

# THERMODYNAMICS

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# Definition

- Thermodynamics is a macroscopic science that studies the interrelationships of various equilibrium properties of a system and corresponding changes that occur in equilibrium properties in these processes.
- It describes macroscopic properties of equilibrium system.
- Thermodynamics is derived from the Greek words for *thermos* i.e. “heat” and dynamics means “power”. It is the study of heat, work, energy, and the changes produced in the states of systems by them. On a wider range, thermodynamics studies the relationships between the macroscopic properties of a system.
- The key factor in thermodynamics is related with temperature, and therefore thermodynamics can often be defined as the study of the relation of temperature to the macroscopic properties of matter.

# Systems and Surroundings

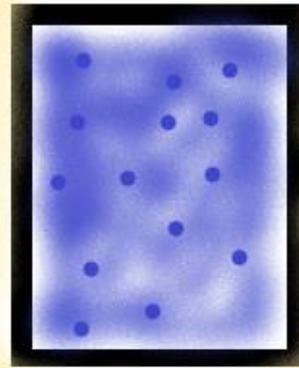
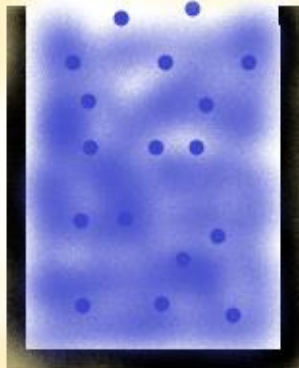
- A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The part of universe excluding the system is known as surroundings. System and the surroundings together constitute the universe.

$$\text{Universe} = \text{System} + \text{Surrounding}$$

- The entire universe other than system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighborhood of the system constitutes its surroundings.
- The surface that separates system from surroundings is known as **boundary**.

# Types of Systems

- **Open System:** The system which exchanges matter as well as energy with the surroundings is known as open system.
- **Closed System:** The system which exchanges energy but not the matter with the surroundings is known as closed system.
- **Isolated System:** The system which neither exchanges energy nor exchanges matter from the surroundings is known as isolated systems.



# Laws of thermodynamics

Thermodynamics can be explained on the basis of four laws which in brief can be summarized as follows:

0<sup>th</sup> law is based on the concept of temperature.

1<sup>st</sup> law is based on the concept of energy.

2<sup>nd</sup> law is based on the concept of entropy.

3<sup>rd</sup> law is general calculation term of entropy.

**These are the universal laws and can not be circumvented at any given condition.**

# How to define a system

**To describe any given system we require the following entities:**

- A set of few macroscopic properties: pressure ( $p$ ), temperature ( $T$ ), Volume ( $V$ ), number of moles ( $n$ ), ....
- Deciding if the System is Homogeneous or Heterogeneous
- Knowing if System is in Equilibrium State
- Knowledge of the number of components of the system.

**Two classes of Properties:**

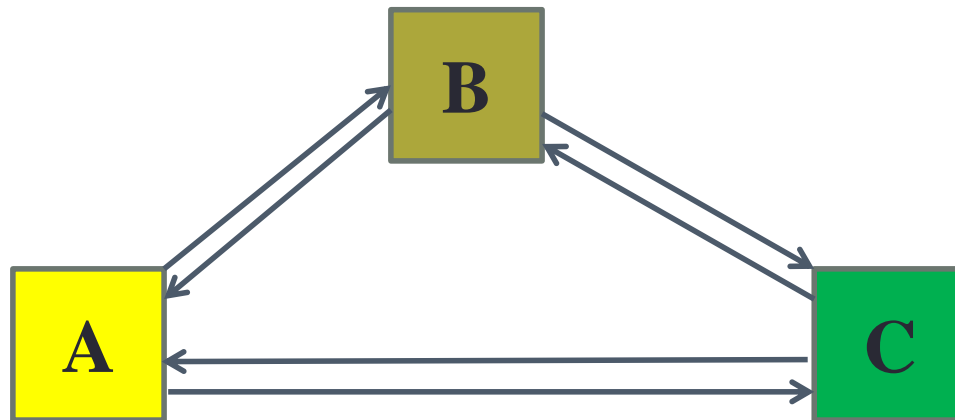
- Extensive Properties: They mainly depend on the size of the system such as concentration, volume, number of moles ( $n$ ,  $m$ ,  $V$ ,...)
- Intensive: Independent of the size of the system such as Temperature, pressure etc.

# Zeroth Law of Thermodynamics

Consider three systems A, B and C where

- A is in thermal equilibrium with B
- B is in thermal equilibrium with C

Then according to this law A and C are said to be in thermal equilibrium with each other. B can be labelled as a thermometer here.



- In Thermodynamic calculations, 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. The system must be specified before and after the change.
- The state of the system can be defined either by state functions or by state variables. The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties such as pressure ( $p$ ), volume ( $V$ ), temperature ( $T$ ), amount ( $n$ ) etc.



- Variables such as  $p$ ,  $V$ ,  $T$  are called state variables or state functions because their values depend only on the state of the system (initial and final state) and not on the pathway it follows to attain the state.
- In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system.
- The minimum number of macroscopic properties are fixed, others automatically have definite values. The state of the surroundings can never be completely specified.