Thermodynamics

① Basic Concepts -obj.

② Ist law of TD

③ IInd law of TD

④ Entropy Concepts

(obj + conv)

⑤ AE / UAE -obj

⑥ PS - obj

⑦ Mixture of Gases - obj

⑧ TD Relation (only in Gate) → Gate ✓ ↳ ESE X

- Basic concepts
- 1st law of TD
- 2nd law of TD
- Entropy Concepts
- AE/UAE
- Pure substance
- Mixture
- TD relation

Basic Concepts.

Thermodynamics :- It is the branch of the science which deal with the steady of energy interaction of the system with w.r.t. surrounding and it's impact on the properties of system. or

→ It is the branch of science which deals with the study of 3E's i.e. Equilibrium, Energy and entropy.

→ It is the branch of science which deals with the conversion of disorganised form of energy into organised form.

System :- Anything under consideration or it is control region in space over which our attention is focused.

Surrounding :- Anything external to the system.

Boundary :- which seprate's system from surrounding.

NOTE :- ① Boundary may be real or imaginary. Real boundaries are represented by countinuous line or curves where as imaginary boundaries are represented by dotted lines or curve

② Boundary may be fixid (Rigid) or movable.

③ It ~~so~~ should be considerd of nearly zero thicknes

Universe:- system + surroundings

Types of System:-

Open System:- It is the system in which both mass interaction and energy interaction takes place b/w System and surrounding.

Ex:- Boiler , Turbine, Condensor, pump, Compressor evoporator, nozzel, diffusure, piston Cylinder arrangement with valves.

Close System:- It is the system in which only energy interaction takes place between System and surrounding.

Ex:- Piston Cylinder arrangement without Valves.

Isolated System:- In which neither mass Interaction nor energy interaction takes place between System and surrounding.

Ex:- Universe, thermoflask.

Microscopic Approach V/s Macroscopic Approch.

In the case of microscopic approach individual molecule partical under consideration and it is also know as statistical approach whereas In the case of macroscopic approch time average behaviour of molecule is under considaration and it also known as classical approach.

Note:- In our thermodynamics we are generally dealing with macroscopic approach.

Continuum Approach :- In this approach we are considering over matter as continuous.

{ it means you have 1 lakh
if one missing, still you say very 1 lakh is
macroscopic

Note:- In the Case of Rarefied Gases theory the Concept of continuum app. is not valid.

Thermodynamic Properties :-

It represents the Characteristics of the system.

Types of Property

① Intensive/Intrinsic :- These properties are independent of mass.

Eg. Pressure, Temp., Conductivity, Specific heat, Ratio of two extensive property like desity, specific energy (energy per unit mass), Coefficient of thermal expansion (α), ② Extensive/Ex-trinsic :- These are dependent on mass.

Ex:- Volume, All forms of energy like, K.E. P.E., enthapy, entropy. Heat capacity(mc).

Thermodynamic equilibrium:-

A system is said to be in thermodynamic equilibrium when they are in Thermal eq^m, mechanical eq^m, chemical e

Themal equilibrium means equality of Temp.,
Mechanical equilibrium means equality of forces & pressure
chemical equilibrium means equality of chemical potential.

Pure Subtance:- it is subtance of constant chemical ~~Pure substance~~ Composition through-out its Volume of mixture irrespective of phase

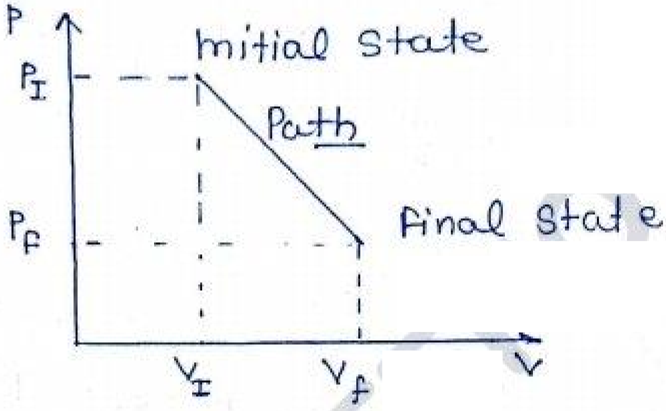
Eg. → H_2O, ice, steam
→ H_2O + ice, H_2O + steam ice + Steam.
→ H_2O + ice + Steam

eg → Gases air

Note:- Atmospheric air is not a pure substance because the percentage of water vapour contained varies from place to place. as we have seen that at some place there is a high humidity and at some places there is a low humidity.

Thermodynamic State :- it represent the Conditions of the System.

Path :- it is obtained by joining two equilibrium state's



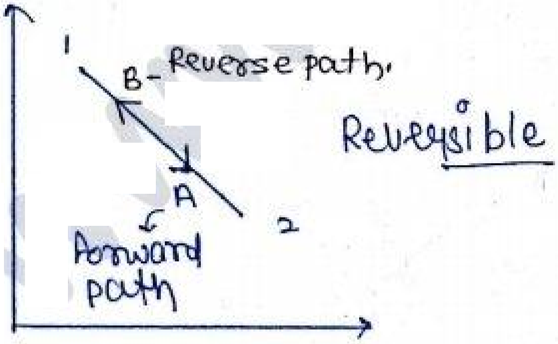
Reversible Process and Irreversible Process :-

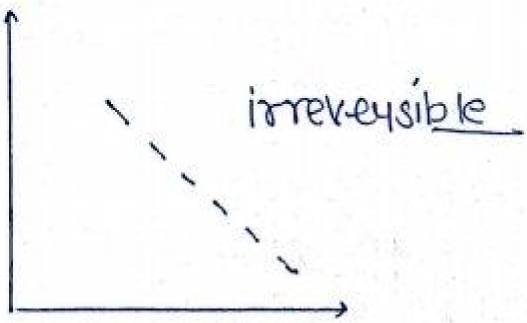
A process is said to be reversible in which System returns to it's origional States without leaving any effect on the surrounding. { P & T can change continuosly }

Note :- ① for the reversible process to occur both forward and reverse path has to be same.

② Reversible process are shown by continuous line. whereas irreversible process are repersanted by dotted lines/curve

③ Reversible process is impossible to achiveve practically.





Rev: Isothermal expansion of stirling cycle
- slow heating, evaporation

Methods which makes the process Irreversible

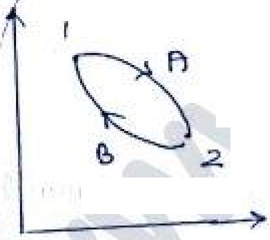
① Friction:
② free expansion.
③ mixing of fluid.
④ Heat transfer through a finite temp. differance.

- Gradual heating of water from a hot source
- isentropic compression
- transfer of electricity through a resistor

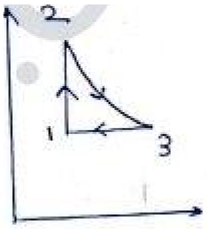
Cyclic Process:→ A process is said to be cyclic in which initial state and final state are same

Note:- minimum number of process require to make a cycle are 2.

eq.

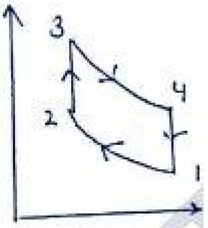


2 process cycle

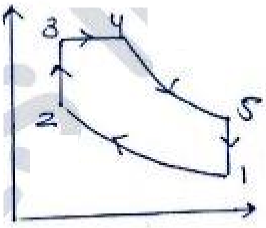


3 processes cycle

(knoir) cycle



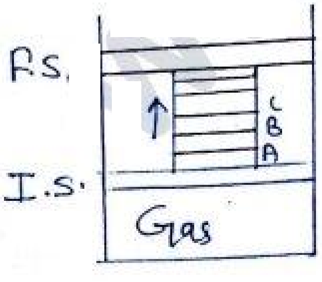
4 process cycle

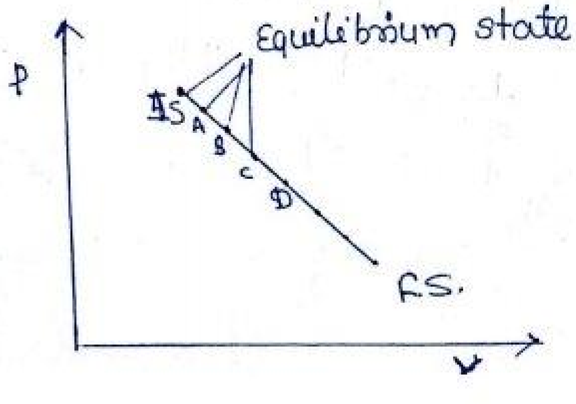


5 process cycle.

Quasi-Static Process:- Infinite (∞) slowness is the characteristic of quasi static process or it is obtained by joining of series of equilibrium states. (slow heating - quasi state rev.)

Note:- Quasi-static without friction is a reversible process





Thermometric Properties :-

It is the property with the help of which we are able to calculate the values of temp.

for Example - ① in case of Constant Volume Gas thermometry pressure will plays the role of thermometric property.

$$PV = mRT$$

At low pressure

$$P = \left(\frac{mR}{V}\right)T \Rightarrow P \propto T \Rightarrow T = f(P)$$

② In case of constant pressure Gas thermometer Volume will plays the role of thermometric property.

$$PV = mRT$$

$$V = \left(\frac{mR}{P}\right)T \Rightarrow V \propto T \Rightarrow T = f(V)$$

③ In case of electric resistance thermometer, resistance will plays the role of thermometric property

④ In case of thermocouple, electro motive force (EMF) or Voltage diff. plays the role of thermometric property

⑤ In case of ordinary thermometer (i)- length

(ii) Volume

Ideal Gas Equation :- Any Gas behavious as an ideal Gas under low pressure and high temp.

The mathematicle expression of ideal Gas equation is

$$\boxed{PV = mRT}$$

where - P = absoulate pressure

V = Volume , m = mass

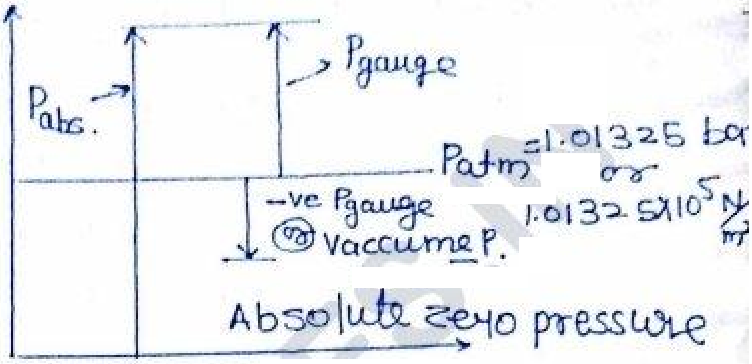
R = characteristic Gas Constant

T = Absoulate temp. in K

$$\boxed{P_{Abs} = P_{atm} + P_{Gauge}}$$

P_{abs} cannot be -ve

P_{gause} can be -ve



1atm = 1 bar = 1atm
= 10^5 Pa
= 10^5 N/m²

The other form of ideal Gas is

$$PV = n\bar{R}T$$

$$n = \text{no. of mole} = \frac{\text{mass}}{\text{Molecular wt}}$$

$$PV = \text{mass}\left(\frac{\bar{R}}{\text{Mol wat}}\right)T$$

$$\boxed{PV = m\ R\ T} \qquad \boxed{R = \frac{\bar{R}}{\text{Mol. wat}}}$$

$$\boxed{\bar{R} = 8.314\ \text{kJ/kmole k}}$$

where $\bar{R}$ is known as universal Gas Constant.

① t → 0°C

② T → K

③ 0°C → 273.15 K

Triple point ④ $(TP)_{\text{temp } H_2O}$ = 273.16 K or 0.01°c

⑤ $(TP)_{\text{pressure } H_2O}$ = 4.587 mm Hg

$$\frac{kg}{m^3} \times \frac{m}{sec^2} \times m = \frac{kg}{m\,sec^2} = \frac{N}{m^2}$$

$$P = \rho g h = 13.6 \times 1000 \times 9.81 \times 4.587 \times 10^{-3}$$

$$\Rightarrow P = 611.97\ N/m^2$$

Temprature Measurment Scale:-

Case-1 Method use before 1954

In this method two refreeanance state at its ice point and steam point taken into consideration

$$\boxed{t = ax + b}$$

$$t_{ice} = 0^\circ C \longrightarrow x = x_i \Rightarrow 0 = ax_i + b \Rightarrow b = -ax_i$$

$$t_{steam} = 100^\circ C \longrightarrow x = x_s \Rightarrow 100 = ax_s + b$$

$$100 = a(x_s - x_i)$$

$$\text{So} \quad a = \frac{100}{x_s - x_i}$$

$$b = \frac{-100x_i}{x_s - x_i}$$

$$t = \frac{100x}{x_s - x_i} - \frac{100x_i}{x_s - x_i}$$

$$\boxed{t = \frac{100(x - x_i)}{(x_s - x_i)}}$$

* if no relation Given b/w temp. & thermometric property then use this

Case-2 Method use after 1954

In this method a single fixed refrerence temp. is take Into consideration. that is triple point.

For ex⇒ In case of Constant Volume Gas thermometer

Ex. for constant Volume Gas thermometer

$$PV = mRT$$

$$P = \left(\frac{mR}{V}\right) T$$

$$T \propto P$$

$$T = KP$$

At triple Point $T = T_{TP}$

$P = P_{TP}$

$$T_{TP} = KP_{TP} \Rightarrow K = \frac{T_{TP}}{P_{TP}}$$

$$T = T_{TP}\left(\frac{P}{P_{TP}}\right)$$

So.

$$\boxed{T = 273.16\left(\frac{P}{P_{TP}}\right)}$$

Ideal Gas thermometer:-

It is the only thermometer which is independent of material of construction.

1k(kelvin) is defined as :-

$$1k = \frac{1}{273.16}\left(\overset{\text{triple point}}{TP} \text{ temp of } H_2O\right)$$

Define such that the triple pt of water is exactly 273.16 K

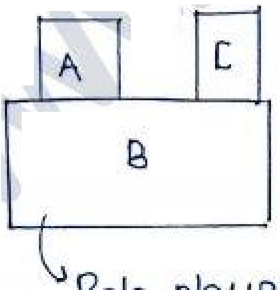
Zero th law of thermodynamics :-

It was given by RH Fowler.

"According to Zero th law of thermodynamics if body A is in thermal equilibrium with body B, and body B is in thermal equilibrium with body C separtely than body A and C will be in thermal equilibrium with each other.

The Role played by the common body is of thermometer.

Note:- Zero th law of thermodynamics provides the Concept of thermal equilibrium.



Role played by the common body is thermometer

$T_A = T_B$ — ①

$T_B = T_C$ — ②

Compare eq ① & ②

$$\boxed{T_A = T_C}$$

Point function & Path function :-

Point Function are the variables whose Value does not depend on the path followed by the system.

Ex. Pressure, Volume

Path Function are the Variables whose Value depends on the past history of the system.

Ex. Heat & work.

Exact differential:-

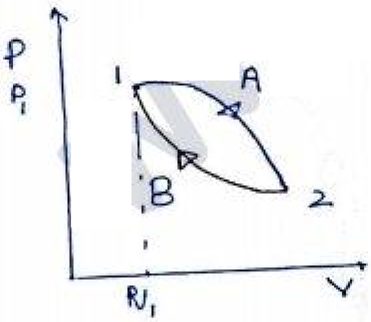
The cyclic integral of the variable is equal to zero. Ex. Pressure, Volume.

Inexact differential:-

The cyclic integral of the variable is not equal to zero. Ex Heat and work

Note:- ① All properties are point function and exact differential

② Heat and work are path function and inexact differential.



$$\left\{\begin{matrix} W_{1-A-2} \\ W_{1-B-2} \end{matrix}\right\} \quad \left\{\begin{matrix} P_1 \\ V_1 \\ T_1 \end{matrix}\right\} \quad \left\{\begin{matrix} dQ,\ \delta Q \\ dw,\ \delta w \end{matrix}\right\}$$

☆ $\oint d(\text{variable}) = 0 \Rightarrow \text{exact}$

$\neq 0 \Rightarrow \text{Inexact}.$

$\oint dP = P_F - P_I$

$\Rightarrow P_1 - P_2 = \underline{0}$

Gibbs Phase Rule:-

$$P + F = C + 2$$

P - Phase
F - DoF
C - No. of Component

DoF:- It is the minimum no. of independent or intensive variable are require to locate or fix the state of any system

Case-1 Single Phase Single Component system:-

Example:- ice, steam

$$1 + F = 1 + 2$$

$$\boxed{f = 2}$$

Case-2 Two phase Single component system:-

Example = ice + water

$$2 + f = 1 + 2$$

$$\boxed{F = 1}$$

Case-3 Three phase Single component system

Example- ice + water + steam

$$3 + F = 1 + 2$$

$$\boxed{F = 0}$$

* it is the unique reference point having zero DoF know as triple point where all of three phases are co-existing.

CH-1 workbook

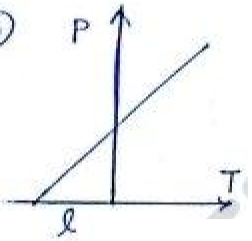
1. A
2. C
3. B
4. D
5. a
6. b
7. c
8. c
9. d
10. c
11. b
12. c
13. d
14. d
15. c
16. d
17. c
18. d
19. d

⑥ $P+F = C+2$

$2+F = 2+2$

$F = 2$

⑨

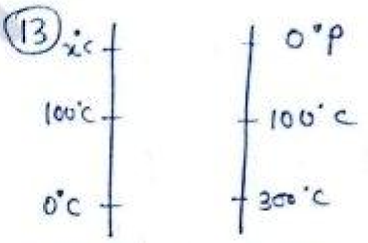


$PV = mRT$

$T = 0K$

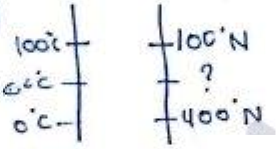
$T = -273.15$

⑬



More then 100°C → ⓓ

㉑



$t = ax + b$, $100 = 100a + b$, $t = -\frac{x}{3} + \frac{400}{3}$

$0 = 400a + b$, $100 = +100a - 400a$

$b = -400a$ $a = -\frac{1}{3}$, $b = \frac{400}{3}$

$60 = -\frac{x}{3} + \frac{400}{3}$

$180 - 400 = -x$

~~$x = 220°N$~~

$x = 220°\underline{N}$

$\underline{t = x}$

$t = -\frac{t}{3} + \frac{400}{3}$

$\frac{4t}{3} = \frac{400}{3} \Rightarrow t = \underline{100}°c$

~~⑲~~ ⑳ $\left.\begin{matrix} 0 - 100 \\ 32 - 212 \end{matrix}\right\} - 1.80$

$= 18 \times 10$

$= 18$ Ans

㉓ $t_A = L + m t_B + n t_B^2$

$0 = L + 0 + 0 \Rightarrow L = 0$

$100 = m(100) + n(100)^2$

$51 = 0 + m(50) + n(50)^2$

$100n + m = 1$

$(50)^2 n + 50m = 51$

$(50)^2 n - 50 \times 100 n = \cancel{5}1$

$-n(2500) = \cancel{500}-1$

$n = -\frac{[illegible]}{2500}$

$m = +\frac{26}{25}$

$t_A = \frac{26}{25} t_B - \frac{1}{2500} t_B^2$

$t_A = \frac{26}{25} \times 25 - \frac{1}{2500} \times 25 \times 25$

$t_A = 26 - 0.25$

$t_A = 25.7\underline{5°C}$

$t_A = t_B = 0^\circ C$

$t_A = t_B = 100^\circ C$

$t_A = 51^\circ C$ $t_A = 25.75^\circ C$

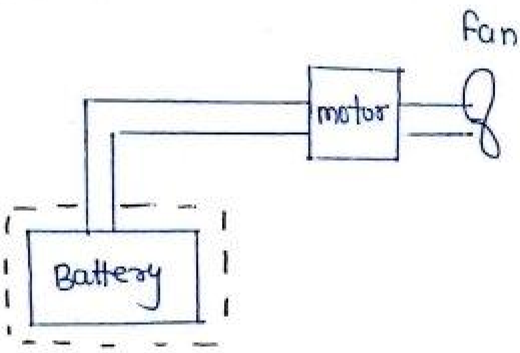
$t_B = 50^\circ C$ $t_B = 25^\circ C$

Both the thermometers are correct because the temp. scales are arbitrary

-:- Energy Interaction :-

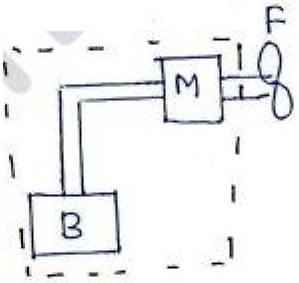
Work :- work is said to be done by the system if sole effect (net) on the things external to the system gets reduced to the raising to weight. (weight may not be actually raised)

Case-1



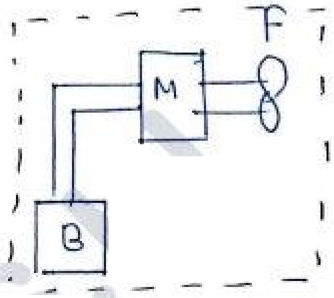
System- Battery
work = ✓

case-2



System = B+M
work = ✓

Case -3



System = B+M+f
work = 0

Sign convention :-

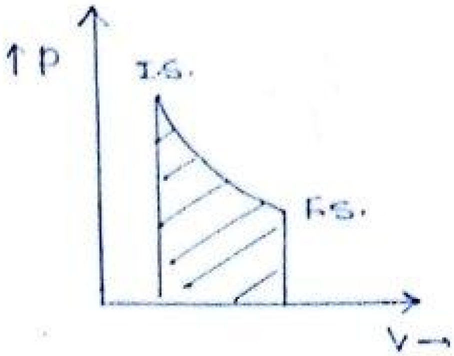
work done on the system = -ve

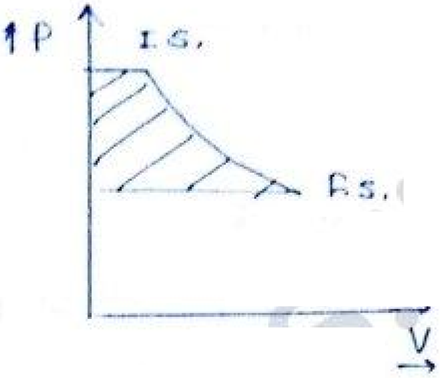
work done by the system = +ve

Types of Work :-

① closed system work/Non-flow work :- To obtain the close system work area under p-v should be projected on volume axis

② open system work/ steady work :- To obtain the open system work area under p-v should be projected on pressure axis



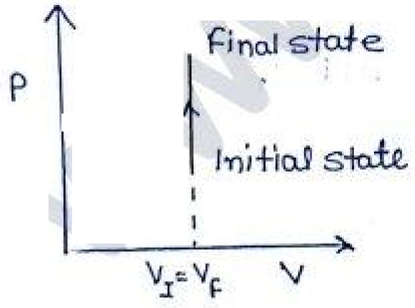


$$\boxed{W_{close} = \int PdV}$$

$$\boxed{W_{open} = -\int VdP}$$

Expression of closed system work for different pressure

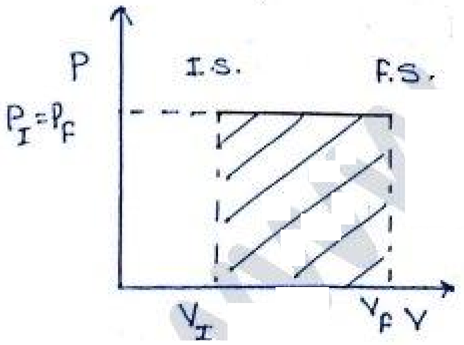
① Constant Volume process :- V = constant
Isochoric / Isometeric.



work = 0

$\int Pdv = 0$

② Constant Pressure process :- P = constant
Isobaric / Isopiestic



$$W = \int PdV = P\int dV = PV\Big|_{V_I}^{V_F}$$

$$\boxed{W = P(V_F - V_I)}$$

③ Constant temprature process (T= Constant

Isothermal / Rectangular hyperbola.

$$PV = mRT$$

$$PV = C = \text{Constant}$$

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

$$\therefore \text{Work} = W = \int P dV = \int \frac{C}{V} dv = C\int_{V_I}^{V_F} \frac{dV}{V}$$

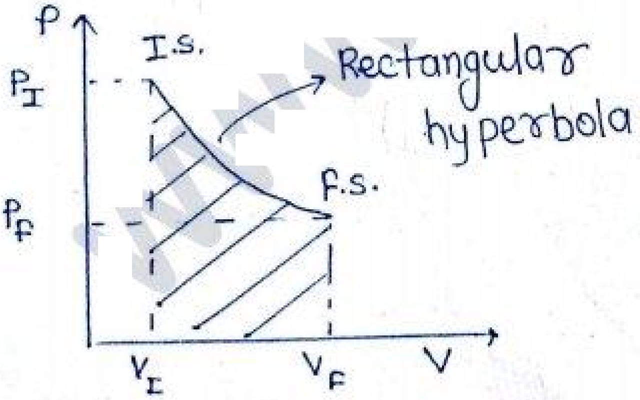
$$W = C \ln V \Big|_{V_I}^{V_F} = C\left[\ln V_F - \ln V_I\right]$$

$$W = C \ln \frac{V_F}{V_F}$$

$$C = P_I V_I = P_F V_F = mRT_I = mRT_F$$

$$\frac{V_F}{V_I} = \frac{P_I}{P_F}$$

$$\boxed{W = C\ln\left(\frac{V_F}{V_I}\right) \text{ or } C\ln\left(\frac{P_I}{P_F}\right)}$$



$$PV = mRT$$

$$T = C$$

$$PV = C$$

$$P \propto \frac{1}{V}$$

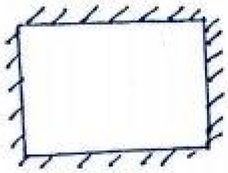
Note:- During isothermal expansion (Volume Increases) by using the expression of close system work for isothermal process we will get positive sign. i.e. work done by the system

$$V_F > V_I \quad , \quad \frac{V_F}{V_I} > 1 \quad , \quad W = c \ln \frac{V_F}{V_I}$$

$$W = \underline{\underline{+ve}}$$

④ Adiabatic process :- A process is said to adiabatic In which there is no heat interaction takes place between system and surrounding. E.g. Insulated tank.

It will follows a law $PV^{\gamma} = C$ where γ = Adiabatic Index which is defined as the ratio of specific heat at constant pressure to specific heat at constant volume.



Insulated.

$$PV^{\gamma} = C$$

$$\gamma = \frac{C_p}{C_v}$$

Air:— $C_p = 1.005$ kJ/kgK

$C_v = 0.718$ kJ/kgK

$R = C_p - C_v = 0.287$ kJ/kgK

$\gamma = 1.4$

$$PV^{\gamma} = C = P_I V_I^{\gamma} = P_F V_F^{\gamma}$$

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

$$W = \int P dV = \int \frac{C}{V^{\gamma}} dV = C \int_{V_I}^{V_F} V^{-\gamma} dV$$

$$W = C \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_I}^{V_F} = \frac{C}{1-\gamma} \left[V_F^{1-\gamma} - V_I^{1-\gamma} \right]$$

$$W = \frac{\left[C V_F^{1-\gamma} - C V_I^{1-\gamma} \right]}{1-\gamma} \qquad C = P_I V_I^{\gamma} = P_F V_F^{\gamma}$$

$$W = \frac{\left[P_F V_F^{\gamma} V_F^{1-\gamma} - P_I V_I^{\gamma} V_I^{1-\gamma} \right]}{1-\gamma}$$

$$\boxed{W = \frac{P_I V_I - P_F V_F}{\gamma - 1} \quad \text{or} \quad \frac{mR(T_I - T_F)}{\gamma - 1}}$$

⑤ Polytropic Process :- It is exactly similary to adiabatic process except heat interaction takes place. It will follows $\boxed{PV^n = C}$

$\boxed{Q \neq 0}$ where n = polytropic Index

expression

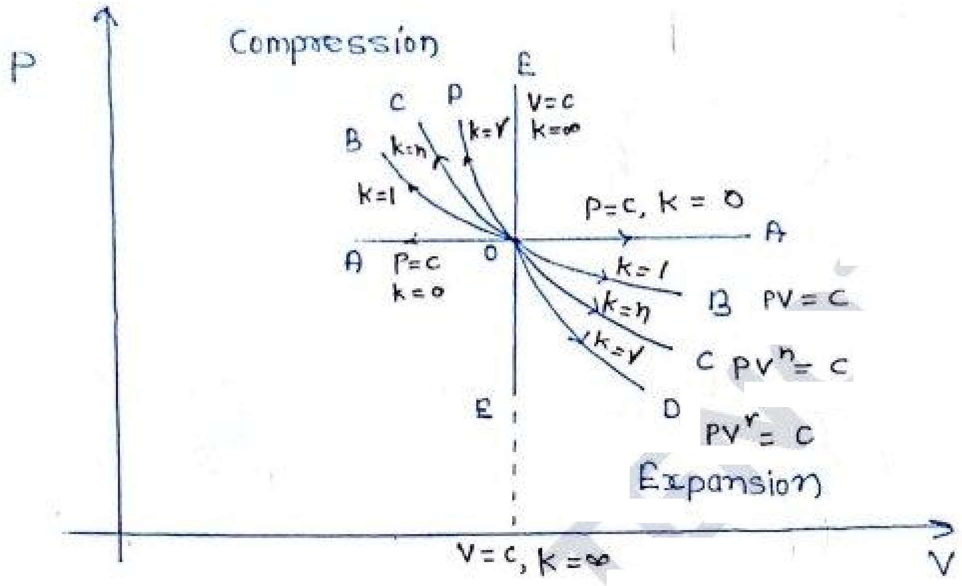
$$\boxed{W = \frac{P_I V_I - P_F V_F}{n - 1} \quad \text{or} \quad \frac{mR(T_I - T_F)}{n - 1}}$$

n - Can be anything

Generally

$\gamma > n > 1$

Representation of All processes on Same P-V Curve.



$$\boxed{r > n > 1}$$

$pv^k = c$

$k = 1 \rightarrow pv = c \rightarrow$ Isothermal process $\left(\frac{dp}{dv}\right)_T = -\frac{p}{v}$

$k = n \rightarrow pv^n = c \rightarrow$ Polytropic process $\left(\frac{dp}{dv}\right)_{pv^n} = n\left(-\frac{p}{v}\right)$

$k = r \rightarrow pv^r = c \rightarrow$ Adiabatic process $\left(\frac{dp}{dv}\right)_{pv^r} = r\left(-\frac{p}{v}\right)$

$$\Downarrow$$

$$\boxed{\left(\frac{dp}{dv}\right)_{pv^r} = r\left(\frac{dp}{dv}\right)_T}$$

$pv^k = c$

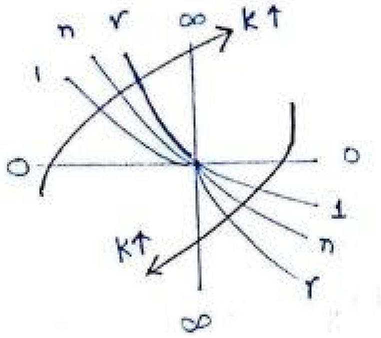
To get slop differentiate w.r.t. v

$dp\, v^k + p k v^{k-1} dv = 0$

$$\boxed{\frac{dp}{dv} = k\left(-\frac{p}{v}\right)}$$

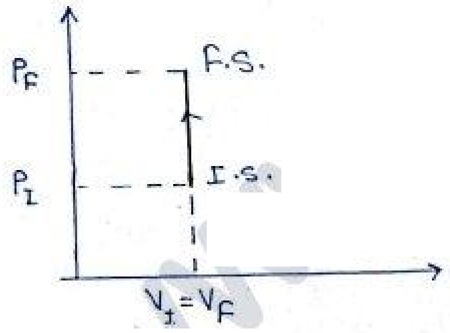
$$\left.\frac{dp}{dv}\right)_{adiabatic} = r \left.\frac{dp}{dv}\right)_{isothermal}$$

Note:- The value of index is increasing in CW dir^n.



Expression of open system work for different process:-

① Constant Volume :- (V = c)

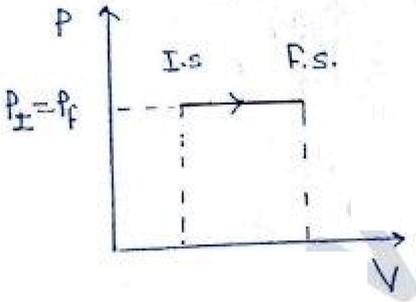


$$W = -\int V dP = -V\int_{P_I}^{P_F} dP = -VP\Big|_{P_i}^{P_f}$$

$$W = -V(P_F - P_I)$$

$$\boxed{W = V(P_I - P_F)}$$

② Constant pressure (P=c)



Work = 0

③ Constant temprature (T = c) isothermal

$$PV = mRT$$

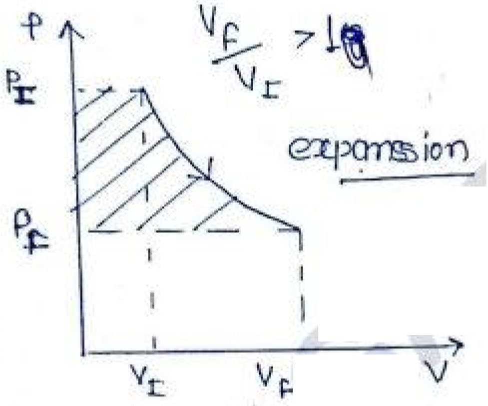
$$PV = C$$

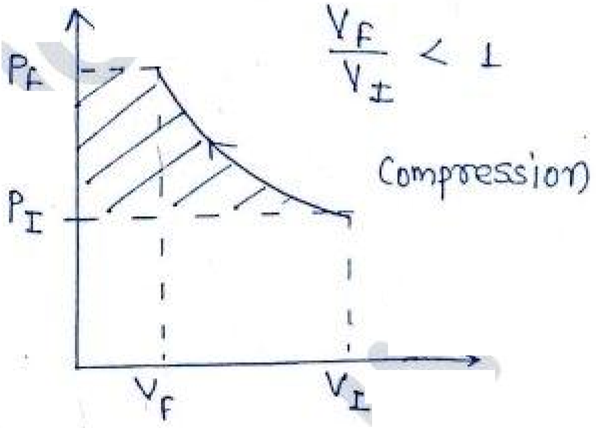
$$V = \frac{C}{P}$$

$$W = -\int V\,dP = -\int_{P_I}^{P_F} \frac{C}{P}\,dP$$

$$W = C\ln\frac{P_I}{P_F} \quad \text{or} \quad W = C\ln\frac{V_F}{V_I}$$

$$C = P_I V_I = P_F V_F = mRT_I = mRT_F \qquad \frac{V_F}{V_I} = \frac{P_I}{P_F}$$





* During isothermal expansion as the volume increasing so by using the expression of open system work for isothermal process we will get positive sign i.e. work done by the system.

Note:- The expression of open system work and close system work for isothermal process is same.

$$PV = mRT = C$$

$$P\,dV + V\,dP = 0$$

$$P\,dV = -V\,dP$$

$$\boxed{\int P\,dV = -\int V\,dP}$$ for isothermal process

$$W_{close} = W_{open}$$

⑪ Adiabatic Process

$$PV^{r} = C$$

$$V^{r} = \frac{C}{P} \Rightarrow V = \left(\frac{C}{P}\right)^{1/r}$$

$$W = -\int V dP = -\int_{P_I}^{P_f} \frac{C^{1/y}}{P^{1/y}} dP$$

$$W = -C^{1/y}\left[\frac{P^{-1/y+1}}{1-1/y}\right]_{P_I}^{P_f}$$

$$W = \frac{-C^{1/r}}{\left(\frac{r-1}{r}\right)}\left[P_f^{1-\frac{1}{r}} - P_I^{1-1/r}\right]$$

$$W = \frac{r}{r-1}\left[-C^{1/r} P_f^{1-1/r} + C^{1/r} P_I^{1-1/r}\right]$$

$$W = \frac{r}{r-1}\left[-\left(P_f V_f^{r}\right) P_f^{1-\frac{1}{r}} + \left(P_I V_I^{r}\right) P_I^{1-\frac{1}{r}}\right]$$

$$\boxed{W = \frac{r}{r-1}\left[P_I V_I - P_f V_f\right]}$$

$$\boxed{W_{open} = r W_{close}.}$$

⑤ Polytropic Process :- $PV^n = C$

$$W_{open} = \frac{n\,[P_I V_I - P_F V_F]}{n-1}$$

$$\boxed{W_{open} = n\,W_{close}}$$

Heat :- It is the form of energy interaction ~~intraction~~ due to due to temp diff. The mathematical expression of Heat is :.

$$Q = mc\Delta T$$

where m = mass

ΔT = temp. diff. in °C or k

C = Specific Heat

Specific Heat :- It is the amount of heat which is require to raise the temp. of unit mass by unit temp. differance.

$$C = \frac{Q}{m\Delta T} = \frac{Q}{1 \times 1} = Q \; \frac{kJ}{kg\,k}$$

$$\boxed{C \text{ unit } \frac{kJ}{kg\,k}.}$$

Note:- ① In the case of Solids and Liquid there is a single Value of specific heat where as in the case of Gas it depends on process

$C_{H_2O} = 4.187\ \frac{kJ}{kgK}$

Air

$C_p = 1.005\ kJ/kgK$

$C_v = 0.718\ kJ/kgK$

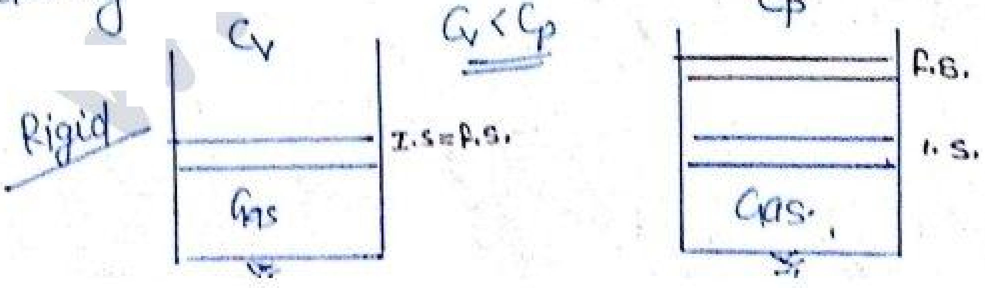
② The value of isothermal specific heat is ∞, and adiabatic heat is zero

$\Delta T = 0, \quad C_{isothermal} = \infty \qquad C = \frac{Q}{m\Delta T}$

$Q = 0, \quad C_{Adiabatic} = 0$

Que:- Why the value of C_p is always greaten then C_v?

Ans:- When the heat is supplied at Constant Volume, Complate heat is utilize to increase the Internal energy of gaseous molecule. where as In the case of constant pressure process some part of heat is utilize to increase the internal energy and some in doing some external work.



Sign convention:-

$Q_{supplied} = +Ve$ Heat supplied to the system

$Q_{Rejected} = -Ve$ Heat rejected from the system.

$$Q = mc\,(T_F - T_I)$$

Types of Heat:-

① **sensible heat** :- It is the form of energy interaction by the virtue of temp. differance.

② **latent Heat**: Heat required to cause the phase change

sensible heat = $mc\Delta T$

latent Heat = $m(LH)$

eg

$$\underset{\text{ice}}{-10^\circ C} \xrightarrow{SH} \underset{\text{ice}}{0^\circ C} \xrightarrow{LH} \underset{H_2O}{0^\circ C} \xrightarrow{SH} \underset{H_2O}{100^\circ C} \xrightarrow{LH} \underset{\substack{H_2O\\ \text{Vapour}}}{100^\circ C} \xrightarrow{SH} \underset{\substack{\text{Superheated}\\ \text{steam}}}{150^\circ C}$$