

-: STATISTICAL

THERMODYNAMICS :-

* SYSTEM -

In a collection of particles, a single particle is known as system.

* Assembly -

Collection of identical entities are called Assembly.

* Ensemble -

Ensemble is defined as a collection of a very large no. of assemblies which are independent of each other but which have been made macroscopically as identical as possible.

In short - Assembly of Assemblies is called Ensemble.

Depending upon the nature of constant, Ensemble are divided into three category.

- (i) Micro Canonical Ensemble
- (ii) Canonical Ensemble
- (iii) Grand Canonical Ensemble.

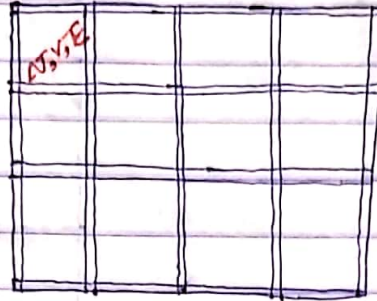
(i) * MICRO CANONICAL ENSEMBLE -

It is defined as the collection of a very large no. of assemblies in which energy (E), Volume (V) and no. of system (N) remains constant.

In other words -

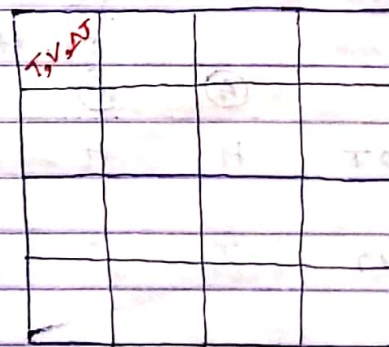
In a micro canonical ensemble, all the system are of the same types, i.e. such an ensemble in which the individual

assemblies are separated by rigid and well insulated walls so that E, V & N for a particular assembly are not affected by the presence of other assemblies.



(ii) * CANONICAL ENSEMBLE -

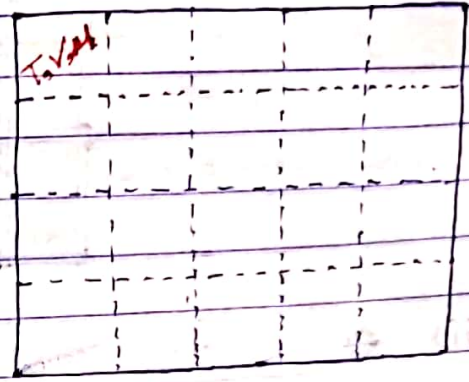
It is defined as the collection of a large no. of independent assemblies in which temperature (T), Volume (V) and no. of identical system (N) are constant. As all the assemblies possess ^{acts at} same temperature (T). It means that one could bring them a thermal contact with each other and also a large heat reservoir at the same temperature. Thus in a canonical ensemble, system can exchange energy but not particle.



(iii) * GRAND CANONICAL ENSEMBLE -

It is defined as the collection of large no. of independent assemblies, having temperature (T), Volume (V) and chemical potential (μ) remains constant.

Thus a grand canonical ensemble in which the individual assemblies are separated by rigid, permeable and conducting walls. Each of these assemblies can exchange both energy and particle with one another.



* Configurations :-

Various equivalent ways of achieving a state is called configurations of the system.

For examples -

There are four coins A, B, C & D. Their state, no. of configurations and results are shown below:-

No. of states	No. of Configuration of the coin				Results
	(A)	(B)	(C)	(D)	
(1). 4H + 0T	H	H	H	H	1
(2). 0H + 4T	T	T	T	T	1
(3). 3H + 1T	H	H	H	T	4
	H	H	T	H	
	H	T	H	H	
	T	H	H	H	

No. of States	No. of Configuration of the coin				Results
	(A)	(B)	(C)	(D)	
(4) 1H + 3T	T	T	T	H	4
	T	T	H	T	
	T	H	T	T	
	H	T	T	T	
(5) 2H + 2T	H	H	T	T	6
	T	T	H	H	
	H	T	T	H	
	T	H	H	T	
	H	T	H	T	
	T	H	T	H	

Thus total no. of configuration available to the system

$$= 1 + 1 + 4 + 4 + 6$$

$$= 16.$$

* Thermodynamic Probability -

The thermodynamic probability of a macrostate is defined as the no. of microstates corresponding to that macrostates.

In general this is a very large no. & denoted by ω or P .

thus,

$$\text{Thermodynamic probability } (\omega) =$$

$$= \text{no. of Configuration leading to that particular state.}$$

Total no. of Configuration available to the system.

Four coins system:-

Since, In the [above configurations]-

Total no. of configuration available to this system. = 16.

Thus -

$$\text{Probability of 4H} = \frac{1}{16}$$

$$\text{" " 4T} = \frac{1}{16}$$

$$\text{" " 3H+1T} = \frac{4}{16}$$

$$\text{" " 1H+3T} = \frac{4}{16}$$

$$\text{" " 2H+2T} = \frac{6}{16}$$

In several cases of N phase, the thermodynamic probability 'p' or ω is given by-

$$p \text{ or } \omega = \frac{N!}{N_0! N_1! N_2!}$$

where,

N_0, N_1, N_2 are the no. of molecular distribution in E_0, E_1 & E_2 energy level of an assembly of N identical particles of a gas at temperature (T) volume (V) and energy (E).

N_0, N_1 & N_2 are distributed in E_0, E_1 & E_2 in such a way that the total no. of molecules and total energy are constant.

$$\text{i.e. } N = \sum N_i$$

$$\text{where } N = (N_0 + N_1 + N_2 + \dots)$$

$$\text{and } E = \sum_{i=0} N_i E_i$$

$$\text{where } E = (N_0 E_0 + N_1 E_1 + N_2 E_2 + \dots)$$

* Most probable state -

More configuration obtained to the system is called most probable state.