Thermodynamics: Some Basic Concepts

What is Thermodynamics?

- The word '**thermodynamics'** is derived from two words: **thermo** and **dynamics.** 'Thermo' stands for heat while 'dynamics' is used in connection with a mechanical motion which involves 'work'. Therefore, Thermodynamics is the branch of physics that deals with the relationship between heat and other forms of energy.
- Broadly speaking, thermodynamics is a branch of science that deals with heat, work and temperature, and their relation to energy, radiation and physical properties of matter. It explains how thermal energy is converted to or from other forms of energy and how matter is affected by this process. (Thermal energy is the energy that comes from heat). This heat is generated by the movement of tiny particles within an object, and the faster these particles move, the more heat is generated.
- Thermodynamics is not concerned about how and at what rate these energy transformations are carried out. It is based on the initial and final states undergoing the change. It should also be noted that Thermodynamics is a macroscopic science. This means that it deals with the bulk system and does not deal with the molecular constitution of matter.

Distinction Between Mechanics and Thermodynamics

The distinction between mechanics and thermodynamics is worth noting. In mechanics, we solely concentrate on the motion of particles or bodies under the action of forces and torques. On the other hand, thermodynamics is not concerned with the motion of the system as a whole. It is only concerned with the internal macroscopic state of the body.

Different Branches of Thermodynamics:

Classical Thermodynamics

In classical thermodynamics, the behaviour of matter is analyzed with a macroscopic approach. Units such as temperature and pressure are taken into consideration, which helps the individuals calculate other properties and predict the characteristics of the matter undergoing the process.

Statistical Thermodynamics

In statistical thermodynamics, every molecule is under the spotlight, i.e. the properties of every molecule and how they interact are taken into consideration to characterize the behaviour of a group of molecules.

Chemical Thermodynamics

Chemical thermodynamics is the study of how work and heat relate to each other in chemical reactions and in changes of states.

Equilibrium Thermodynamics

Equilibrium thermodynamics is the study of transformations of energy and matter as they approach the state of equilibrium.

Some Important Thermodynamic Terms and Definitions

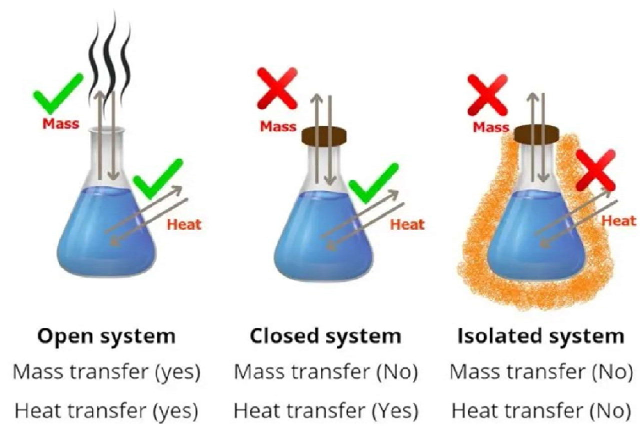
Thermodynamics has its own unique vocabulary associated with it. A good understanding of the basic concepts forms a sound understanding of various topics discussed in thermodynamics preventing possible misunderstandings.

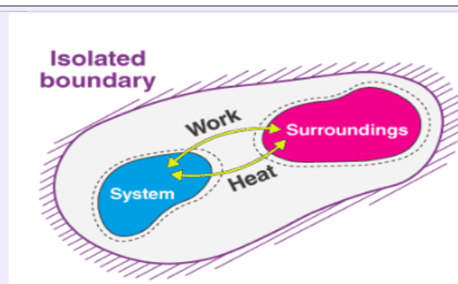
Thermodynamic Systems

A thermodynamic system is a specific portion of matter with a definite boundary on which our attention is focused. The system boundary may be real or imaginary, fixed or deformable.

There are three types of systems:

- **Isolated System –** An isolated system cannot exchange energy and mass with its surroundings. The universe is considered an isolated system.
- **Closed System –** Across the boundary of the closed system, the transfer of energy takes place but the transfer of mass doesn't take place. Refrigerator, compression of gas in the piston-cylinder assembly, etc., are examples of closed systems.
- **Open System –** In an open system, the mass and energy both may be transferred between the system and surroundings. A steam turbine is an example of an open system.





Interactions of thermodynamic systems

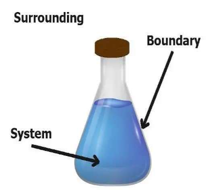
Type of system	Mass flow	Work	Heat
Isolated System	×	×	×
Open System	✓	✓	✓
Closed System	×	✓	✓

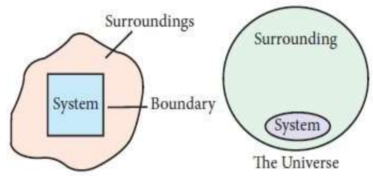
Surrounding

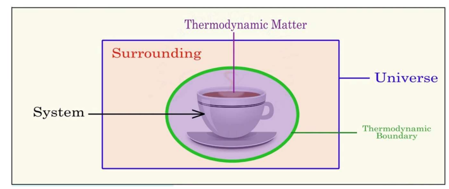
Everything outside the system that has a direct influence on the behaviour of the system is known as a surrounding.

Boundary

The system and surroundings are separated by a boundary. It may be fixed or movable or imaginary. It will not occupy any volume or mass in space.







Thermodynamic state variables:

To define the state of a system in thermodynamics, we use various parameters. These parameters are called state variables. These include:

- Temperature T
- Pressure P
- Volume V
- Entropy S
- Enthalpy H
- Internal Energy U (or E)
- Mass m
- Density ρ

It must be noted that the state variables do not depend on the path taken to reach that state.

State vs. Path Functions

A ***state function*** is a property whose value does not depend on the path taken to reach that specific value. In contrast, functions that depend on the path from two values are called ***path functions.*** Both path and state functions are often encountered in thermodynamics.

Thermodynamic Process

A system undergoes a thermodynamic process when there is some energetic change within the system that is associated with changes in pressure, volume and internal energy.

There are four types of thermodynamic processes that have their unique properties, and they are:

- **Adiabatic Process** – A process where no heat transfer into or out of the system occurs.
- **Isochoric Process** – A process where no change in volume occurs and the system does no work.
- **Isobaric Process** – A process in which no change in pressure occurs.

- **Isothermal Process** – A process in which no change in temperature occurs.

Thermodynamic cycle

A thermodynamic cycle is a process or a combination of processes conducted such that the initial and final states of the system are the same. A thermodynamic cycle is also known as cyclic operation or cyclic processes.

Thermodynamic Equilibrium

At a given state, all properties of a system have fixed values. Thus, if the value of even one property changes, the system's state changes to a different one. In a system that is in equilibrium, no changes in the value of properties occur when it is isolated from its surroundings.

- When the temperature is the same throughout the entire system, we consider the system to be in **thermal equilibrium**.
- When there is no change in pressure at any point of the system, we consider the system to be in **mechanical equilibrium**.
- When the chemical composition of a system does not vary with time, we consider the system to be in **chemical equilibrium**.
- **Phase equilibrium** in a two-phase system is when the mass of each phase reaches an equilibrium level.

A thermodynamic system is said to be in thermodynamic equilibrium if it is in chemical equilibrium, mechanical equilibrium and thermal equilibrium and the relevant parameters cease to vary with time.

Thus, the concept of thermodynamic equilibrium is very important in thermodynamics, as in thermodynamic equilibrium, there is no tendency for the state of a system to change spontaneously. For example, the gas in a cylinder with a movable piston will be at equilibrium if the temperature and pressure inside are uniform and if the restraining force on the piston is just sufficient to keep it from moving. The system can then be made to change to a new state only by an externally imposed change in one of the state functions, such as the temperature by adding heat or the volume by moving the piston. A sequence of one or more such steps connecting different states of the system is called a process.

In general, a system is not in equilibrium as it adjusts to an abrupt change in its environment. For example, when a balloon bursts, the compressed gas inside is suddenly far from equilibrium, and it rapidly expands until it reaches a new equilibrium state. However, the same final state could be achieved by placing the same compressed gas in a cylinder with a movable piston and applying a sequence of many small increments in volume (and temperature), with the system being given time to come to equilibrium after each small increment. Such a process is said to be reversible because the system is at (or near) equilibrium at each step along its path, and the direction of change could be reversed at any point. This example illustrates how two different paths can connect the same initial and final states. The first is irreversible (the balloon bursts), and the second is reversible.

The concept of reversible processes is something like motion without friction in mechanics. It represents an idealized limiting case that is very useful in discussing the properties of real systems. Many of the results of thermodynamics are derived from the properties of reversible processes.

Thermodynamic Properties

Thermodynamic properties are defined as characteristic features of a system, capable of specifying the system's state. Thermodynamic properties may be **extensive** or **intensive**.

Intensive properties: These are properties that do not depend on the quantity of matter. Density, Pressure, Temperature, Specific Volume, Specific Entropy, Thermal conductivity, Thermal Expansion, Compressibility, etc., are intensive properties.

Extensive properties: In the case of extensive properties, their values depend on the mass of the system. Mass, volume, internal energy, enthalpy, heat capacity, entropy, Gibbs free energy, etc. are extensive properties.

Heat

Heat is energy transferred between substances or systems due to a temperature difference between them. As a form of energy, heat is conserved that means it cannot be created or destroyed. It can however, be transferred from one place to another. Heat can also be converted to and from other forms of energy.

For example, a steam turbine can convert heat to kinetic energy to run a generator that converts kinetic energy into electrical energy. A light bulb can convert this electrical energy to electromagnetic radiation which, when absorbed by a surface, is converted back into heat. By convention, heat is given to a body is taken as positive while that taken out of the body is taken as negative.

Sign conventions for heat in internal energy:-

ΔU is taken as positive if the internal energy of the system increases.

ΔU is taken as negative if the internal energy of the system decreases.

Work

In a process, the work done by the system or on the system depends not only on the initial and final states of the system but also upon the path adopted for the process. Work is done when a force acting on a system displaces the body in its own direction.Work 'W' done on or by a system is the product of force and displacement.

For example, a man pushing a car may feel that he is doing a lot of work, but no work is actually done unless the car moves. The work done is the product of the force applied by the man multiplied by the distance through which the car moves. If there is no friction and the surface is level, then the car, once set in motion, will continue rolling indefinitely with constant speed. The rolling car has a kinetic energy of motion equal to the work required to achieve that state of motion.

Internal energy

Internal energy is the sum of the kinetic energies and the potential energies of the molecules. We denote the internal energy of the system by U. Energy possessed by the atoms or molecules by virtue of their motion is kinetic energy. Since there is a force of attraction between two molecules, they possess some potential energy. The sum of total kinetic and potential energies of atoms or molecules constituting a system is the internal energy of the system.

The internal energy of a system depends upon the state of the system. It has a definite value for a definite thermodynamic state. It is not a measurable quantity. If a system starting from one state passes through different states and finally returns to its initial state, then the change in its internal energy will be zero.

Enthalpy

Enthalpy is the measurement of energy in a thermodynamic system. The quantity of enthalpy equals the total heat content of a system, equivalent to the system's internal energy plus the product of volume and pressure.

Mathematically, the enthalpy, H, equals the sum of the internal energy, U, and the product of the pressure, P, and volume, V, of the system.

$$\mathbf{H = U + PV}$$

Entropy

Entropy is a thermodynamic quantity whose value depends on the physical state or condition of a system. In other words, it is a thermodynamic function used to measure the randomness or disorder. For example, the entropy of a solid, where the particles are not free to move, is less than the entropy of a gas, where the particles will fill the container.

→ Entropy is the measure of the number of possible arrangements the atoms in a system can have.

→ Enthalpy is the measurement of energy in a thermodynamic system.

Thermodynamic Potentials

Thermodynamic potentials are quantitative measures of the stored energy in a system. Potentials measure the energy changes in a system as they evolve from the initial state to the final state. Different potentials are used based on the system constraints, such as temperature and pressure.

Laws Of Thermodynamics

Thermodynamics laws define the fundamental physical quantities like energy, temperature and entropy that characterize thermodynamic systems at thermal equilibrium.

These thermodynamics laws represent how these quantities behave under various circumstances.

There are four laws of thermodynamics and are given below:

- **First law of thermodynamics**: Energy can neither be created nor be destroyed, it can only be transferred from one form to another.
- **Second law of thermodynamics:** The entropy of any isolated system always increases.
- **Third law of thermodynamics:** The entropy of a system approaches a constant value as the temperature approaches absolute zero.
- **Zeroth law of thermodynamics:** If two thermodynamic systems are in thermal equilibrium with a third system separately, then they are in thermal equilibrium with each other.