CHEMICAL ENGINEERING (GATE & PSUs)

Postal Correspondence

STUDY MATERIAL (Handwritten Notes)

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Chemical Engineering Thermodynamics-I

GATE-2022 Syllabus: Chemical Engineering: Thermo-I

First and Second laws of thermodynamics. Applications of first law to close and open systems. Second law and Entropy. Thermodynamic properties of pure substances: Equation of State and residual properties, properties of mixtures: partial molar properties, fugacity, excess properties and activity coefficients; phase equilibria: predicting VLE of systems; chemical reaction equilibrium.

BASIC THERMODYNAMICS COURSE CONTENT

1. **Introduction**
2. **Thermodynamics Properties**
3. **First Law of Thermodynamics**
4. **Work and Heat Transfer**
5. **Second Law of Thermodynamics**
6. **Entropy**
7. **Thermodynamics/Maxwell Relations**
8. **Pure Substance and Properties of Fluids**

Note for Student:

1. Full GATE Syllabus covers in Notes.

2. Total number of pages in Thermo-I Notes = 306 Pages

3. No. of Questions solved in Notes = 105+ Questions

(GATE PYQs & other good quality question)

THERODYNAMICS

Phase Equilibrium	Chemical Equilibrium
(Mass Transfer)	(Chemical Reaction Engineering)
Roult's Law	- Gibb's free energy
(L — V) → Phase change	

* <u>Thermodynamics</u>:- Whether the reaction is possible or not

$$A + B \longrightarrow C$$

* <u>Chemical Rxn Engg</u>:- Till what extent conversion etc.

→ Thermodynamic does not tell anything about <u>rate</u>

→ Driving force of thermodynamics: properties

→ Rate is not a thermodynamic property

$$\left[\text{Rate} = \frac{\text{Driving force}}{\text{Resistance}} \right] \quad \text{Ex: } q = \frac{\Delta T}{x/kA}$$

(x/kA ↳ Resistance)

* Resistance is a non-thermodynamic property

ΔT = Temperature

x = Length; (m)

k = thermal conductivity; ($W/m \cdot k$) : material property

A = cross-sectional Area; (m^2)

* Thermodynamic → Develops power from Heat

(Heat → work → power)

* THERMODYNAMICS *

Heat → THERMO; DYNAMICS → Motion of particles

Basic concepts :-

→ The science of thermodynamics deals with <u>Energy</u> and its <u>transformation</u>.

→ It tells us about the direction in which changes take place in nature.

→ It also determines the conditions under which a proposed change attains a state of equilibrium. a state in which no further change is possible under the given conditions.

* Chemical Engineering
  - ① unit operations (physical)
  - ② unit process (chemical)

→ Thermodynamics enables us to determine the maximum yield of product obtained under given conditions of temperature and pressure.

* "Thermodynamics is a fundamental subject that describes the laws of governing the occurence of physical associated with transfer of energy of transformation of energy"

It also establishes the relationship b/w different physica properties which has been effected by the process.

* **Process :-** The changes taking place within the system is referred to as a process.

Example. combustion chamber (Hydrocarbon fuel + oxygen)

system :- combustion chamber

process :- combustion of fuel to form water and carbon dioxide

(CH_4) $\quad C_xH_y + O_2 \longrightarrow CO + 2H_2O$

Homogeneous and Heterogeneous system :-

* **Homogeneous system :-**

This system is also called a phase. Here the properties are the same throughout or the properties vary smoothly without showing any surface of discountinuity.

Example :- i) Liquid water in a beaker

ii) A column of dust free air above the earth's surface

* **Heterogeneous system :-**

This is a system which consists of two or more distinct homogeneous phases or regions. There is a sudden change in properties at the phase boundaries.

Example (i) water and water vapour in a closed container.

ii) A liquid mixture of benzene and water forms a heterogeneous system made up of two immiscible liquid phases.

➔ A systems consisting of only gases and vapours are always homogeneous.

Thermodynamics property :-

Identifable and obeservable characterstics feature of the system by which a system can be specified called thermodynamics property.

Example - Pressure, temperature and volume etc.

But it's also important How the system can specified and it will be clear from states of system called thermodynamics states.

* There are two types of thermodynamics property

1) Extensive property (Depend on mass)
2) Intensive property

* i) Extensive property :- The properties that depends upon the mass of the system or extent of the system called Extensive property. These property is found to be zero when mass of the system contract to the point,

Extensive property – Volume, mass, Enthalpy, Entropy, Internal energy etc.

* 2) **Intensive property**:- (Independent of mass)

Property that does not depends on the mass and as when a system contract to a point it has a finite value.

Example – Density, temperature, pressure, thermal conductivity, specific heat, chemical potential etc.

* All specific extensive properties are intensive

Ex:- specific volume $v = \frac{V}{m}$

specific entropy $= S/m$

specific enthalpy $h = H/m$

specific internal energy $u = \frac{U}{m}$

(Thermodynamic) properties

Intensive properties
(do not depend on Mass)

P, T	P, T
P, T	P, T

but volume ; V/4

→ ① pressure (P)
② Temperature (T)
③ Density ($\rho = m/v$) (specific)
④ Thermal conductivity (k)
⑤ Chemical potential (μ)
⑥ specific heat capacity (C_p)

Note → All specific heat capacity are intensive property

⑦ specific volume, specific entropy, specific enthalpy, specific internal energy
⑧ concentration
⑨ color
⑩ melting point
⑪ Boiling point
⑫ fugacity (f)
⑬ Activity coefficient (γ)
⑭ steam quality (x)
⑮ molality
⑯ magnetic permeability

Extensive properties
(depend on the mass)

→ ① Volume (V), m^3 or lit
② Mass
③ Energy (E), J
④ Enthalpy (H), J
⑤ Internal energy (U); Jule
⑥ Entropy (S); J/K
⑦ length
⑧ shape
⑨ Gibbs energy (G)
⑩ Helmholtz energy (A)
⑪ Heat capacity (C_p) $\frac{kJ}{kg \cdot K}$
⑫ Amount of substance (mol)

Note → All energy are Extensive property

* (Note) - most of the above are not thermodynamic properties

Thermodynamic state :-

The system is said to be state when the following two condition is satisfied —

1) The properties should be uniform throughout the system (all Intensive properties should be uniform throughout the system) → (do not depend on Mass)

2) They (Intensive properties) invarient with time atlest temporarily for the moment when the state of system is defined.

Thermodynamic system

1) closed system (control mass system) [$\dot{m} = 0, E \neq 0$]
2) open system (control volume system) [$\dot{m} \neq 0, E \neq 0$]
3) Isolated system

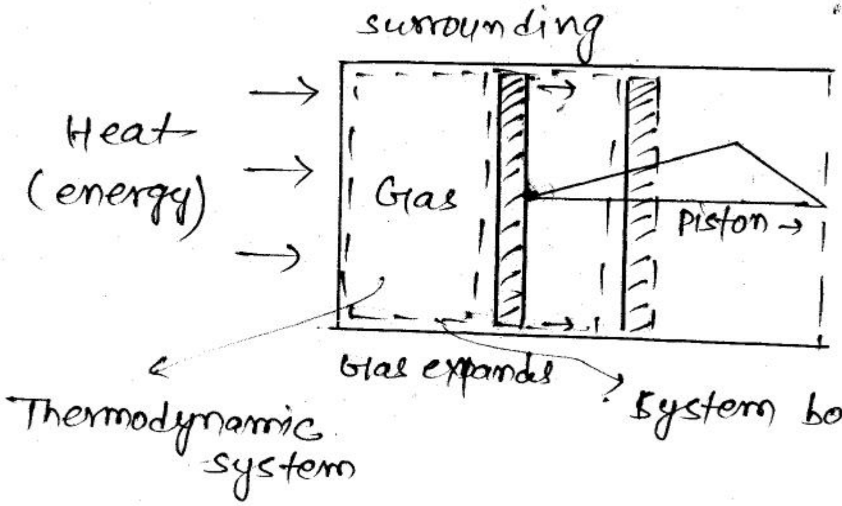
* closed system :- systems that can exchange energy with the surroundings but which cannot transfer matter across the boundaries are known as closed system. (matter → mass)

* open system :- system that can exchange both energy and matter with their environment.

* Isolated system :- Theres is neither matter nor energy transfer across the boundary of the system.

1) closed system :-

- No mass transfer
- only energy transfer takes place.



(A closed system with moving boundaries)

(i) Heat cross the system boundaries.
↳ Gas expand in the system and the piston moves backward.

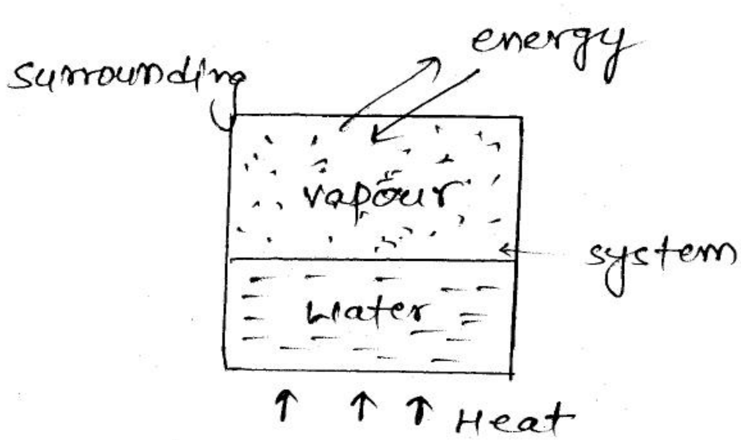
(ii) Work crosses the system boundaries.

(iii) Mass of the gas remains fixed

(iv) Non flow process (Because gas does not cross system boundaries)
↳ Non flow system

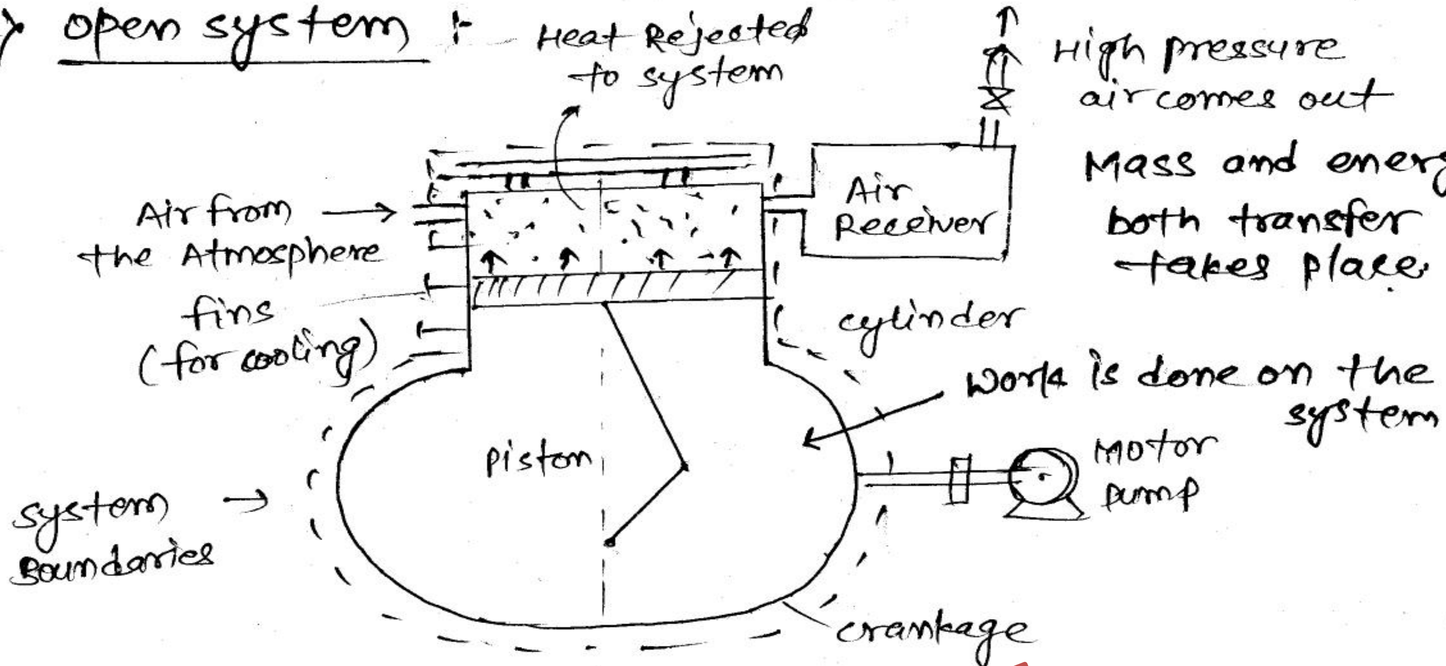
* Example :- A batch reactor, cyclical processes like power and refrigeration cycles.

*



- cooking with pressure cooker is closed system while it's not whistling

2) Open system :-



Mass and energy both transfer takes place

- Motor is not included in the system boundaries

(i) Heat crosses the system boundaries

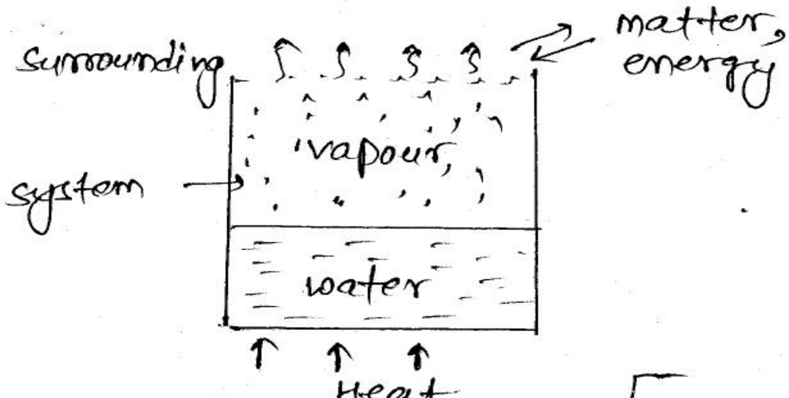
(ii) Work cross the system boundaries

(iii) Mass of air is not fixed.

(iv) flow process

* Example : A tubular flow reactor, each component of the cyclic process such as compressor, pump, and Heat exchanger.

*



- A control volume is a open system with one inlet and one exit.

- cooking in a pot is a open system
[As mass in the form of water vapor is crossing the boundary of system]

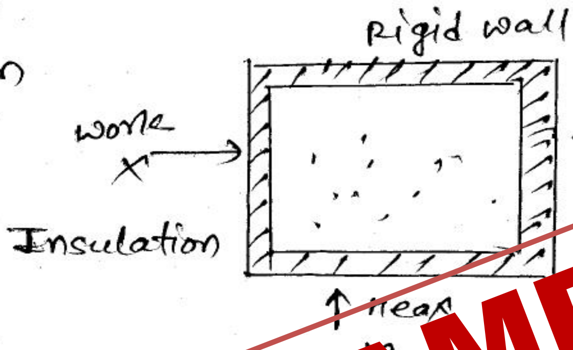
→ system boundaries plays a major role to decide wheather system is open or closed.

* 3) Isolated system :-

A system where neither energy nor mass transfer takes place.

- No Heat transfer
- No Mass transfer

Dead system



system boundaries don't allow to transfer heat and Mass.

→ A perfectly isolated system is an ideal concept.

State and properties :-

→ The condition defined by certain specificatons (like pressure, temperature and volume) is called the state of the system.

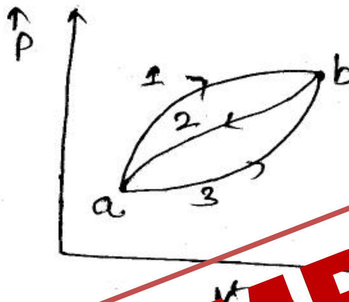
→ The variables used to define the state are called the state functions or the properties of the system.

→ We already study about intensive and extensive properties.

State and path functions :→

*) State function :-

Property that are fixed for a particular state of the system and do not in any way depend upon the past history or the path by which the state was arrived at.



→ for a cyclic process the initial and final states are the same and the change in property will be zero.

*) Path functions :-

The values of heat and work accompanying a given change in state vary with the path from the initial to the final state.

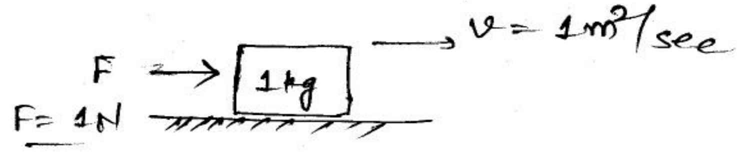
→ Heat and work involved in a given change of state are not to be determined solely by the initial and final states; they also depend on the manner in which the change is carried out.

→ Heat and work are therefore not thermodynamic properties of the system.

{ Heat and work → Path functions }

Important terms :-

1) Force ⇒



Force = Rate of change of momentum

$$F \propto \frac{d}{dt}(mv)$$

$$F \propto \left(m\frac{dv}{dt} + v\frac{dm}{dt}\right) \quad \left(v\frac{dm}{dt} \to 0\right) \qquad m = \text{constant}$$

$$F \propto m\frac{dv}{dt}$$

Acceleration (a) = Rate of change of velocity

$$F \propto ma$$

$$F = k\,ma$$

K = constant of proportionality = 1

$$\boxed{F = ma}$$ Newton's second law of motion

→ When a body of mass 1 kg is accelerated by 1 m/s^2, the force acting on the body is 1 $kg\,m/s^2$, which is designated as 1 newton or (1 N).

unit of Force → Newton

$$\boxed{N = kg\cdot m/s^2}$$

* **Kilogram force (kgf)** : $F = \frac{1}{g_c} ma$

$$\left[g_c = 9.80665 \ kg\cdot m/s^2 ; kgf\right]$$

$$\boxed{1 \ kgf = 9.80665 \ N}$$

2) Pressure :-

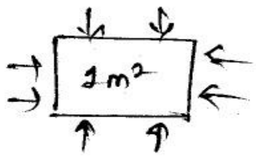
Pressure is defined as the normal component of the force per unit area exerted by the fluid on a real or imaginary boundary.

$$\boxed{P = \frac{F}{A}} = \frac{Newton}{m^2} \rightarrow \text{pascal} \rightarrow$$

$$\boxed{1 \text{ pascal} = 1\ N/m^2}$$

$$\boxed{1 \text{ bar} = 10^5 \text{ Pa.}}$$

* Atmospherical pressure :- The pressure exerted by standard atmosphere on $1\ m^2$ area is called the standard atmospheric pressure.



* Value of 1 atm :-

$$\left\{\begin{array}{l} 1 \text{ atm} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ Pa} \\ 1 \text{ atm} = 760 \text{ mm of Hg} \end{array}\right\}$$

$P = \rho g h$ | Put $\rho_{Hg} = 13.6 \times 10^3\ kg/m^3$

$g \simeq 9.81\ m/s^2$

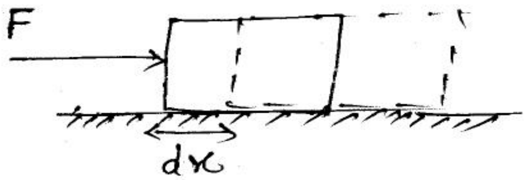
$h = 760$ mm of Hg $= 0.760$ m of Hg

$P = (13.6 \times 10^3)(9.81)(0.760)$

$P = 101325\ N/m^2$

$\left[P = 1.01325 \times 10^5 N/m^2\right] \Rightarrow \left[1 \text{ atm} = 1.01325 \text{ bar}\right]$

WORK ⇒ Energy is expended in the form of work when a force acts through a distance.



Work = force × Displacement

$dW = F \times dx$

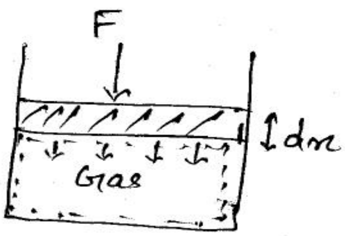
$dW = (P \cdot A)\, dx$

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

↳ volume = dv

$$\boxed{dW = P \cdot dV}$$

*

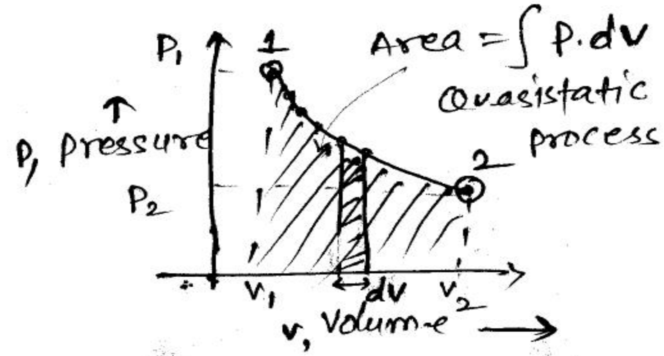


* Example - consider the expansion or compression work in a cylinder, Assume that a gas is confined in a cylinder.

→ The work done on the face of piston if the volume of the gas changes from the initial value V_1 to the final value V_2.

$$\int_1^2 dW = \int_1^2 P \cdot dV$$

Total Area occupied



$W_2 = 0$ (at Equilibrium)

$W_1 = 0$ (Initial system in equilibrium No displacement)

* Work of expansion on the P-V diagram

→ · Area under point 1 ÷ Meaningless

so, $\int_1^2 dW = {}_1W_2$; W state 1 state 2

$$\int_1^2 dW = \int_1^2 P.dV$$

→ Quasi-state process $P = f(V)$

$${}_1W_2 = \int_1^2 P.dV$$ = Area under the P-V curve

- Hence the work done in the compression or expansion of the gas depend on the shape of the PV curve, means work done in a process is a path function.

(i) Work is a path function (depend on path 1 → 2)

(ii) Work is experience by only crossing the boundries of the system.

(iii) Work is a transient phenomenan. (Transfer)

(iv) $\int_1^2 dW = {}_1W_2$; Its differential is inexact or imperfect differential,

${}_1W_2$ ⟶ δW (Imperefect or Inexact differential)

Note:-

* Point function's are perfect differential.

Example - volume, temperature, pressure

$\int_1^2 dV = V_2 - V_1$, | $\int_1^2 dT = T_2 - T_1$ | $\int_1^2 dP = P_2 - P_1$

* **Unit of Work :** Work = force × displacement

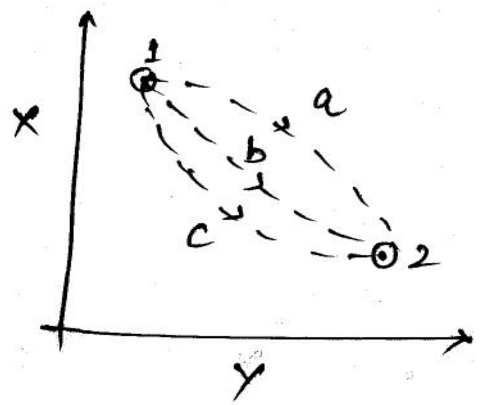
$W \rightarrow N-m$

$W \rightarrow$ Joule S-I unit.

* **Sign convention :-**

1) Work done by the system = +ve Example (Engine)
2) Work done on the system = -ve (compressor)
3) Heat supplied to the system = +ve
4) Heat Rejected to the system = -ve

* Heat and Work both are path function and both depend upon the past History

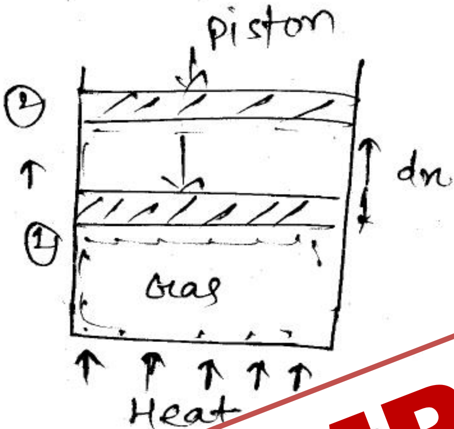


Path ① 1 - a - 2
② 1 - b - 2
③ 1 - c - 2

$$\left\{ \begin{array}{l} W_{1-a-2} \neq W_{1-b-2} \neq W_{1-c-2} \\ Q_{1-a-2} \neq Q_{1-b-2} \neq W_{1-c-2} \end{array} \right\}$$

* Quasi-static process :-

It is one in which the deviation from thermodynamic equilibrium or infinitesimally small and the state the system passes through may be regarded as equilibrium state

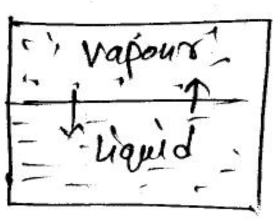


Quasi → almost / nearest
static → stop / slow

* Infinitly slow process is said to be quasi-static process.

* Reversible process :-

A process in which the system and surrounding both will come back to initial state following the same path if we are trying to reverse the process.



* Here the system is Reversible but not the surrounding

$$\text{Work} \Rightarrow \boxed{{}_1W_2 = \int_1^2 P\,dV} = \text{Area under the P-V curve}$$

→ for Reversible & quasi-static process

$dW = PA \cdot dx$

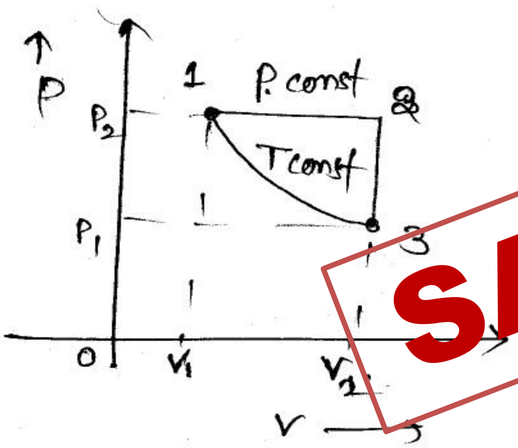
$dW = P\,dV$

$${}_1W_2 = \int_1^2 P\,dV$$

valid for (quasi-state process)

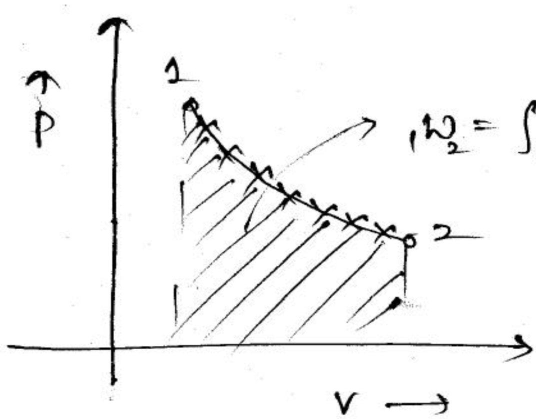
$$P = f(V)$$

* Every state is in thermodynamic equilibrium, so internal pressure is equilibrium with external pressure.

* 

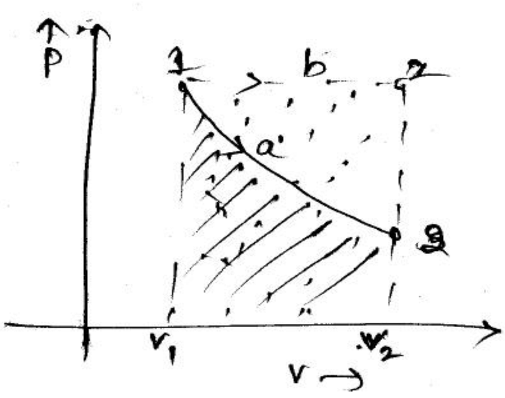
→ Expansion can be carried out by isobaric or isothermally

→ But work ~~done~~ can be different for the different path.

* 

$\to {}_1W_2 = \int_1^2 P\,dV$; ${}_1W_2 > 0$

* Area under the curve will gives the value of displacement work

* 

$W_{1-a-2} \neq W_{1-b-2}$

(Path function)

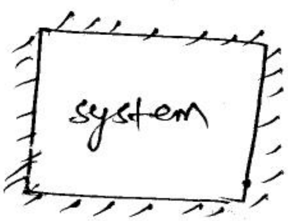
Different type of thermodynamic process :-

1) Adiabatic process ($Q = const.$)
2) Isothermal process ($T = const.$)
3) Isobaric process ($P = const.$)
4) Isochoric process ($V = const.$)
5) polytropic process

* 1) Adiabatic process :- ($Q = 0$)

There is no heat interaction b/w the system and the surroundings.

$$\boxed{dQ = 0}$$



$$\boxed{dU = dQ - dW}$$

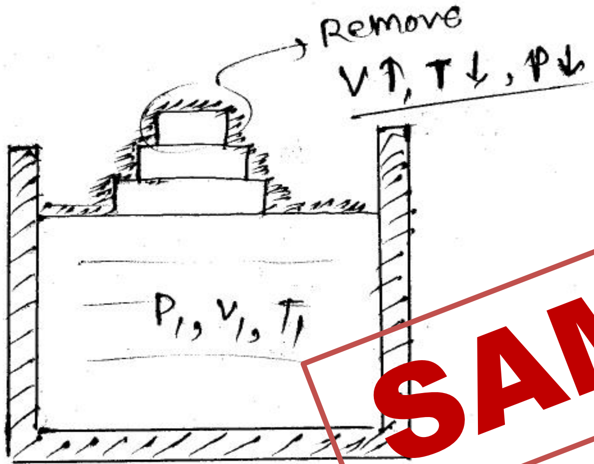
$$\Rightarrow \quad dU = -dW = -PdV$$

* - Adiabatic process in which no heat is supply or rejected
- system should be thermally insulated.
- process should be extremely fast.

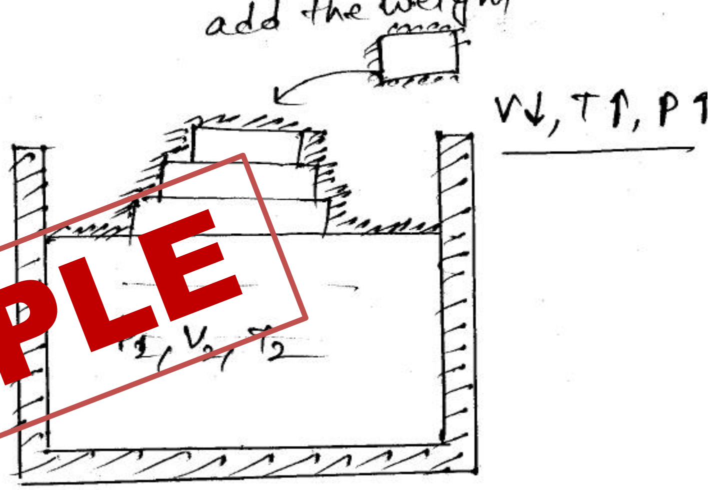
* (i) P-V-T relationship
(ii) P-V diagram
(iii) change in internal energy.
(iv) Work done
(v) Heat transfer

} We talk about these five parameters.

* Adiabatic process ($\dot{Q} = 0$)



Adiabatic expansion



Adiabatic compression

(i) P-V-T relationship :- ($dQ = 0$)

* P-V :-

$$dU = \cancel{dQ}^{0} - dW$$

$$dW + dU = 0$$

$$\delta W + dU = 0$$

$$Pdv + C_v dT = 0$$

$$\Rightarrow P dv + C_v \left(\frac{P dv + v dP}{R} \right) = 0$$

$$\Rightarrow RP dv + C_v (P dv + V dP) = 0$$

$\because \delta W = P dV$

$dU = C_v dT$

for ideal gas

$$PV = RT$$

$$Pdv + vdP = RdT$$

$$\left(\frac{P dv + vdP}{R} = dT \right)$$

$\Rightarrow \quad RP\,dv + C_v(P\,dv + v\,dP) = 0$

for ideal gas $\boxed{C_p - C_v = R}$ & $\boxed{\dfrac{C_p}{C_v} = \gamma}$

where C_p & C_v constant

$\Rightarrow \quad (C_p - C_v)P\,dv + C_v(P\,dv + v\,dP) = 0$

$\Rightarrow \quad C_p P\,dv + C_v v\,dP = 0$

dividing by $C_v \cdot P \cdot V$

$\Rightarrow \quad \dfrac{C_p}{C_v}\dfrac{dV}{V} + \dfrac{dP}{P} = 0 \quad \left(\text{put } \dfrac{C_p}{C_v} = \gamma\right)$

$\Rightarrow \quad \gamma \dfrac{dV}{V} + \dfrac{dP}{P} = 0$

Integrating

$\Rightarrow \quad \gamma \ln V + \ln P = \ln C$

$\Rightarrow \quad \ln V^{\gamma} + \ln P = \ln C$

$\Rightarrow \quad \ln P \cdot V^{\gamma} = \ln C$

$\Rightarrow \quad \boxed{PV^{\gamma} = C}$; constant ——— (1)

* $\boxed{V - T}$ $\quad PV = RT \Rightarrow P = \dfrac{RT}{V}$

$\Rightarrow \quad \left(\dfrac{RT}{V}\right) V^{\gamma} = C$

$\Rightarrow \quad RT\,V^{\gamma-1} = C$

$\Rightarrow \quad T\,V^{\gamma-1} = \dfrac{C}{R} = C'$

$\Rightarrow \quad \boxed{TV^{\gamma-1} = C'}$; constant ——— (2)

* T-P , $PV^{\nu} = C$

$PV = RT$

$V = \frac{RT}{P}$ $\Rightarrow P\left(\frac{RT}{P}\right)^{\nu} = C$

$\Rightarrow P^{1-\nu} R^{\nu} T^{\nu} = C$

$\Rightarrow \frac{T^{\nu}}{P^{\nu-1}} = \frac{C}{R^{\nu}}$

$\Rightarrow \left(\frac{T^{\nu}}{P^{\nu-1}}\right)^{1/\nu} = \left(\frac{C}{R^{\nu}}\right)^{1/\nu} = C''$

$\Rightarrow \frac{T}{P^{(\nu-1)/\nu}} = C''$ } constant ——— (3)

(a) $PV^{\nu} = C$ ——— (*) PV - relationship

(b) $TV^{\nu-1} = C'$ ——— (*) V-T Relationship

(c) $\frac{T}{P^{(\nu-1)/\nu}} = C''$ ——— (*) T-P Relationship

$PV = RT$

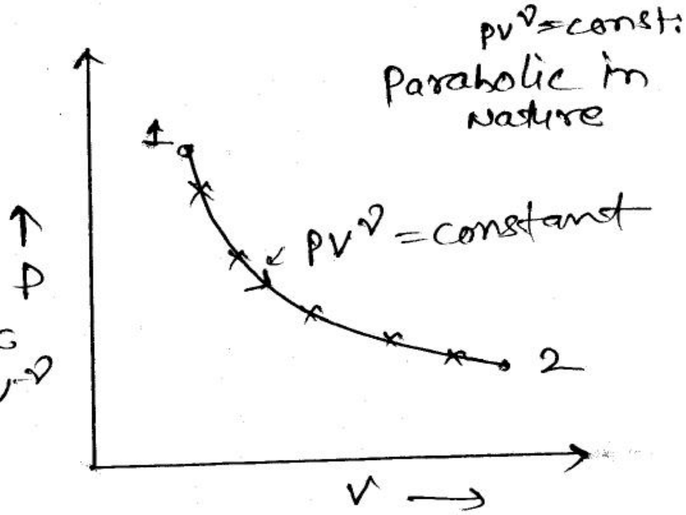
$\frac{PV}{T} = \text{constant}$

$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

(ii) **p–v diagram for adiabatic process**

$$pv^{\gamma} = \text{constant}$$

$$p \propto \frac{1}{v^{\gamma}}$$



$$\text{Slope} = \tan\theta = \frac{dy}{dx} \quad \Big| \quad pv^{\gamma} = c, \quad p = cv^{-\gamma}$$

$$\text{slope} = \frac{dp}{dv} = c(-\gamma)\, v^{-\gamma-1}$$

$$\frac{dp}{dv} = (pv^{\gamma})(-\gamma)\, v^{-\gamma-1} \quad \Big| \quad \text{put } pv^{\gamma} = c$$

$$\frac{dp}{dv} = -\gamma \frac{p}{v}$$

$$\left[\text{slope} = \frac{dp}{dv} = \left(-\gamma\frac{p}{v}\right)\right] \quad \Big| \quad \gamma = \frac{C_p}{C_v} = (+)\text{ve term}$$

(Or) $pv^{\gamma} = c$ differentiate

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

$$\left(\frac{dp}{dv} = -\gamma \cdot \frac{p}{v}\right)$$

(iii) **Change in Internal Energy :-**

$$(dU = C_v\, dT) \longleftarrow \text{for any closed system}$$

$$\boxed{U_2 - U_1 = C_v (T_2 - T_1)}$$

(iv) Work done (for adiabatic process)

$$\dot{Q} = 0$$

$$dU = dQ - dW$$

$$\Rightarrow \quad dW = P\,dV$$

$$\int_1^2 dW = \int_1^2 P\,dv \qquad \text{put } PV^{\gamma} = C, \quad P = C\,V^{-\gamma}$$

$$\int_1^2 dW = \int_1^2 C \cdot V^{-\gamma}\,dV$$

$$_1W_2 = C \int_1^2 V^{-\gamma}\,dV$$

$$_1W_2 = C\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_1^2$$

$$_1W_2 = C\left[\frac{V_2^{-\gamma+1} - V_1^{-\gamma+1}}{-\gamma+1}\right]$$

$$_1W_2 = \frac{C V_2^{-\gamma+1} - C V_1^{-\gamma+1}}{-\gamma+1}$$

$$_1W_2 = \frac{C}{-\gamma+1}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$$

$$PV^{\gamma} = C \Rightarrow P_1V_1^{\gamma} = P_2V_2^{\gamma} = C$$

$$_1W_2 = \frac{(P_2V_2^{\gamma})\,V_2^{-\gamma+1} - (P_1V_1^{\gamma})\,V_1^{-\gamma+1}}{-\gamma+1}$$

$$_1W_2 = \frac{P_2V_2 - P_1V_1}{-\gamma+1} \Rightarrow \boxed{_1W_2 = \frac{P_1V_1 - P_2V_2}{\gamma - 1}}$$

Imp.

$$\boxed{{}_1W_2 = \frac{P_1V_1 - P_2V_2}{\gamma - 1}} \quad ; \quad PV = nRT$$

$${}_1W_2 = \frac{nR(T_1 - T_2)}{\gamma - 1}$$

$$\boxed{{}_1W_2 = \frac{nR(T_1 - T_2)}{\gamma - 1}}$$

$$C_p - C_v = R$$

$$\frac{C_p}{C_v} - 1 = \frac{R}{C_v}$$

$$\left(\gamma - 1 = \frac{R}{C_v}\right) \Rightarrow \frac{R}{\gamma - 1} = C_v$$

$$\boxed{{}_1W_2 = nC_v(T_1 - T_2)}$$

(IV) Heat transfer for adiabatic process

We know $\boxed{\delta Q = 0}$

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

$${}_1Q_2 = {}_1W_2 + (U_2 - U_1) \qquad dU = C_v\,dT$$

$$\Rightarrow {}_1Q_2 = \left[\frac{P_1V_1 - P_2V_2}{\gamma - 1}\right] + C_v(T_2 - T_1)$$

$$\because PV = RT, \quad C_p - C_v = R, \quad \left(C_v = \frac{R}{\gamma - 1}\right)$$

$$\Rightarrow {}_1Q_2 = \frac{R(T_1 - T_2)}{\gamma - 1} + \frac{R}{\gamma - 1}(T_2 - T_1)$$

$${}_1Q_2 = \frac{R(T_1 - T_2)}{\gamma - 1} - \frac{R}{\gamma - 1}(T_1 - T_2)$$

$\boxed{{}_1Q_2 = 0}$ Hence proove, Heat transfer is zero in Adiabatic process.