrow -ve$



Q is +ve



Q is -ve

(b) Energy is a property of system
from eqn (A): $Q_{2b1} - Q_{2c1} = W_{2b1} - W_{2c1}$

or $[Q_{2b1} - W_{2b1} = Q_{2c1} - W_{2c1}]$
 $[(Q-W)_{2b1} = (Q-W)_{2c1}] = \Delta E$

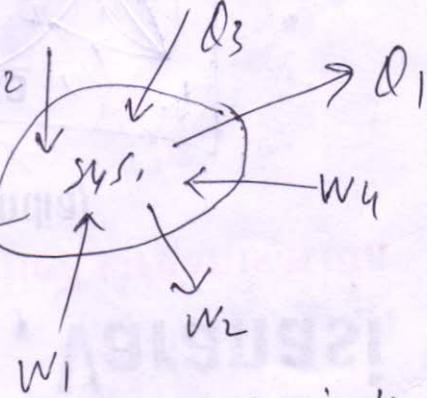
Hence the quantity $(Q-W)$ is a path independent quantity & depends only on the initial state & final state; so it shows the change in a property (ΔE) of the system. This property is known as Energy (E) of the system. In differential form:

$$[\delta Q - \delta W = dE]$$

I law for a thermodynamic process:

$$Q-W = \Delta E$$

$$(Q_2 + Q_3 - Q_1) = (W_2 + W_3 - W_1 - W_4) + \Delta E$$



Now Energy $E = U + K.E. + P.E.$ -- (U is internal)

$$\Delta E = \Delta U + \Delta K.E. + \Delta P.E.$$

For a stationary thermodynamic system,

$$\Delta K.E. = 0 ; \Delta P.E. = 0$$

$$\Rightarrow \Delta E = \Delta U$$

$$\Rightarrow Q-W = \Delta U$$

$$\delta Q - \delta W = dU$$

$$\Rightarrow \boxed{\delta Q = dU + \delta W}$$

Ques. Points Regarding Energy (E or U):

- Energy is a property of system,

- " " Point fn.

- " " an exact differential

For a closed system:

$$\delta Q = dU + \delta W$$

$$\& \delta W = P.dV$$