CHEMISTRY CLASS -XI

UNIT -6
THERMODYNAMICS

MODULE -1/5

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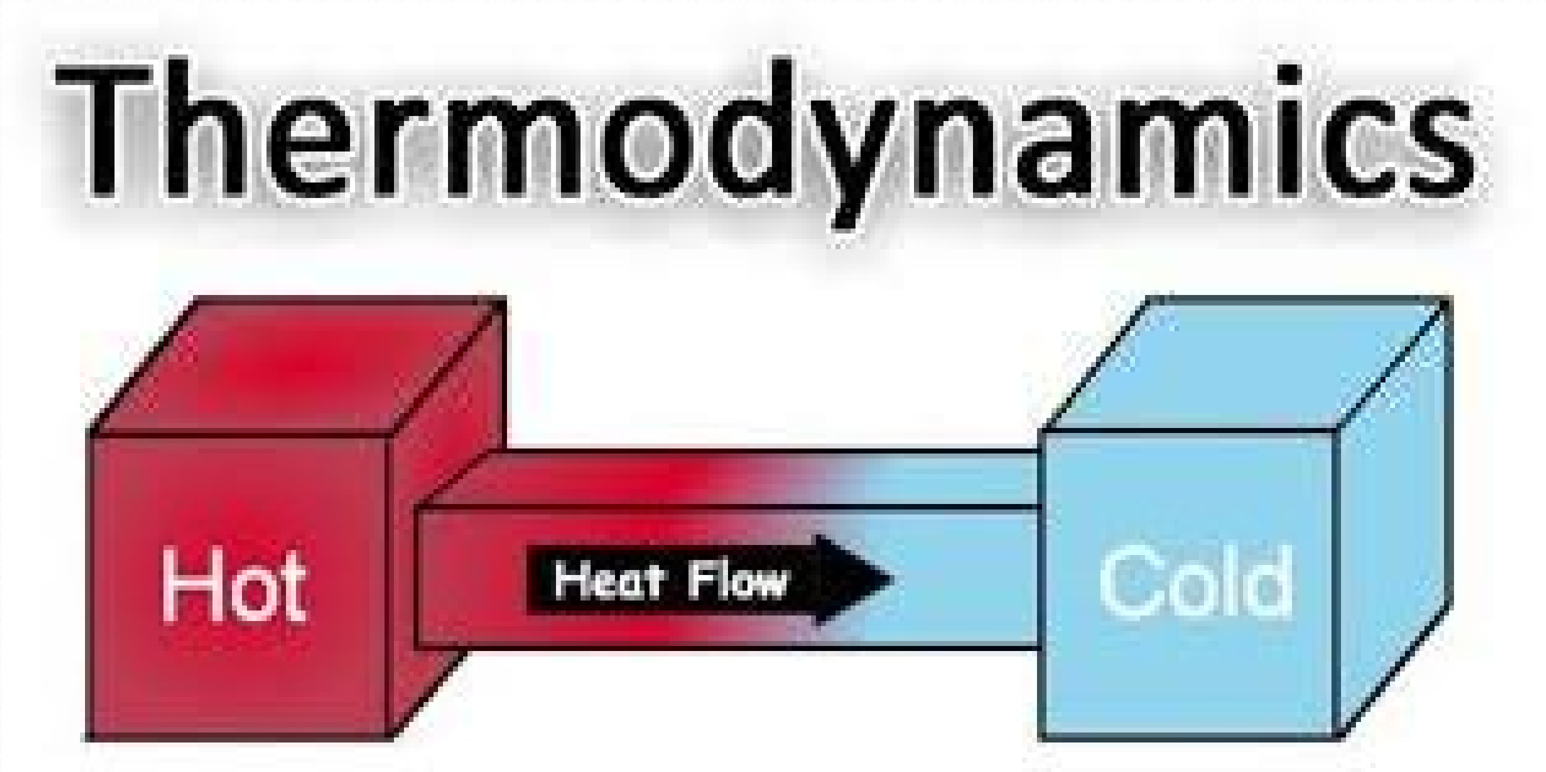
OUTLINE

- Introduction to thermodynamics
- Basic terminologies involved in thermodynamics
- System
- Surroundings
- Intensive and Extensive Properties
- State Function
- State variables
- Reversible and irreversible process


Thermodynamics
Hot
Heat Flow
Cold

INTRODUCTION

- Thermodynamics is all about energy transformation
- Various types of energies are inter related .Under certain conditions these energies may be transformed from one form to another. Energy stored in the molecules can be released as heat during chemical reactions ,when a fuel like methane, cooking gas or coal burns in air.
- The chemical energy may also be used to do mechanical work when a fuel burns in an engine or to provide electrical energy through a galvanic cell like dry cell.
- The study of these energy transformations forms the subject matter of thermodynamics.
- The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules.
- Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change.

LIMITATIONS OF THERMODYNAMICS

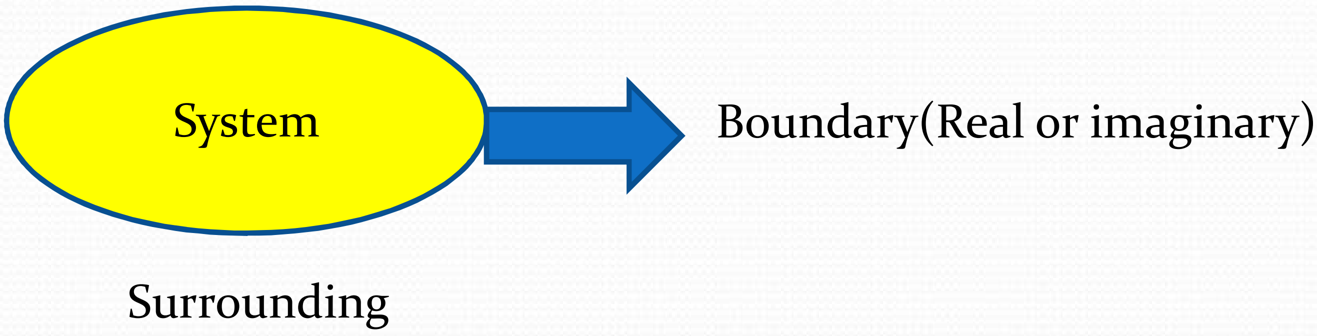
- Its Laws are applicable to the bulk of matter and does not provide any information about individual atom.

- It predicts feasibility of the reaction but fails to suggest the rate of reaction.

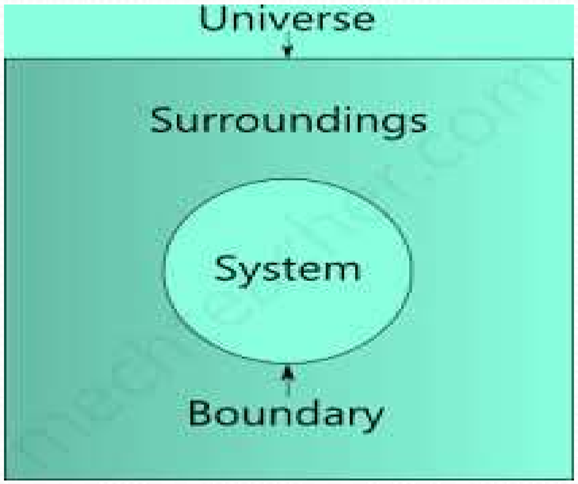
- Does not deals with microscopic entities

SOME BASIC TERMS

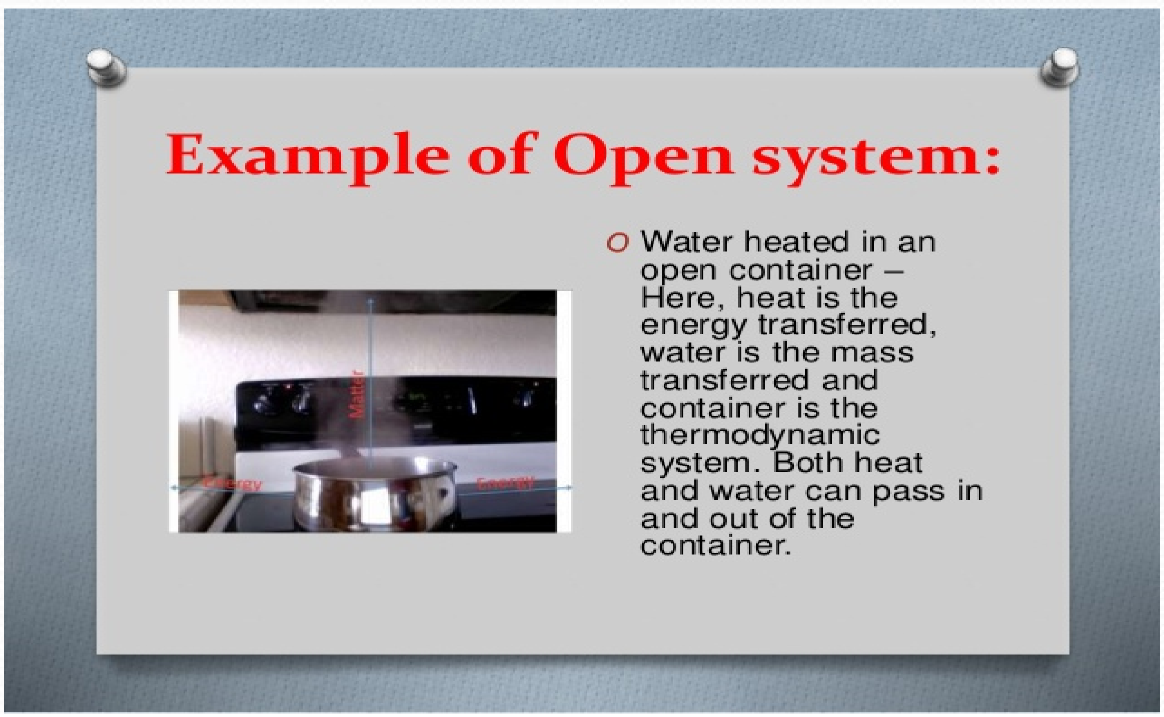
- **System**-A system in thermodynamics refers to that part of universe in which observations are made.System is part of the universe with real or imaginary bounderies.eg-A room,an engine,Human body etc.



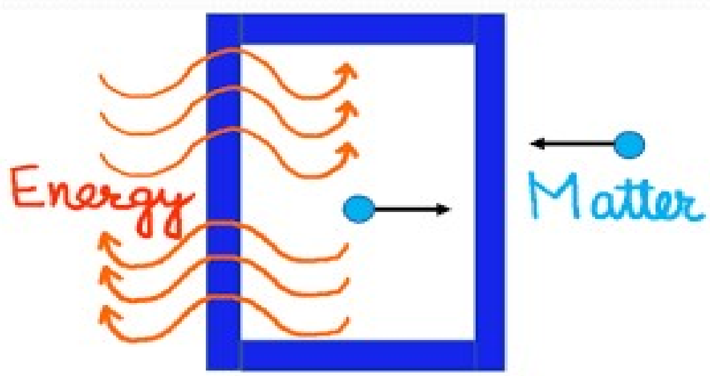
- **Surrounding**- The surroundings include everything other than the system.
- System and the surroundings together constitute the **universe** .Surrounding is adjacent to real or imaginary boundary
- **universe = system + surrounding**



- **Types of System**-We, further classify the systems according to the movements of matter and energy in or out of the system.
- **Open system-**
- In an open system, there is exchange of energy and matter between system and surroundings The presence of reactants in an open beaker is an example of an open system. Here the boundary is an imaginary surface enclosing the beaker and reactants.
- Example- Thermos flask and Stainless steel flask which is open

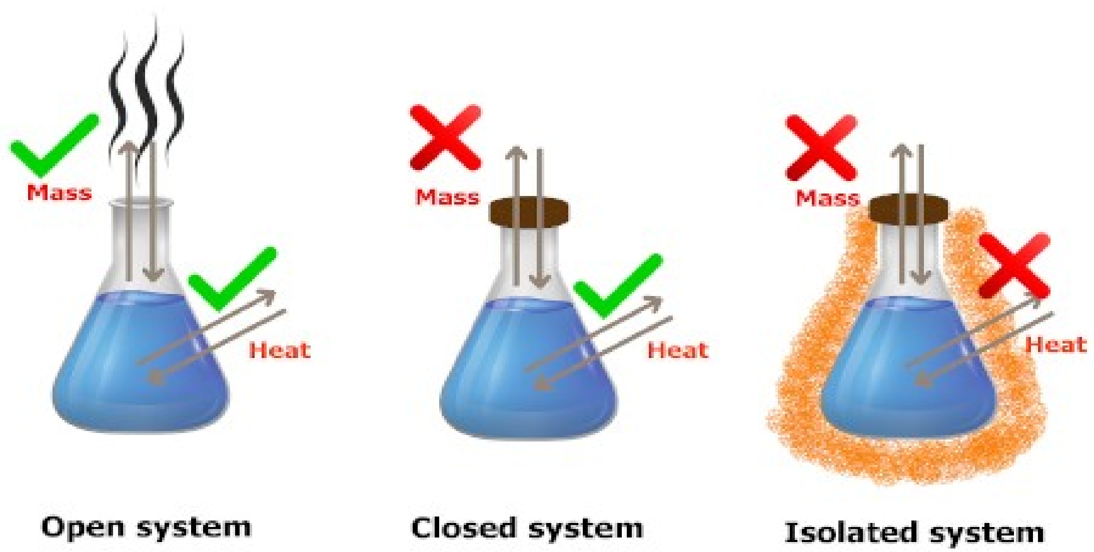


- **Closed System**
- In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings. The presence of reactants in a closed vessel made of conducting material e.g.copper or steel is an example of a closed system.
- Coffee in closed stainless steel is an example of closed system.
- A rubber balloon filled with air and tightly closed.



A closed system

- **3.Isolated System**
- In an isolated system, there is no exchange of energy or matter between the system and the surroundings The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.Eg –Coffee in Thermos Flask



Isolated system

- Thermos flask

Closed, Open, and Isolated Systems

Types of	Energy	Mass Transfer	Examples
Closed System	Yes	No	Gas in a sealed container
Open System	Yes	Yes	Turbines, pumps, valves etc.
Isolated System	No	No	Universe, Thermoflask

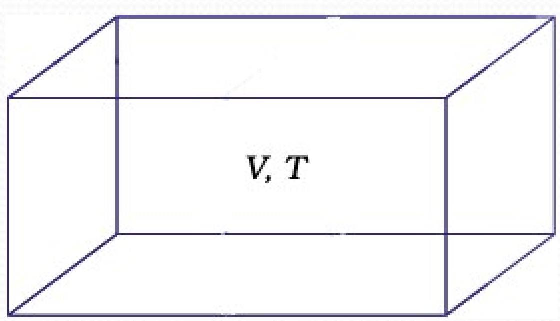
Properties of the system

- State of system is defined by a particular set of measurable quantities called properties by which the system can be described. For example Temperature,pressure,volume defines the thermodynamic state of the system.
- Properties can be categorised into intensive and extensive properties on the basis of dependence on the size or mass of the system.

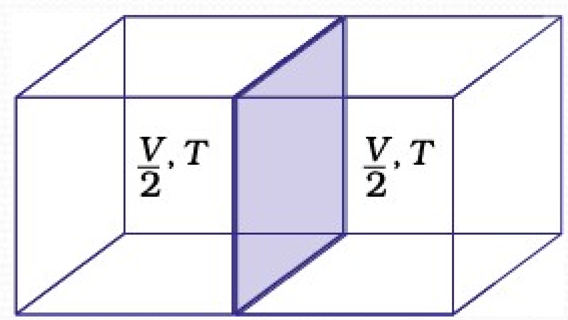
- **Intensive properties**-Property whose value is independent of the size or mass of the system.For example Temperature,Density,Pressure etc.
- **boiling point of water is 100ºC , irrespective of volume of 1 liter or 2 liters at 1 atm. pressure. So boiling point is intensive property.**

- **Extensive Properties**—Property whose value depends on the size or mass of the system. For example-mass, volume internal energy, heat capacity ,number of moles etc.
- **volume of one mole of gas at STP is 22.4 dm^3, but two moles of gas occupies 44.8 dm^3 at STP. So volume is extensive property.**

- Other examples of intensive property are molar volume, *V*m and molar heat capacity, *C*m, viscosity, surface tension.
- Let us understand the distinction between extensive and intensive properties by considering a gas enclosed in a container of volume *V* and at temperature *T(fig 1)*. Let us make a partition such that volume is halved, each part now has one half of the original volume, *V/2* but the temperature will still remain the same i.e., *T(fig2)*. It is clear that volume is an extensive property and temperature is an intensive property



(fig 1)



(fig2).

- **Extensive and Intensive Properties**

Intensive property	Symbol
Specific volume	v
Specific internal energy	u
Specific entropy	s
Specific enthalpy	h
Specific Gibbs free energy	g
Specific heat capacity at constant volume	c_V
Specific heat capacity at constant pressure	c_P

Extensive property	Symbol
Volume	V
Internal energy	U
Entropy	S
Enthalpy	H
Gibbs free energy	G
Heat capacity at constant volume	C_V
Heat capacity at constant pressure	C_P

- **Extensive and Intensive properties**
- Extensive properties are additive intensive properties are non additive
- Ratio of two extensive properties gives an intensive property.

  Eg –Density=Mass/Volume

  Molarity=Number of moles of solute/volume of solution
- An extensive property can be converted into intensive property by defining it per gram ,per mole per litre

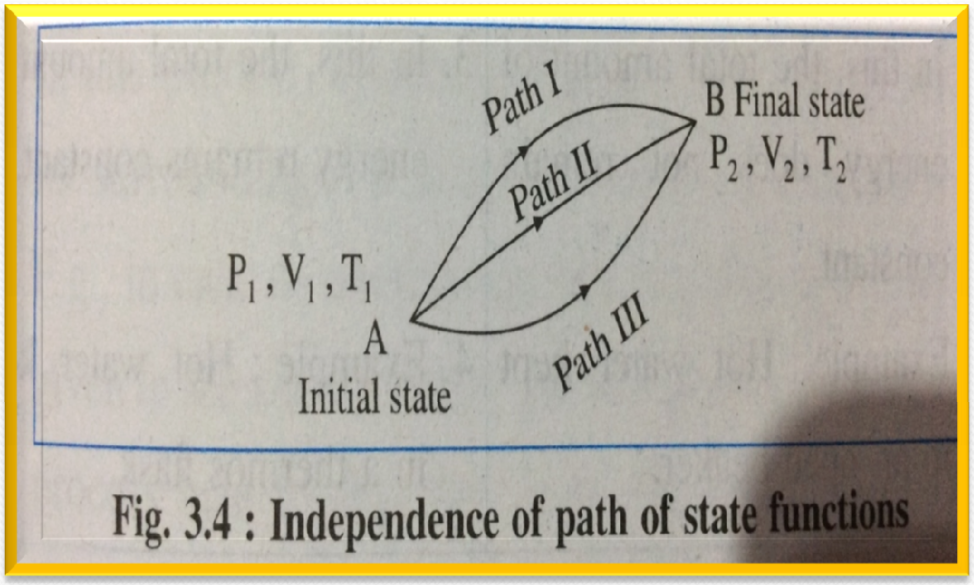
State of the system

- It implies the conditions of existence of a system when its macroscopic properties have definite values
- **Macroscopic properties are Pressure(P) volume(V) temperature(T) amount (n).**
- **Important features**
- Variation in one or more macroscopic properties brings a change in the state of the system ,when other macroscopic properties attain new values .thus these properties are called **state variables or state functions.**
- Initial state refers to the starting state of system in equilibrium. After interaction with surrounding the system attains another equilibrium state which is referred as final state of the system.
- Thermodynamic state should not be confused with physical state or phase.
- A system is said to be in thermodynamic equilibrium if its macroscopic properties do not change with time

State function Or State variable

- The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (*p*), volume (V), and temperature (T) as well as the composition of the system. We need to describe the system by specifying it before and after the change.. We specify the state of **the system by state functions or state variables**.
- State function is thermodynamic property whose value depends only on initial and final states of the system. These are independent of manner as to how the change is brought about.
- For example if 'h' is the height of a mountain between top to bottom, then h is independent of the path followed in reaching the top of the mountain. so we can say 'h' is analogous to state function .
- Some common state functions in thermodynamics are Internal Energy(U) ,Enthalpy(H),Entropy(S),Gibb's Free Energy(G),Pressure(P) ,Temperature(T), Volume(V)

STATE FUNCTION



in all the three paths followed

$\Delta P = P_2 - P_1$

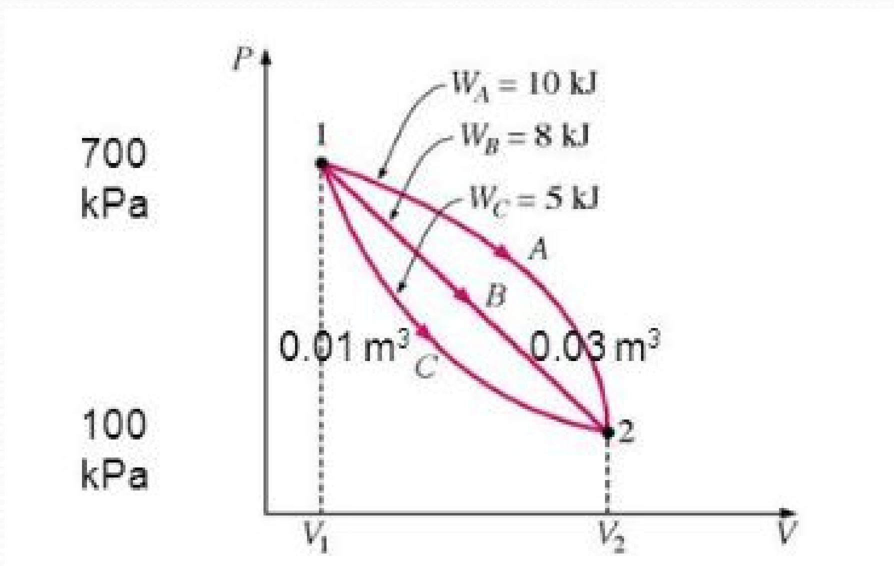
$\Delta V = V_2 - V_1$

$\Delta T = T_2 - T_1$

- ✓ **Changes are independent of path followed**
- ✓ **It depends on initial and final state**

Path Function

- Function which depends on path i.e. how the process i.e. carried out to reach a state from another state depends on path.
- Example-Work,Heat,Loss of energy to due to friction



THERMODYNAMIC FUNCTIONS

All state functions and paths functions are referred as thermodynamic functions

What if all the thermodynamic functions doesn't change with time in the system????????

_Here system is said to achieve a thermodynamic equilibrium

Equilibrium Types

Thermal equilibrium:- system and surrounding are at same temperature Ex:- water in equilibrium with its vapour at constant temperature.

Chemical equilibrium :-When chemical composition of the system does not change. Ex:

$N_2 + 3H_2 = 2NH_3$ (all are gases)

$PCl_5 = PCl_3 + Cl_2$ (all are gases)

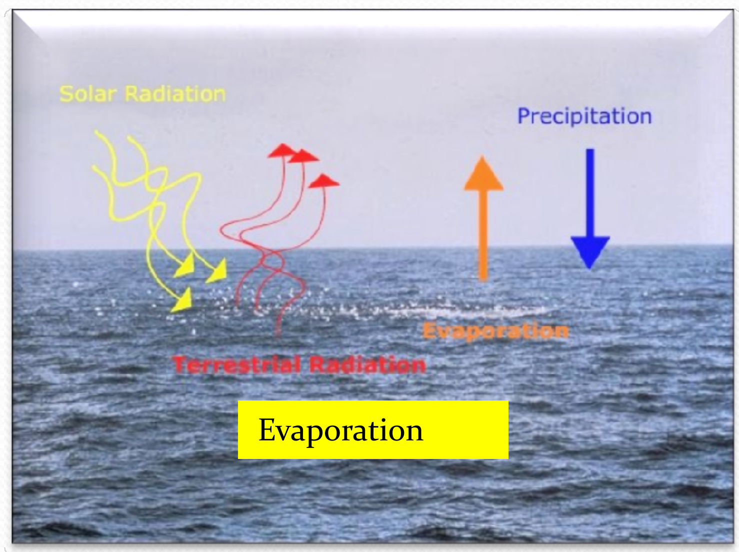
Mechanical equilibrium:- there is no macroscopic movement with in the system.(equality of pressure between system and surrounding)

i.e. there is no movement of matter in the system with respect to its surrounding

Thermodynamic Process

- It is the operation which brings change in the state of the system.
- Thermodynamic processes are of following types-
- (i) **Isothermal process** In which temperature remains constant, i.e., (dT = 0, Δ U = 0).
- **internal energy depends on temperature of system as there is no change in temperature**
- **∴ $U_1 = U_2$**
- **∴ $\Delta U = 0$**

Melting Of Ice



Isothermal process

Consider an example of refrigerator

We know that temperature of refrigerator remains constant even though many reaction are taking place inside it.

what does that mean????????

refrigerator is designed in such a way that heat generated is constantly thrown out in surrounding to maintain its temperature constant.

thus refrigerator carries isothermal process inside it.

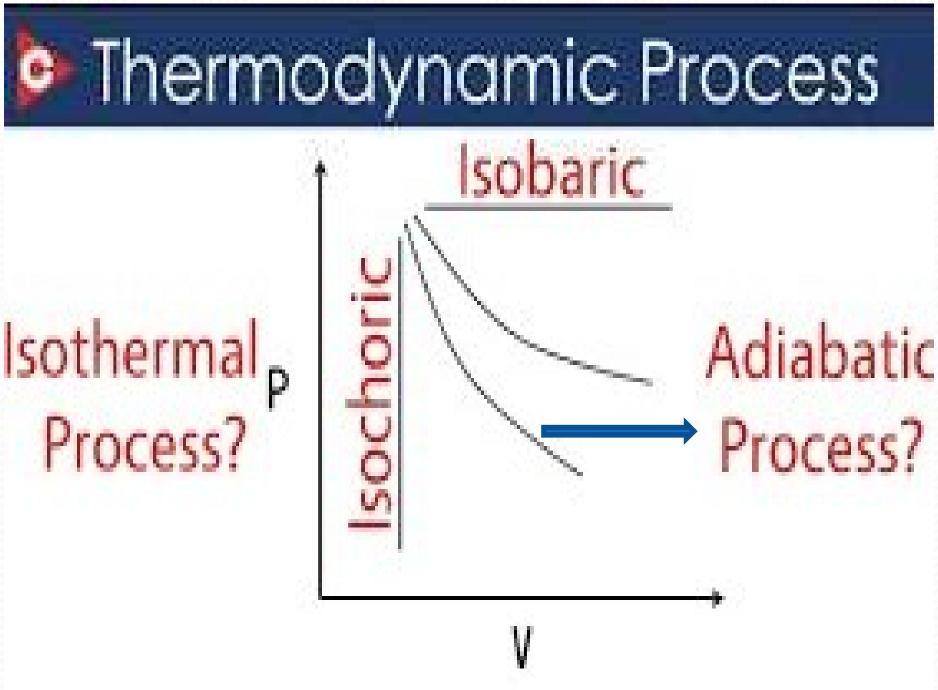
- (ii) **Isochoric process** In which volume remains constant, i.e., ($\Delta V = 0$).

- (iii) **Isobaric process** In which pressure remains constant, i.e., ($\Delta p = 0$).
- **All the process carried out in natural environment are isobaric as atmospheric pressure remains constant**

- (iv) **Adiabatic process** In which heat is not exchanged by system with the surroundings, i.e., ($\Delta q = 0$).

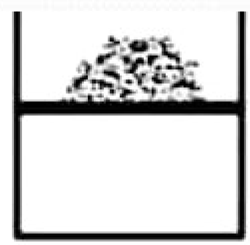
  It can be achieved by insulating system bounderies for heat transfer
- (v) **Cyclic process** It is a process in which system returns to its original state after undergoing a series of change,
- i.e., Δ U cyclic = 0; Δ H cyclic = 0

Thermodynamic Process



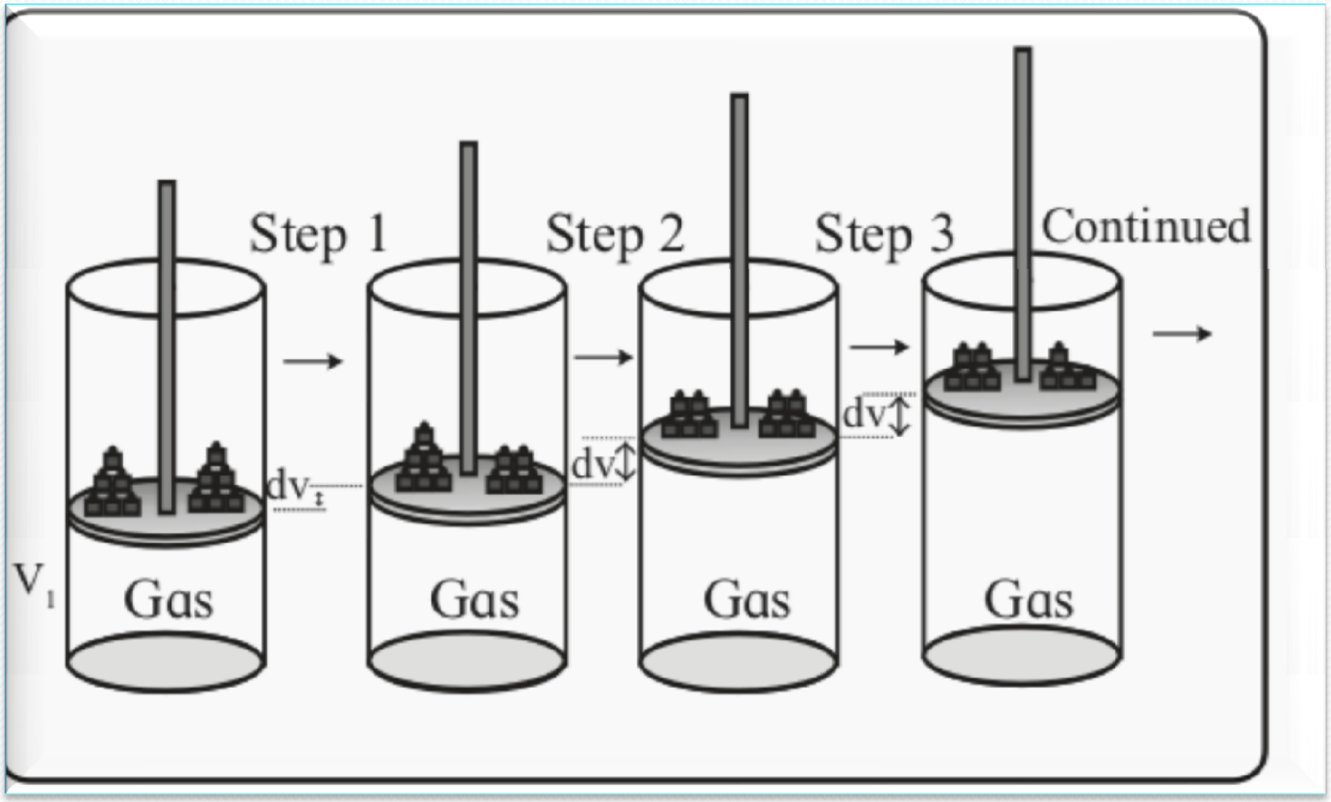
Reversible Process

- **Reversible process A process that follows the reversible path, i.e., the process which** occurs in infinite number of steps in this Way that the equilibrium conditions are maintained at each step, and the process can be reversed by infinitesimal change in the state of functions.
- **Important features of reversible process**
- Driving force is infinitesimally small
- PV work is done across the pressure difference dp
- A reversible heat transfer takes place across temperature difference dT
- It takes infinite time for completion of process
- It is an imaginary process and cannot be realised in actual practice
- Throughout the process ,the system remains infinitesimally closer to state of equilibrium and exact path of process can be drawn
- It's an ideal process



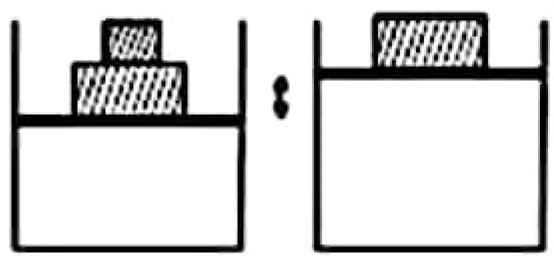
Reversible process

Reversible process



Irreversible process

- **Irreversible process The process which cannot be reversed and amount of energy** increases. All natural processes are Irreversible.
- **Important features of reversible process**
- Driving force is large and finite
- PV work is done across the pressure difference ΔP
- A reversible heat transfer takes place across temperature difference ΔT
- It takes finite time for completion of process
- It is an natural process and takes place in particular direction under given conditions.
- the system is far away from state of equilibrium and exact path of process cannot be defined as different part of the system are in different conditions.
- It's a real process.



irreversible process

Summary

Universe	• System(open, closed, isolated) • surrounding
State function/state variable	• Temperature • Pressure • Enthalpy • Gibbs energy • Internal energy
Process	• Isothermal • Isochoric • Isobaric • Adiabatic • Reversible(ideal) • Irreversible(real)

THANK YOU