THEMODYNAMICS

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Introduction Thermodynamics

- is the branch of science which deals with all types of energy transformations that accompany physical and chemical processes.
- is primarily based upon four fundamental generalizations called the Zeroth, First, Second and Third Laws of thermodynamics.
- laws are not derived from more fundamental concepts; they are assumed universal principles based purely on natural human observation and experience on the behaviour of bulk matter.

BASIC TERMINOLOGY OF THERMODYNAMICS

1. **System -** to the specified part of the physical world or "universe" chosen for investigation and separated from the rest of the universe by a real or imaginary boundary.

- It may be a

  - -gas enclosed in a container

  -- a solution of a salt taken in a vessel, a reaction vessel, a galvanic cell. a heat engine. a biological cell, and so on.

  --- contain matter, radiation or both.

2, <u>Surroundings</u> The portion of the universe excluded from the system, i.e., the region outside the system, is called surroundings.

e.g., When we study the energy change that accompanies a chemical reaction in the laboratory, the reactants and products constitute the system. The container and everything beyond it are considered the surroundings.

In thermodynamic studies, the realm of the surroundings is usually restricted to a limited portion of the region around the system which can interact with the system.

- **Universe**. the system and the surroundings together constitute what is known as the universe.
- The universe = The system + The surroundings
- A system is said to be a *homogeneous* system if it contains only one phase
- It will be uniform throughout.

Phase is defined as any homogeneous, physically distinct and separable part of a system which is separated from other parts of the definite bounding surfaces.

In short, a phase is a part of a system which has same properties and composition throughout.

e.g., --one liquid layer constitutes one phase.

--an unsaturated solute in water(sugar+water)

-- a mixture of two miscible liquids (e.g., water + ethanol)

--a two or more gases constitutes a single phase

Homogeneous & Heterogeneous

- **Homogeneous --**a single phase

  eg:, mixture of a two or more gases constitutes
- **Heterogeneous --** system consisting of two or more phases is called a heterogeneous.

  -- will not be uniform throughout.

e.g.,1. A system of two immiscible liquid layers in contact

2. water + its vapc.

3. $CaCO_3(s) + CaO(s) + CO_2(g)$-three phases — two solid phases ($CaCO_3$ and CaO) and one gas phase

Types of systems

- The type of system depends on the characteristics of the boundary.
- **Open system-** A system which can exchange both matter and energy with its surroundings through the boundary is called an open system.
- e.g., Boiling water in an open beaker on a gas stove or water in an open tank or tea in an open cup forms an open system
- it can absorb heat energy from the surroundings and evaporate, giving out its vapours to the surroundings and eventually reach equilibrium.

- **Closed system :** A system which can exchange energy, but not matter, with the surroundings through the boundary is called a closed system.
- Eg:, Hot tea enclosed in a vessel with conducting walls.
- here, since the vessel is closed, matter cannot leave the system or enter the system, but since the walls are conducting, energy can be exchanged with the surroundings to reach thermal equilibrium eventually.

- **Isolated system -**A system which can exchange neither matter nor energy with its surroundings through the boundary .
- Hence, the energy and matter remain constant for such a system. It is thus a closed system that has neither mechanical nor thermal contact with its surroundings .
- Eg:,Hot tea enclosed in an insulated vessel such as a thermos flask approximates an isolated system; here, since the vessel is closed as well as insulated, there cannot be an exchange of either matter or energy with the surroundings.
- But the tea eventually cools because a thermos flask is not an ideally insulated vessel; so the system is not perfectly isolated after all.
- There is no such perfectly isolated system other than our universe itself.

Macroscopic properties — Intensive and extensive properties

- The physical characteristics which are experimentally measurable and which enable us to define a system are called the thermodynamic properties of the system.
- A thermodynamic property associated with the collective behaviour of a large number of particles (atoms, molecules, ions, etc.) is called a macroscopic property.

Eg: pressure, volume, temperature, density, viscosity, refractive index, surface tension, composition, etc. are some of the macroscopic properties of a system.

- **Intensive properties -**Properties which are independent of the quantity or size of matter present in the system .

  eg:,Temperature, pressure, viscosity, density, surface tension, refractive index, etc. are intensive properties.
- e.g., A glass-full of water and a tank-full of water will have the same density.

- **Extensive properties-** Properties which depend upon the quantity or size of matter present in the system.

  e.g.. Mass. volume, surface area, energy, enthalpy, entropy, free energy, heat capacity. etc.

- The important distinguishing feature between the two types of properties is that intensive properties are not additive whereas extensive properties are additive.

State of a system

- The state of a system refers to the set of thermodynamic variables ie.,macroscopic properties (e.g., pressure, volume, temperature, composition,density etc.), whose values describe the system.
- A system is said to be in a definite state when its macroscopic properties have definite values.
- Since the state of a thermodynamic system is defined by the values of its thermodynamic properties, such properties are referred to as state variable or state functions.
- Whenever there occurs a change in one of the macroscopic properties of a it is said to undergo a change in state.

State function and path function

- A state function (or state variable) is a property of a system whose value depend upon the state of the system only and does not depend upon the path by which the state has been attained.

Or

- A physical quantity is said to be a state function (or state variable) if its value during a process depends only upon the initial and final states or system and does not depend upon the path
- Eg:. pressure, volume, temp, mass,. internal energy, enthalpy, entropy, etc.

- **Path function-** A property of a system which depends upon the path followed in attain-=-state is called a (or path variable).
- Eg:.Heat, work, etc.

Process

- A process is defined as the operation by which a system changes from-one state to another.
- A process obviously involves a change in one or more of the state variables of the system and is accompanied by a change in energy.
- A change in a variable that may occur during a thermodynamic process is denoted by adding the Greek letter Δ as a prefix to the symbol of the variable.
- Eg:, finite changes in the variables ΔP, ΔV, ΔT,.....

Thermodynamic processes - different types.

(a) Isothermal process

A process in which the temperature of the system remains constant throughout (i.e., $\Delta T = 0$) is called an isothermal process.

- In such a process, heat can flow from the system to the surroundings and vice-versa.
- This condition is accomplished by keeping the system in thermal contact with a constant temperature bath.

(b) **Adiabatic process-** A process in which no heat enters or leaves the system .

In such a process, the system is thermally insulated from the surroundings.

Here, the temperature of the system either increases or decreases according to the nature of the process.

If heat is evolved in the process, the temperature of the system increases; if heat is absorbed, it is absorbed from the system and hence its temperature decreases.

(c) Isochoric process -A process in which the volume of the system is kept constant (i.e., $\Delta V = 0$).

- A reaction occurring in a sealed container of constant (unchangeable) volume corresponds to such a process.

(d) Isobaric process- A process in which the pressure of the system is kept constant (i.e., $\Delta P = 0$) is called an isobaric process.

(e) **Cyclic process--** If a system returns to its initial state (i.e.. if the thermodynamic properties of a system return to their original values) after a series of different processes, the overall process is referred to as a cyclic process.

(f) **Endothermic and exothermic processes—**

A process in which energy is absorbed as heat is called an **endothermic process**.

During an endothermic process, such as the melting of ice or vaporization of water, heat flows into the system from its surroundings.

A process in which energy is liberated as heat is called an exothermic process. During an **exothermic process.**

-- such as the combustion of gasoline or any other substance, heat exits or flows out of the system and into the surroundings.

Thermodynamic equilibrium

- A system is in an equilibrium state if the variables that specify the state of the system do not change with time.
- This means that a state of equilibrium exists when there is no change in any of the system's macroscopic properties with time.
- A system is said to be in equilibrium with its surroundings if an infinitesimal change in its conditions in opposite directions causes opposite changes in its state.

Reversible and irreversible processes

- **A reversible process** is one which is conducted infinitesimally slowly at every stage, the driving force is only infinitesimally greater than the opposing force, and which can be reversed by increasing the opposing force by an infinitesimal amount.

- **An irreversible process** is one in which the driving force at any stage greater than the opposing force so that it cannot be reversed by an infinitesimally increase in the opposing force.

Energy, work and heat

- **Work and heat** are forms of energy transfer

(a) Energy The energy of a system is its capacity to do work.

- When a system does work, energy is reduced

  when work is done on the system, its energy is increased.

Energy of an object

--kinetic energy (by virtue of its motion)

---potentialenergy (by virtue of its position relative to other objects)

Energy is a state function.

Thank you