Thermodynamic System: Any portion of the material universe which can be isolated completely and arbitrarily from the rest for consideration of the changes which may occur within it under varying conditions.

Surroundings: Refers to the rest of the universe outside the system.

Open system: A system where the exchange of both matter and energy can occur through the boundary.

Closed system: It is a system where only the exchange of energy between it and the surrounding is possible through the boundary. There is no matter exchange.

Isolated System: A system which is thermally insulated and has no communication of heat with the surrounding.

Thermodynamic equilibrium: The system experiences thermal, mechanical and chemical equilibrium.

Diathermal wall: A wall that allows for exchange of heat between the system and the surrounding.

Adiabatic wall: A wall that does not allow for exchange of heat between the system and the surrounding.

State variables: These are directly measurable variables which are sufficient to describe the bulk behaviour of the system. In the case of a gas system, these include pressure (P), temperature (T), volume (V), internal energy (U), Entropy (S) and composition.

Usually, we require at least two state variables to specify the state of a system.

For example, of the 3 measurable variables P, V and T, in a gas system, only two are independent and the third one is a function of the two e.g.,

P is a function of V and T or $P = P(V, T)$

V is a function of P and T or $V = V(P, T)$

State variables are also known as thermodynamic variables or coordinates.

Reversible process: Reversible implies that in any such change, the system must be capable of being returned to its original state with the surrounding unchanged. This requires two conditions:

1. The processes must be quasi-static i.e., it should take place very slowly such that it is always in a succession of equilibrium states at any given time.

2 No dissipative forces such as friction are present to dissipate energy.

Irreversible Process: Any process which is not reversible exactly is an irreversible process. All practical processes such as free expansion, radiation and radioactive decay etc.

Ideal gas: An ideal gas is an abstraction and it is a gas whose properties represent the limiting behaviour of real gases at sufficiently low densities. In an ideal gas, it is assumed that

(i) There are no intermolecular attractions. This implies that the internal energy of the gas is entirely kinetic and would be dependent on temperature

(ii) The molecules do not occupy space.

PV = nRT [Equation of state]

Where R is the universal gas constant = 8.314 J mol-1K-1.

Real gas: (i) there are intermolecular attractions (ii) The gas molecules themselves occupy a finite space.

$$(P + \frac{a}{V2})\ (V\text{-}b) = RT$$

Constants a and b are different for different gases.

The ideal gas obeys the gas law PV = nRT exactly. No such gas exists.

The internal energy of an ideal gas is entirely kinetic and depends only on its temperature.

Zeroth Law: "If body A and body B are each in thermal equilibrium with a third body C, then, A is also in thermal equilibrium with B."

First Law of Thermodynamics: The first law of thermodynamics is the principle of conservation of energy .

Now, If heat dQ is supplied to the system, this heat goes to increase the internal energy (dU) of the gas as well as enable the gas do some mechanical work (dW) on the surrounding
dQ = dU + dW

Thermodynamic Processes:

(i) **Isothermal process:** Processes that occur at constant temperature

(ii) **Isobaric process:** Processes that occur at constant pressure

(iii) **Isochoric process:** Processes that occur at constant volume ($dV = 0$)

(iv) **Adiabatic process:** Processes where no heat enters or leaves the system ($dQ = 0$)

$C_p - C_v = R$ This relation is known as Mayer's relation

C_p is greater than C_v

Degree of Freedom: The number of independent variables required to describe completely the state of motion of a body are called its degree of freedom.

Monoatomic molecule: 3 degrees of freedom (all translational)

Ex. Neon, Helium etc.

Diatomic molecule: 5 degrees of freedom (3 translational and 2 rotational)

Ex. HCl, CO etc.

Triatomic molecule: 6 degrees of freedom (3 translational and 3 rotational)

Ex. H_2S, SO_2 etc.

Average kinetic energy associated with each degree of freedom is $\frac{1}{2}KT$.

The kinetic energy per unit volume of a perfect gas is equal to $\frac{3}{2}P$.