Outline of Ensemble theory :-

A collection of a number of particles is called a System. An ensemble is defined as a collection of a large number of macroscopically identical, it is meant that the system constituting an ensemble satisfies the same macroscopic conditions i.e., volume, pressure, energy, total number of particles etc. By the term independent system, it is meant that the system constituting an ensemble are mutually non-interacting. In an ensemble the system play the role as the non-interacting molecules do in a gas. The macroscopic identity of the systems constituting an ensemble can be achieved by choosing the same values of same set of macroscopic parameters. These parameters uniquely determine the equilibrium state of the system. Accordingly, those types of ensembles are most used. These are —

(i) Microcanonical ensemble :-

The microcanonical ensemble is a collection of essentially independent assemblies having the same energy E, volume V, and number N of systems, all the systems are of the same type. The individual assemblies are separated by rigid, impermeable and well insulated walls such that the values of E, V and N for a particular system are not effected by the presense of other systems.

(ii) Canonical ensemble :-

The canonical ensembles is a collection of essentially independent assemblies having the same temperature T, volume V, and number of identical particles N. In this ensemble, the system can exchange energy but not particles. The individual systems of a canonical ensembles are seperated by rigid, impermeable but conducting walls.

(iii) Grand canonical ensemble :-

An ensemble in which exhange of energy as well as of particles takes place is known as 'grand canonical ensemble'.

The grand canonical ensemble is a collection of essentially independent assemblies having the same temperature T, volume V, and a chemical potential μ. The detailed characteristics of thesese ensembles can be had after a complete study of Liouville's theorem.

The three ensemble are particularly useful for two main reasons —

- They correspond approximately to the types of thermodynamic measurements most frequently made in practices.

- In large assemblies, it is useful to find that the values of thermodynamic quantities which are not very sensitive to the method of measurement.