Thermodynamic

- LECTURE (1)

- ❑ THERMODYNAMIC TERMS AND BASIC CONCEPTS
- ❑ HOMOGENEOUS AND HETEROGENEOUS SYSTEMS
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- ❑ THERMODYNAMIC PROCESSES
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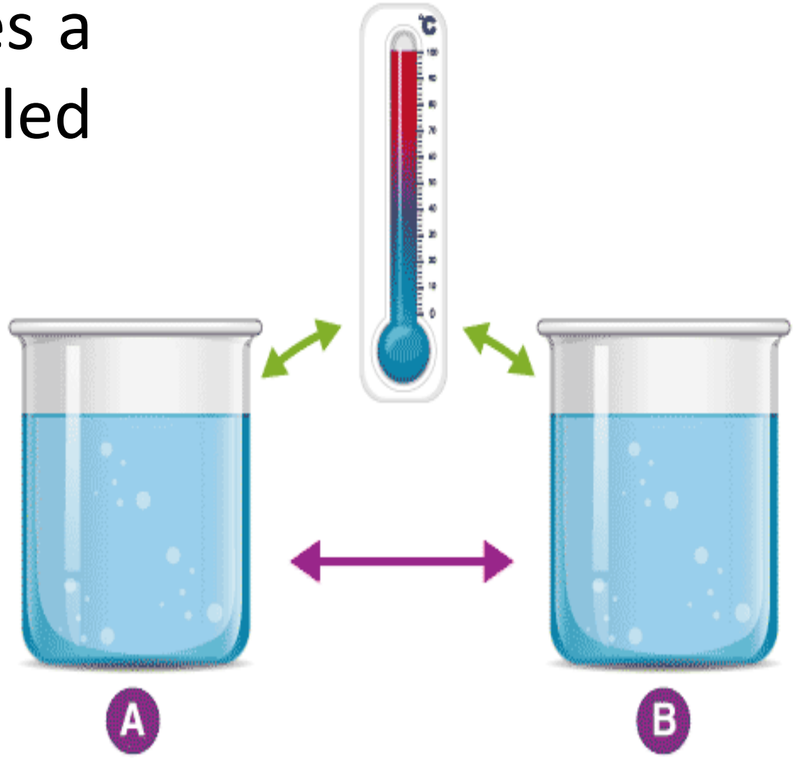
The study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation, is called ***Thermodynamics.***

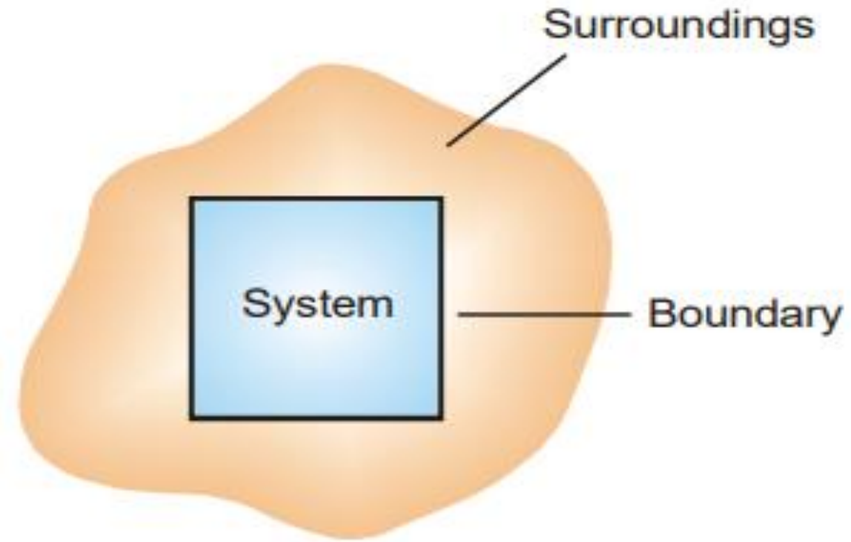


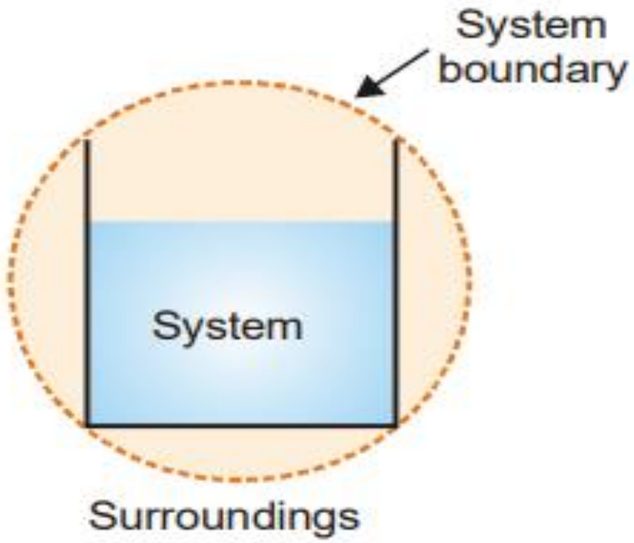
- In studying the flow of energy into or out of a system, considering changes in certain properties of the system.
  - ❑ Temperature
  - ❑ Pressure
  - ❑ Volume
  - ❑ Concentration
- Measuring the changes in these properties from the initial state to the final state, provide information about energy and related quantities such as:
  - ❑ Heat
  - ❑ work

THERMODYNAMIC TERMS AND BASIC CONCEPTS

An important part of the study of thermodynamics is a few terms and definitions which must be understood clearly.

- **SYSTEM** *(part of the universe which is under thermodynamic study)*
- **BOUNDARY** *(the rest of the universe)*
- **SURROUNDINGS** *(The real surface separating the system from the surroundings)*





HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

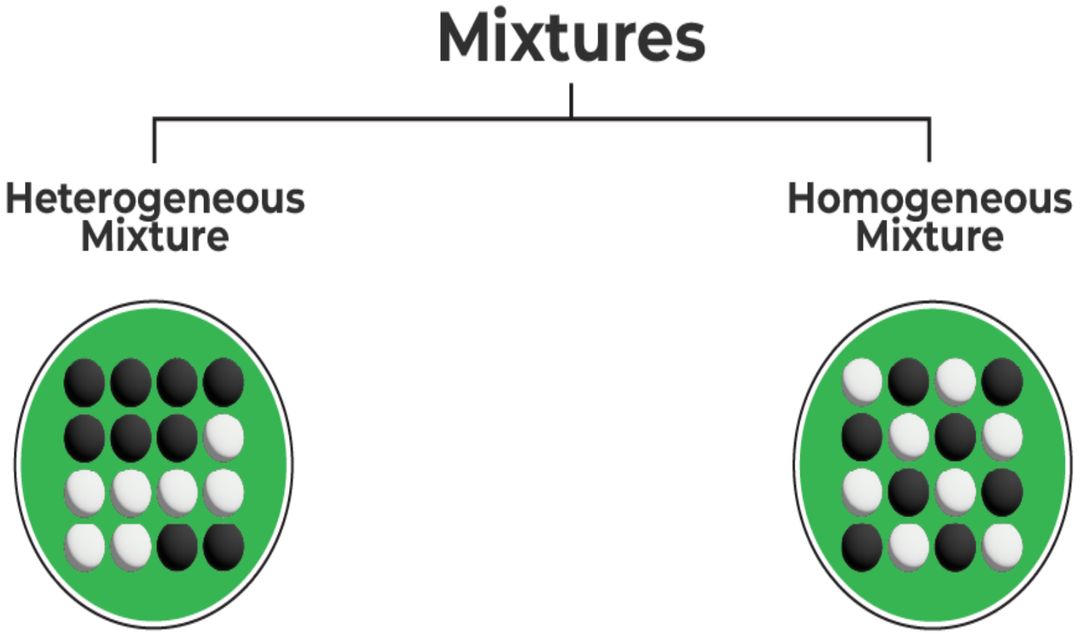
Homogeneous System

- When a system is uniform throughout.

Examples are :

- ❑ pure single solid, liquid or gas
- ❑ mixtures of gases
- ❑ true solution of a solid in a liquid

- A homogeneous system is made of one phase only.



Heterogeneous system

- is one which consists of two or more phases, In other words it is not uniform throughout.

Examples are :

- ❑ ice in contact with water
- ❑ ice in contact with vapour

- Here ice, water and vapour constitute separate phases.

TYPES OF THERMODYNAMIC SYSTEMS

There are three types of thermodynamic systems depending on the nature of the boundary.

(1) Isolated System

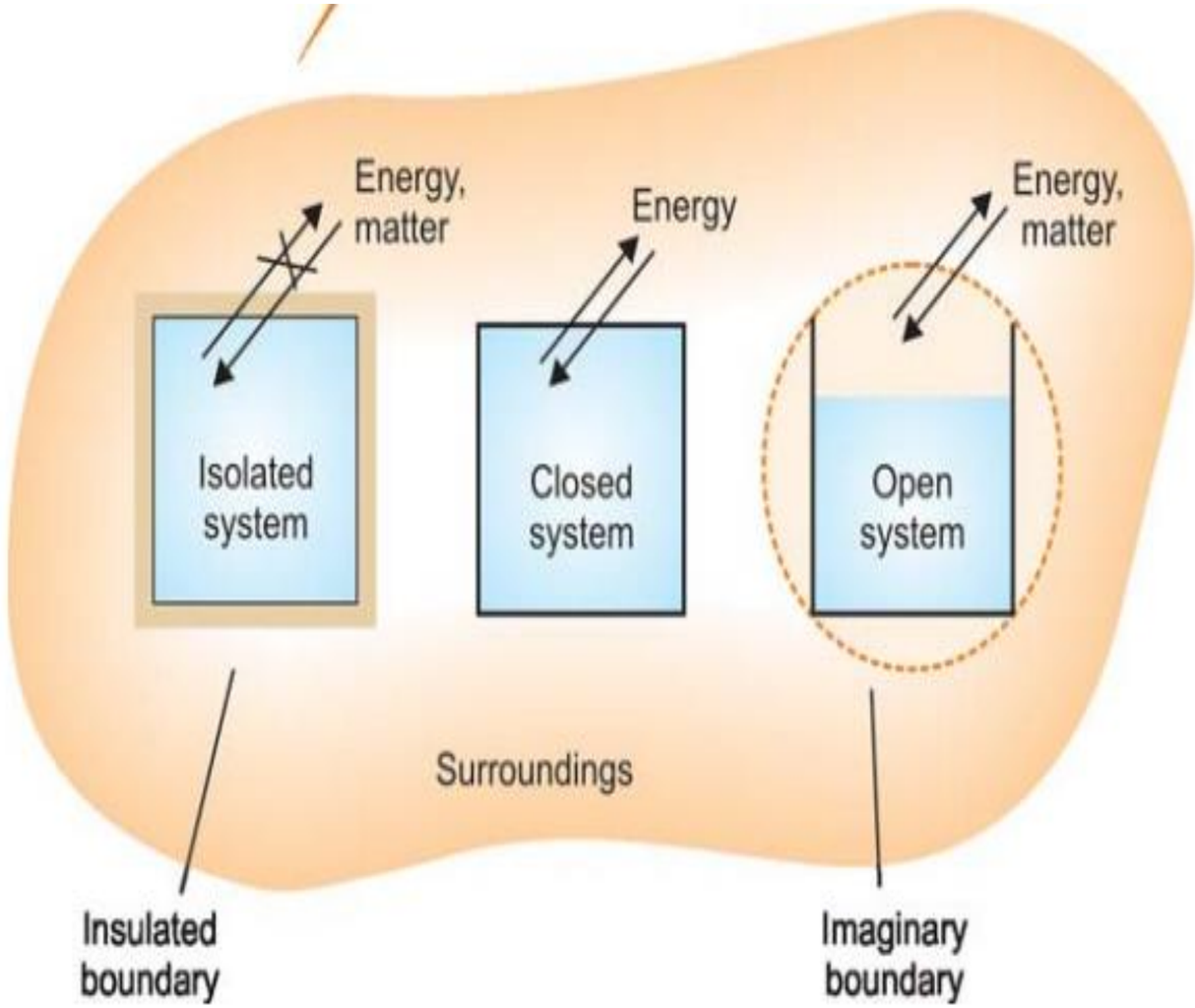
When the boundary is both sealed and insulated, no interaction is possible with the surroundings.
Therefore, it is one that can transfer neither matter nor energy to and from its surroundings.

(2) Closed System

Here the boundary is sealed but not insulated. Therefore it is one which cannot transfer matter but can transfer energy in the form of heat, work and radiation to and from its surroundings.

(3) Open System

In such a system the boundary is open and un-insulated. Therefore, it is one which can transfer both energy and matter to and from its surroundings.



☺ ***Those systems in which no thermal energy passes into or out of the system, are said to be adiabatic systems.***

INTENSIVE AND EXTENSIVE PROPERTIES

The macroscopic or bulk properties of a system (volume, pressure, mass, etc.) can be divided into two classes :

(a) Intensive properties

(b) Extensive properties

Property	Intensive properties	Extensive properties
Definition	A property which does **not depend on** the quantity of matter present in the system, is known as Intensive Property.	A property that does **depend on** the quantity of matter present in the system, is called an Extensive Property.
example	pressure, temperature, density, and concentration	volume, number of moles, enthalpy, entropy, and Gibbs' free energy

THERMODYNAMIC PROCESSES

When a thermodynamic system changes from one state to another, the operation is called a Process.
These processes involve the change of conditions (temperature, pressure and volume).
The various types of thermodynamic processes are

1) Isothermal Processes

Those processes in which the temperature remains fixed, are termed isothermal processes.
This is often achieved by placing the system in a thermostat (a constant temperature bath).
For an isothermal process **dT = 0**

(2) Adiabatic Processes

Those processes in which no heat can flow into or out of the system, are called adiabatic processes.
Adiabatic conditions can be approached by carrying the process in an insulated container such as 'thermos' bottle.
High vacuum and highly polished surfaces help to achieve thermal insulation.
For an adiabatic process **dq = 0**

(3) Isobaric Processes

Those processes which take place at constant pressure are called isobaric processes.

For example, heating of water to its boiling point and its vaporisation take place at the same atmospheric pressure.

These changes are, therefore, designated as isobaric processes and are said to take place isobarically.

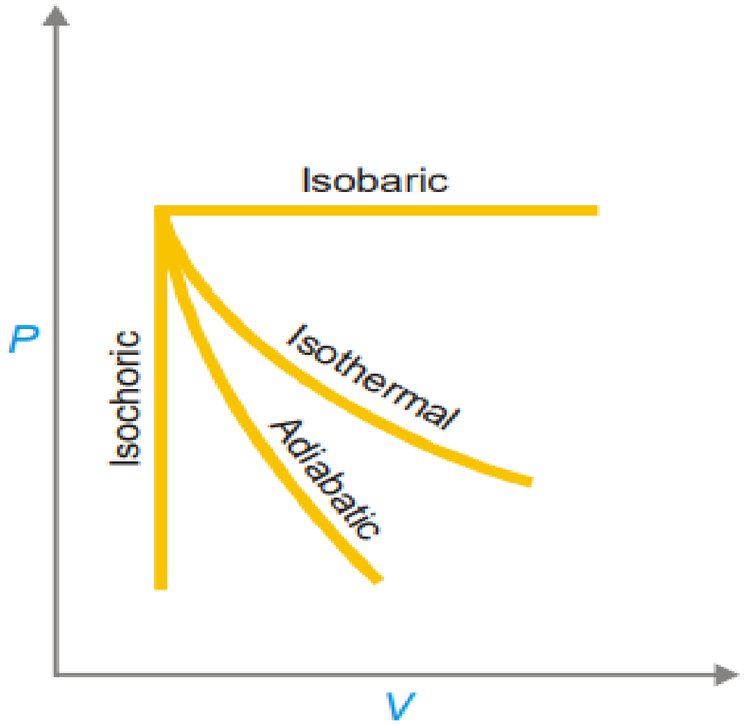
For an isobaric process **dp = 0**

(4) Isochoric Processes

Those processes in which the volume remains constant are known as isochoric processes.

The heating of a substance in a non-expanding chamber is an example of isochoric process.

For isochoric processes **dV = 0.**



(5) Cyclic Process

When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cycle or cyclic process.

For a cyclic process **dE = 0** **dH = 0**

NATURE OF HEAT AND WORK

- When a change in the state of a system occurs, energy is transferred to or from the surroundings.

This energy may be transferred as heat or mechanical work.

We shall refer the term ‘work’ for mechanical work which is defined as **force × distance**

Units of Work

The joule (J)

1 joule =$10^7$107 ergs

or 1 erg = 10^{-7} J

We often use kilojoule (kJ) for large quantities of work

1 kJ = 1000 J

Units of Heat

A calorie is defined as the quantity of heat required to raise the temperature of 1 gram of water by 1º C

SI unit of heat is the joule (J).

1 joule = 0.2390 calories

1 calorie = 4.184 J

or 1 kcal = 4.184 kJ

Sign Convention of Work

- The symbol of work is w. If work is done on a system by the surroundings and the energy of the system is thus increased, it is taken to be positive, **+w**

- If work is done by the system on the surroundings and energy of the system is decreased, it is taken to be negative, **–w**

Summary of Sign Conventions	
Heat flows into the system, q is +ve	Heat flows out of the system, q is –ve
Work is done on the system, w is +ve	Work is done by the system, w is –ve

PRESSURE–VOLUME WORK

- It is important to remember that it is the external pressure, Pext. and not the internal pressure of the gas itself which is used in evaluating work.
- If the gas expands at constant pressure, the piston would move, say through a distance l. We know that

$$\text{work} = \text{force} \times \text{distance (by definition)}$$

$$\text{or } w = f \times l$$

- Since pressure is force per unit area, $f = P_{ext} \times A$
- where A is the cross-section area of the piston.

$$w = P_{ext} \times A \times l$$

$$= P_{ext} \times \Delta V$$

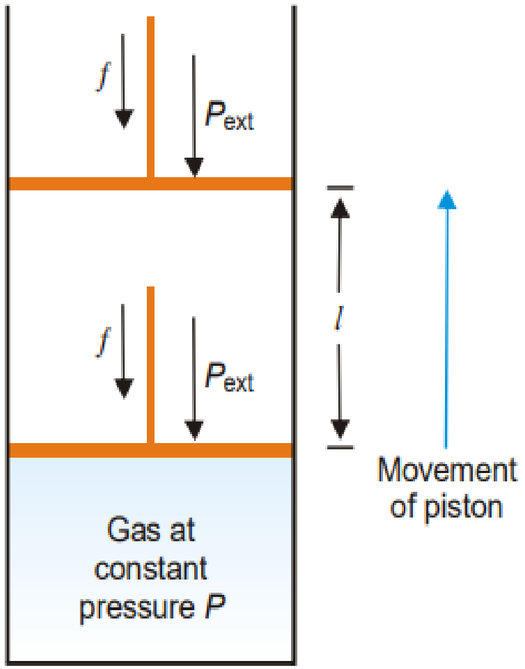
- where ΔV is the increase in volume of the gas.

Since the system (gas) is doing work on the surroundings (piston), it bears negative sign. Thus,

$$w = -P_{ext} \times \Delta V$$

- Proceeding as above the work done in compression of a gas can also be calculated. In that case the piston will move down and sign of the work will be positive.

$$w = P_{ext} \times \Delta V$$



- As already stated, work may be expressed in dynes-centimetres, ergs, or joules.
- PV work can as well be expressed as the product of pressure and volume units in litre or atm .
- It may be noted that the work done by a system is not a state function.
- This is true of the mechanical work of expansion.

- We shall show presently that the work is related to the process carried out rather than to the internal and final states.

EXAMINATION QUESTIONS

Define or explain the following terms :

(a)First law of thermodynamics

(b) An isothermal reversible expansion

(c)Irreversible expansion

(d)Internal energy

Explain the following terms :

(a)State of a System
(b)Extensive Properties
(c)Closed System
(d)Isothermal Process

What do you understand by the terms :

Extensive properties and Intensive properties. Give two examples of each category

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