Ensembles :

→ Gibbs introduced the concept of ensembles.

→ A system is defined as a collection of no. of particles.

→ An ensemble is defined as collection of a large no. of microscopically identical but essentially independent systems.

Types of an ensemble :

Ensemble is classified as three types.

That are,

i) Micro Canonical Ensemble

ii) Canonical Ensemble

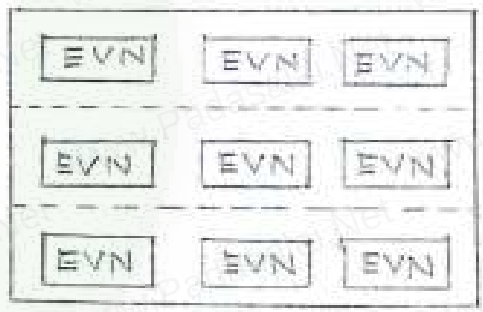
iii) Grand Canonical Ensemble.

i) Micro Canonical Ensemble :

→ It is the collection of large no. of essentially independent system having Same energy (E), Volume (V) & no. of particles (N).

→ All particles are identical

→ The individual Systems are Separated by rigid, impermeable & well insulated walls.



→ Such that the values of E, V, N for a particular system are not affected by the presence of other Systems.

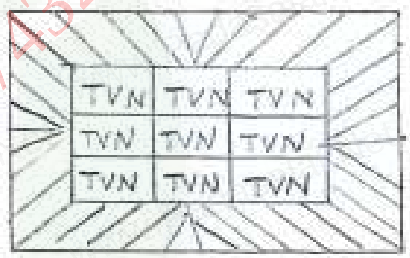
→ An ensemble in which neither energy nor matter is called μ-canonical ensemble.

ii) Canonical Ensemble :

→ It is the collection of large no. of essentially independent systems having the same temperature (T), Volume (V) & no. of particles (N).

→ All particles are identical.

→ The equality of temp. of all systems can be achieved by bringing each in thermal contact



with a large heat reservoirs at const T (or) bringing all of the systems in thermal contact with one another.

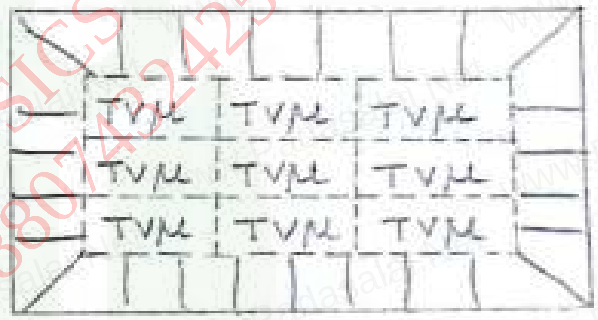
→ The individual system are separated by rigid, impermeable but conducting walls.

→ As the separating walls are conducting, heat can be exchanged b/w the systems. As a result all the system will arrive at the common temp.

iii) Grand Canonical Ensemble :

→ It is the collection of large no. of essentially independent systems having the same temperature (T), Volume (V), chemical properties (μ).

→ The individual systems are separated by rigid, permeable & conducting walls (or) diathermic walls.



→ As the separating walls are conduction & permeable, the exchange of heat energy as well as that of particles b/w systems take place in such a way that all the systems arrives at common temperature (T) & chemical properties (μ)

Micro Canonical	Canonical	Grand - Canonical
E, V, N are Same	T, V, N are same	T, V, μ are Same
Rigid, imepermeable, insulated walls	Rigid, impermeable, conducting walls	Rigid, Permeable, conducting walls.

→ It is the fundamental ensembles which is suitable for isolated systems.

Uses of an ensembles :

→ It is useful for thermodynamical measurements

→ It is used to measure the specific heat of a liquid.

Equation of State (P, V, T)

→ The equation connecting the pressure, volume, temperature of the substance is called equation of state of that substance.

→ The three quantities are connected by a relationship of general form.

$$f(P, V, T) = 0$$

which is called equation of state.

→ The equation of state of an ideal gas,

$$PV = RT$$

R - Universal gas constant (8.314 J/g. mole)

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

→ The equation of state is not applicable to system which is not in thermodynamic equilibrium

→ Every thermodynamic system has its own equation of states independent of the others.

→ An equation of state is not a theoretical deduction from thermodynamics.

Thermodynamic function of an ideal gas equipartition of energy :

→ When system obeying classical statistical mechanics is in thermal equilibrium with a heat bath at temperature T, the total K.E of a dynamical system consisting of a large no. of particle in thermal equilibrium is equally divided among its all degree of freedom.

→ Each degree of freedom - $\frac{1}{2}KT$

→ If the degree of freedom is f the average energy is $\frac{1}{2}fKT$.

→ For free particle at temperature T should be $f = 3$

$$= \frac{1}{2} 3KT$$

$$= \frac{3}{2} KT$$

→ The law of equipartition of energy is applicable only so long as the system can be described classically.

→ This is applicable above room temperature but a very low temperature, where the gas is about to liquify it is not trace.

→ Higher the temp. of the system better the validity of the theorem

→ Translational - $3/2$ KT

Rotational - $2 \times \frac{1}{2}$ KT

Vibrational - $(3N-5)$ KT

→ Linear polyatomic molecule,

$$= (6N-5)\frac{KT}{2}$$

→ Non-linear polyatomic molecule,

$$= (6N-6)\frac{KT}{2}$$