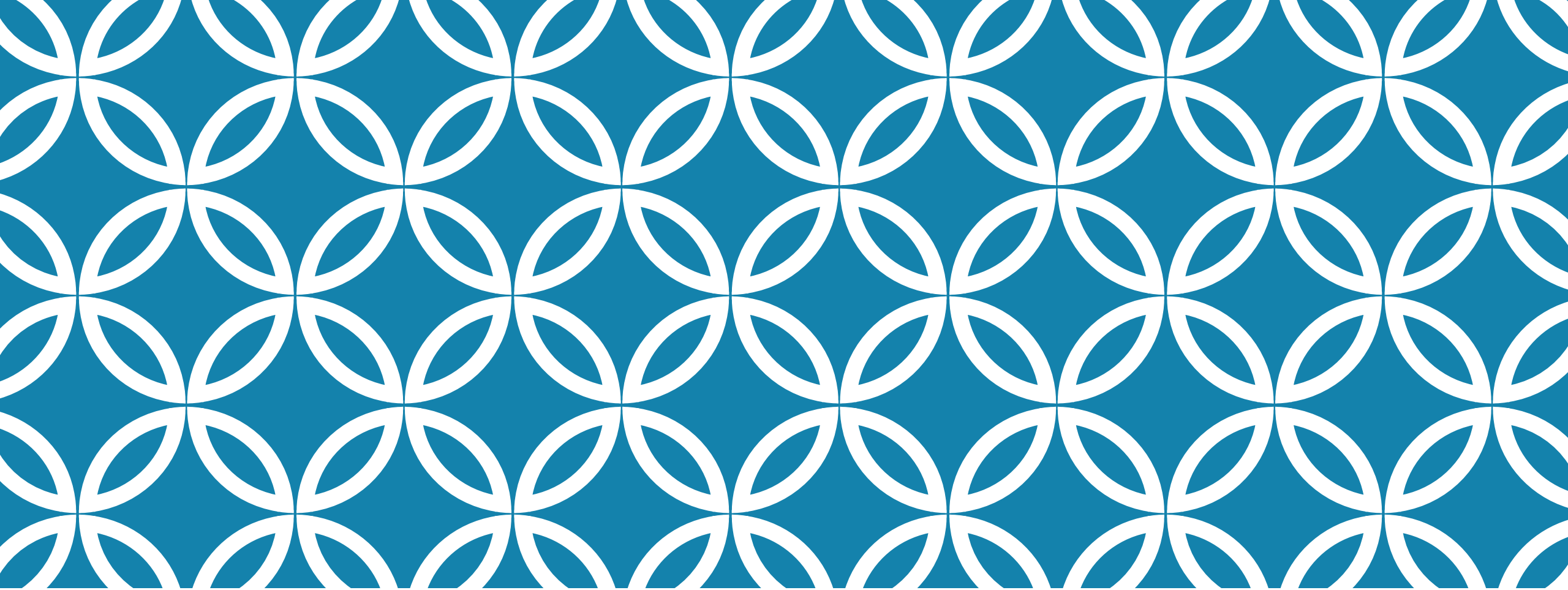

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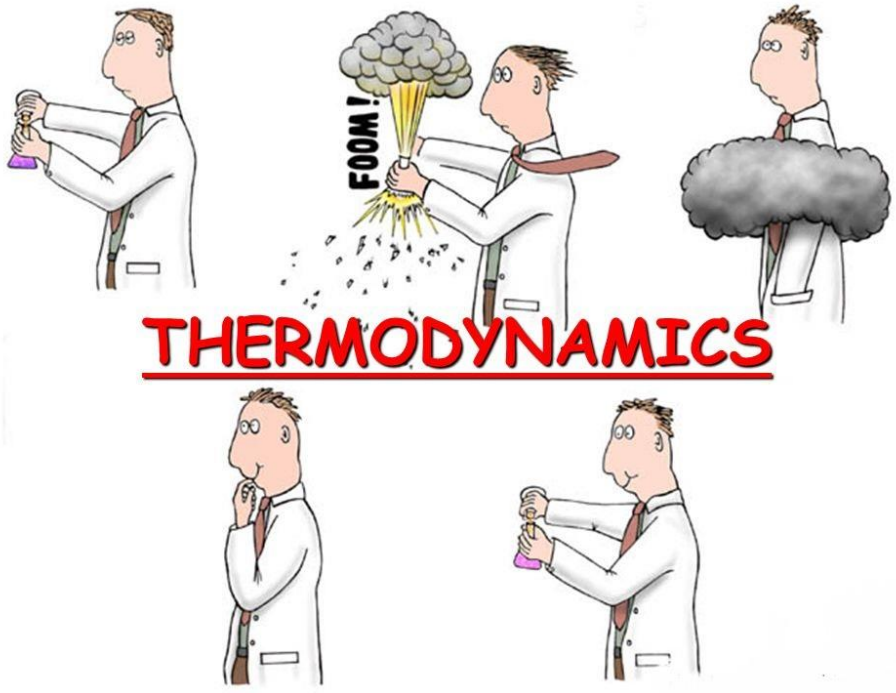
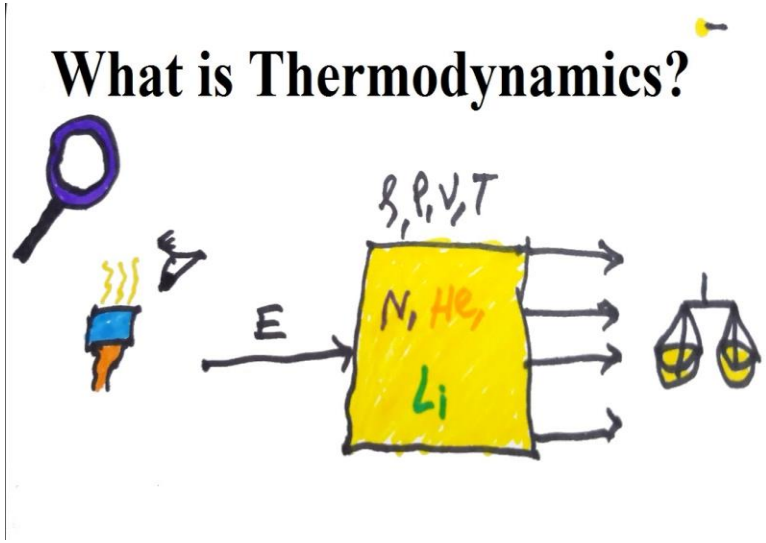
TITLE OF PAPER : PHYSICAL CHEMISTRY

UNIT 2 – CHEMICAL THERMODYNAMICS



DEFINITION OF THERMODYNAMICS

- Thermodynamics is a Greek word which means flow of heat in physical and chemical reactions
- Thermodynamics is a branch of science which deals with study of different forms of energy and their interconversions
- It deals with energy changes in physical and chemical processes



CHEMICAL THERMODYNAMICS : It is the branch of thermodynamics which deals with the study of the processes in which only chemical energy is involved.

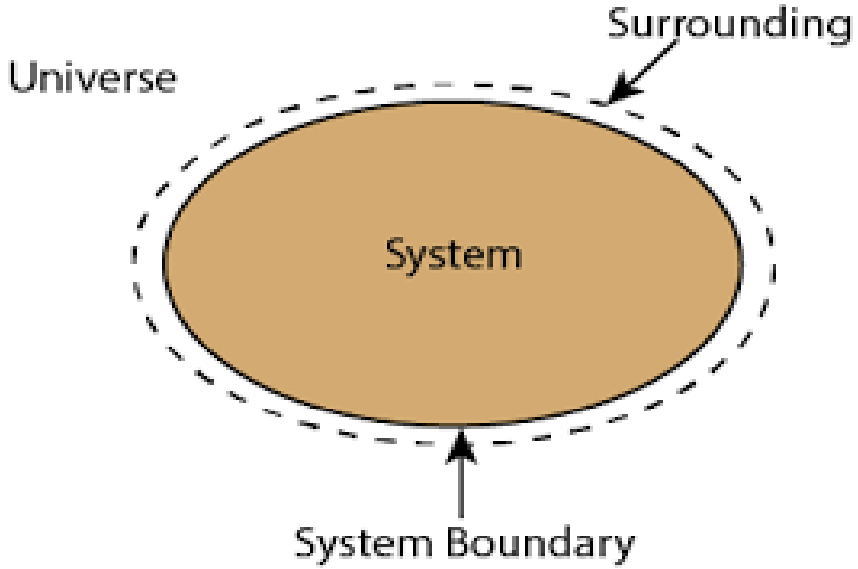
e.g. Heat is evolved when an acid is neutralized by a base, combustion of coal generates heat and light

TERMINOLOGY OF THERMODYNAMICS

SYSTEM : A part of the universe whose properties we wish to study and which is separated from the rest of the part by either real or an imaginary boundary is called system.

SURROUNDING : The remaining portion of the universe excluding the system is called surrounding.

UNIVERSE = SYSTEM + SURROUNDING



TYPES OF SYSTEM

1) Depending on number of phases present in a system

- **Homogeneous System** : A system containing only one phase and which is uniform throughout is called homogeneous system

  e.g. A pure single solid, A uniform solution, A mixture of gases

- **Heterogeneous System** : A system that has more than one phase and which is not uniform throughout is called heterogeneous system

  e.g. Ice in contact with water, A liquid in contact with vapor, mixture of immiscible liquids

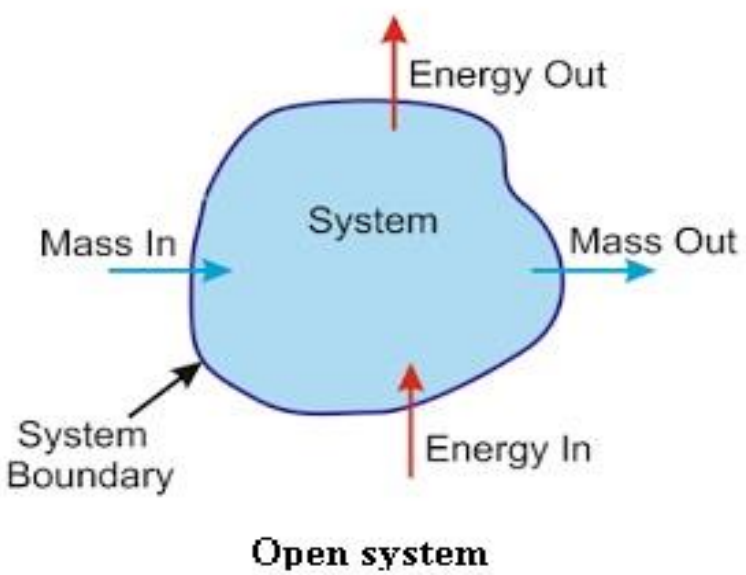
2) Depending on interaction between system and surrounding

- **An Open System** : A system that can exchange the matter as well as energy with its surroundings

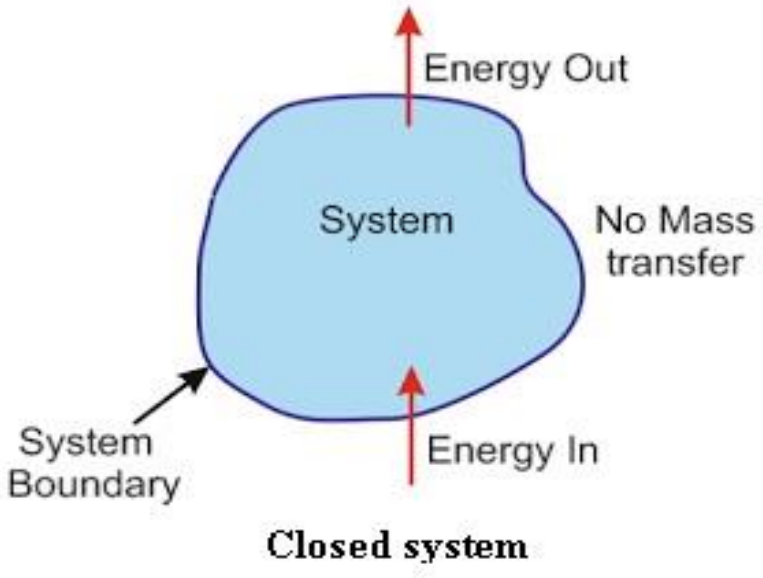
  e.g. A liquid in contact with its vapor in beaker

- **A Close System** : A system that can exchange the energy but not the matter with its surroundings

  e.g. Hot or cold water in a sealed bottle



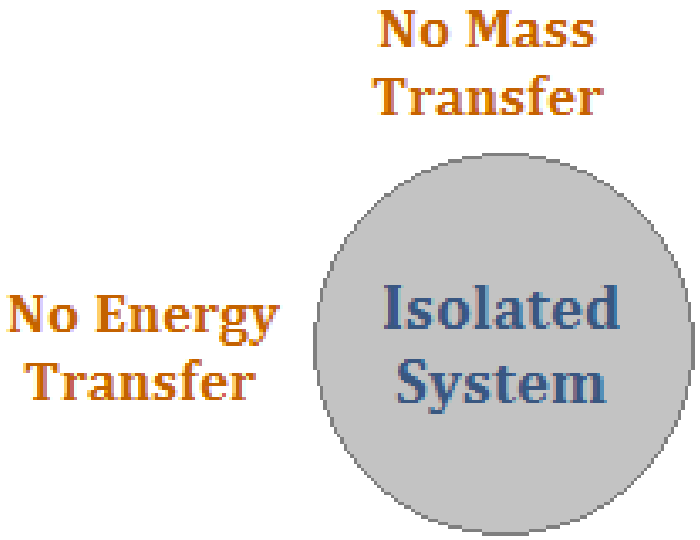
Open system



Closed system

- **An isolated system** : A system that can neither exchange energy nor the matter with its surroundings

  e.g. Thermo flasks



- **Macroscopic System** : A system containing large number of atoms, ions or molecules is called macroscopic system

MACROSCOPIC PROPERTIES

- The properties associated with macroscopic system are called macroscopic properties.

E.g. pressure, volume, temperature, density, viscosity, composition, surface tension, etc.

- Macroscopic properties can be divides into two classes :

1) **Extensive Properties**: The properties of the system which depends on the amount of the substance present in the system

E.g. mass, volume, energy etc.

2) **Intensive Properties**: The properties of the system which is independent of the amount of the substance present in the system

E.g. pressure, temperature, density, viscosity, surface tension etc.

THERMODYNAMIC PROCESS

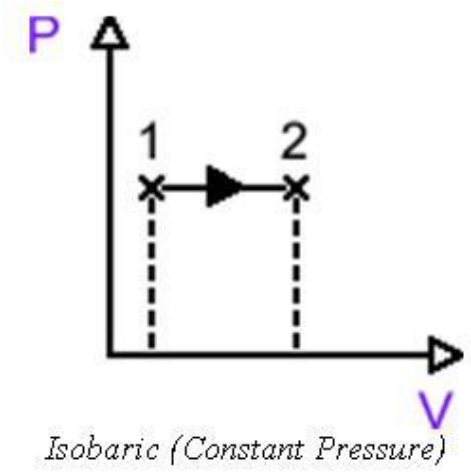
Types of Process:

1) **ISOTHERMAL PROCESS** : It is a process in which the temperature of the system remains constant throughout. i.e. $\Delta T = 0$

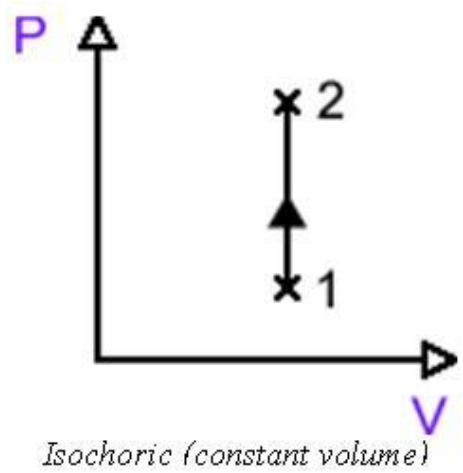
2) **ADIABATIC PROCESS** : If no heat enters or leaves the system during a process than it is called adiabatic process. i.e. $\Delta q = 0$

3) **ISOBARIC PROCESS** : It is a process in which the pressure of the system remains constant throughout. i.e. $\Delta P = 0$

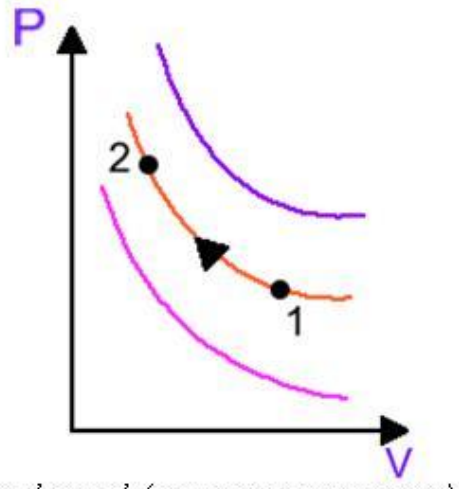
4) **ISOCHORIC PROCESS** : It is a process in which the volume of the system remains constant throughout. i.e. $\Delta V = 0$



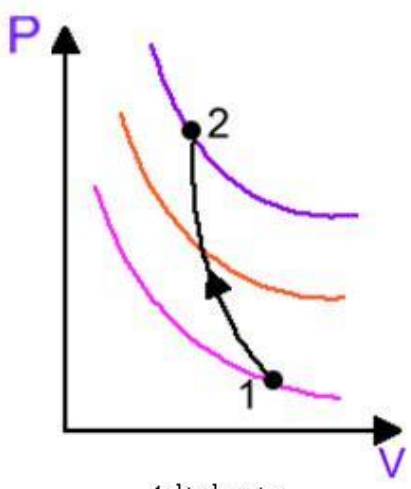
Isobaric (Constant Pressure)



Isochoric (constant volume)

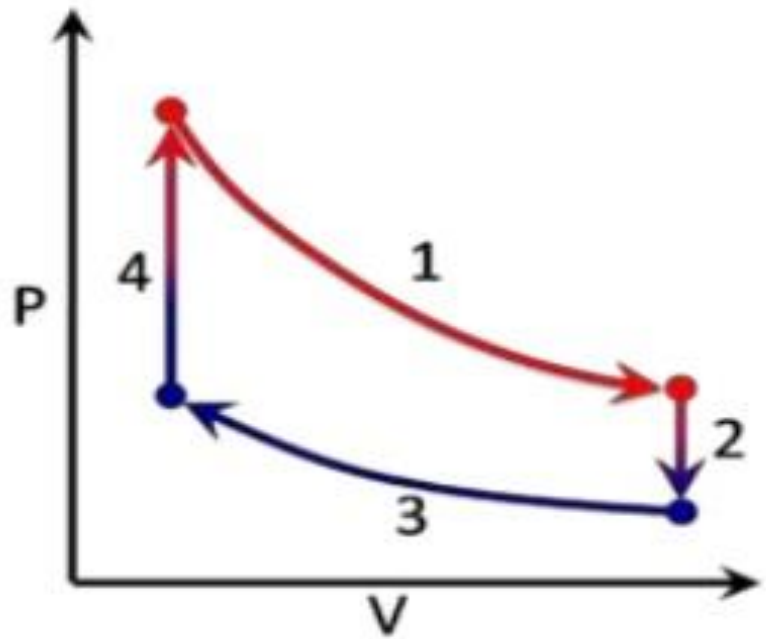


Isothermal (constant temperature)



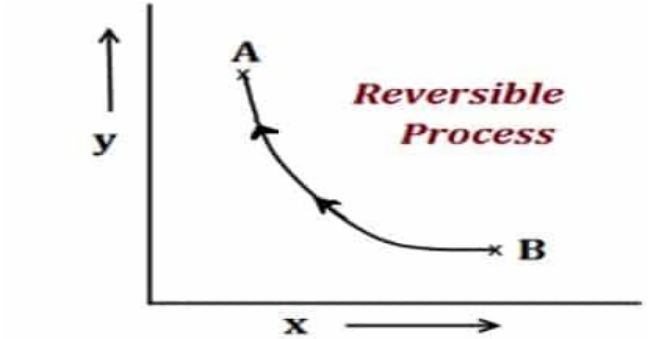
Adiabatic

Cyclic Process



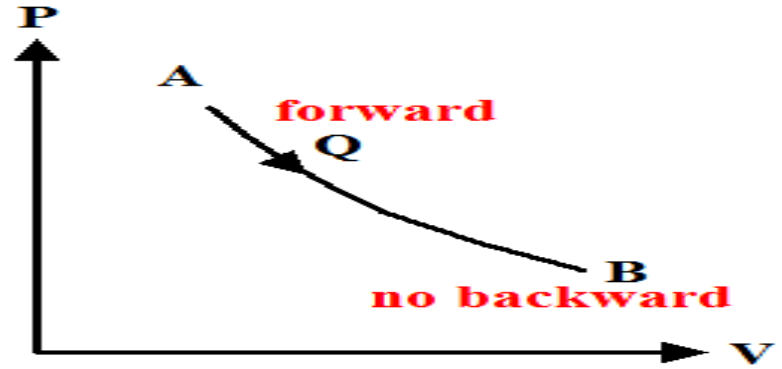
REVERSIBLE PROCESS

- A reversible process is a process that can be reversed in order to obtain the initial state of a system
- Can be reversed
- A reversible process can be made to proceed in forward or backward direction
- Work done in a reversible process is greater than the corresponding work done in irreversible process
- e.g. Working of a Galvanic cell which is made up of a zinc and a copper electrode



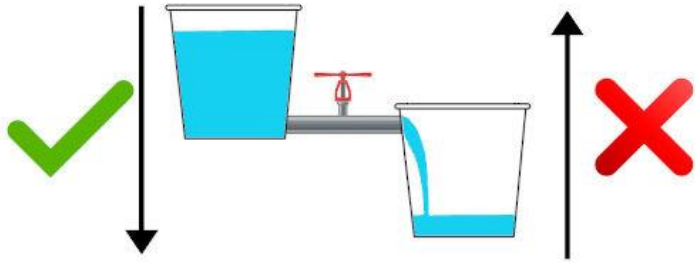
IRREVERSIBLE PROCESS

- An irreversible process is a thermodynamic process that cannot be reversed in order to obtain the initial state of a system
- Cannot be reversed
- Irreversible process can take place in one direction only
- Work done in a irreversible process is always lower than the same kind of work done in a reversible process
- e.g. Most of spontaneous processes are irreversible in nature like water flowing down a hill

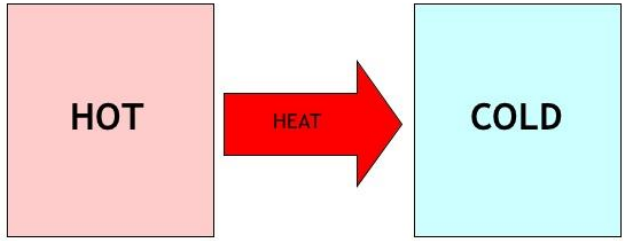


SPONTANEOUS PROCESS

- Those processes which actually occur in nature are known as natural or spontaneous processes.
- In such a process, a change takes place in a system without the aid of any external agency.
- For example;
  i) Liquid flows from a higher to a lower level
  ii) Gas spontaneously moves from a higher to lower pressure
  iii) Heat flows from a hotter body to a colder body
  iv) Dissolution of salt in water
  v) Evaporation of water in open vessel
- All this spontaneous reactions take place in one direction and are irreversible.



Water flows spontaneously from higher level to lower level



- Heat always moves from HOT to COLD.
  hot→cold

- Every system moves towards the state of equilibrium.
- Therefore, we may state that; **all spontaneous processes are irreversible or all spontaneous processes tend to a state of equilibrium.**

CRITERIA FOR SPONTANEOUS CHANGES

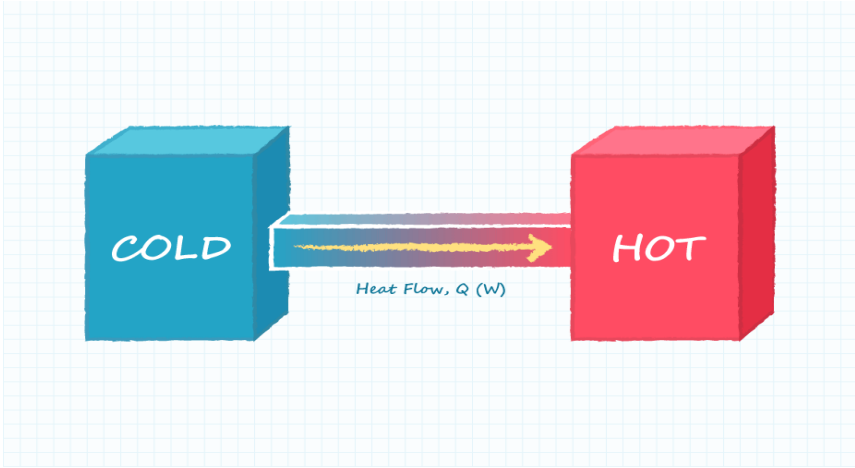
ΔG_{sys} < 0 (negative) , the process is spontaneous.

ΔG_{sys}= 0 (zero) , the process is at equilibrium.

ΔG_{sys}> 0 (positive) , the process is non-spontaneous.

NON-SPONTANEOUS PROCESS

- It is the process which cannot take place by itself.
- Non-spontaneous processes occur by supplying external energy to the system.
- For example;
  i) Flow of heat from cold body to hot body
  ii) When water is pumped from a lower level to a higher level, external energy is required
  iii) Dissolution of sand in water




Spontaneous process


Nonspontaneous process

FIRST LAW OF THERMODYNAMICS

- Energy of Universe is constant
- It law stated as;

> Energy can neither be created nor be destroyed,
> but it can only be converted from one form to another.

- Mathematically, it can be expressed as :

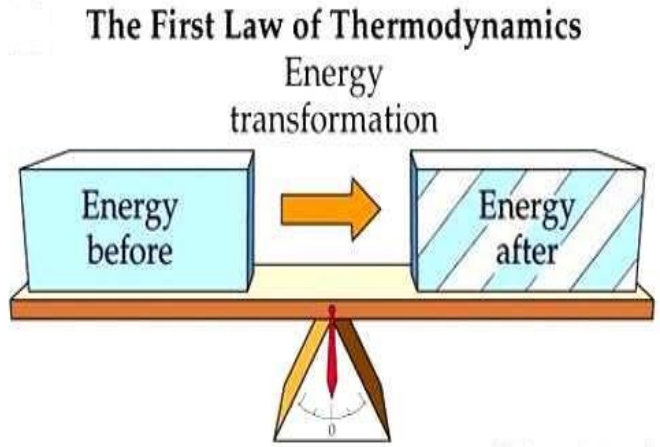
$$\Delta E = q - W$$

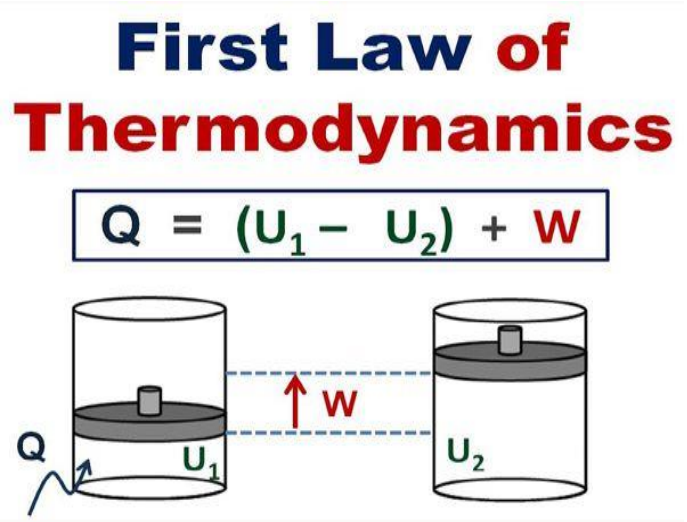
- Where, ΔE = Internal energy

  q = heat

  W = work done

- If the system changed its state without doing any work than W=0 and $\Delta E = q$. This means that absorbed or lost energy is stored as internal energy.
- If a system works without any transfer of energy then q=0, so, $\Delta E = W$. In general, $\Delta E = q + W$.





LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

- First law does not explain why chemical reactions do not proceed to completion and it also does not answer why spontaneous or natural processes are uni-directional. It also does not explain anything about the source of heat and direction of flow of heat.
- First law states that all forms of energy change into one another but does not define the extent of convertibility of one form of energy into another.
- First law cannot explain that while work can be completely converted into heat, heat cannot be completely converted into work without leaving permanent changes in the system or surroundings.
- First law cannot explain as to why all naturally occurring processes always tends to change spontaneously in a direction which leads to equilibrium.
- First law does not contradict the existence of heat engine of 100% efficiency or self- acting machines. But on the basis of human experiences we can say that such heat engines or machines are not attainable in actual practice.


THANK
YOU