Ensemble in Statistical Mechanics:

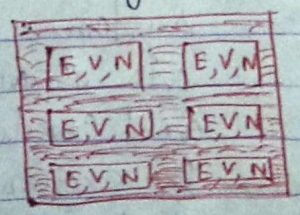
In statistical mechanics, Gibbs introduced the concept of ensemble. An ensemble is defined as the collection of large number of macroscopically identical but independent system. The term macroscopically identical means that each of the system constitutes an ensemble satifies the same macroscopic conditions e.g volume, energy, temperature, pressure, total number of particle etc. The term independent system means that the system constituting an ensemble are mutually non-interacting. In an ensemble the system play the same role as the non interacting molecules do in a gas.

According to Gibb's there are three ensembles —

① The microcanonical ensemble
② The canonical ensemble
③ The Grand Canonical ensemble.

Microcanonical ensemble:

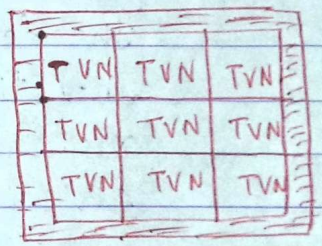
It is the collection of a large number of independent system having the same energy (E), volume (V) and the number of particle (N). For simplicity



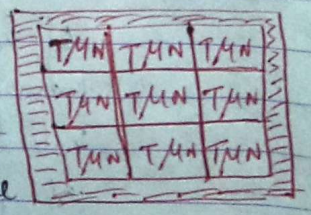
We assume that all particles are identical. The individual systems of a microcanonical ensemble are separated by rigid impermeable and well insulated walls such that the the values E, V, and N for a particular system are not affected by the presence of other systems.

Canonical ensemble:

It is the collection of large number of independent systems having the same temp^r (T), volume (V), and same number of particles (N). The equality of temp^r of all systems can be achieved bringing all the systems in thermal contact with one another. The individual systems of canonical ensemble are saperated by rigid, impermeable but conducting walls.



Grand Canonical ensemble:- It is the collection of large number of independent systems, having the same temperature (T), volume (V), and chemical potential (μ). The individual systems of grand canonical ensemble are separated by rigid, permeable, and conducting walls. As a result the exchange of heat energy and the particles between the systems take place.



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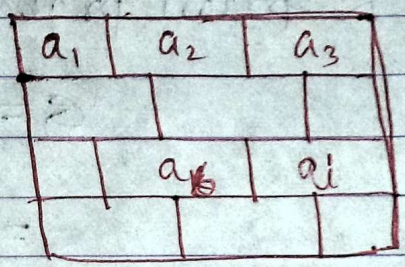
Probability of distribution of particles

Let a large box divided into 'k' no of small box, where surface areas are $a_1, a_2, \ldots\ldots a_k$. Now 'N' identical but distinguishible particles are thrown into the box in a random manner.



The probability that the particles be distributed in a certain way among the small box depends on two factors

1. Priori Probability of the distribution, which is based on the properties of each small box.

2. Thermodynamical probability of the distribution, which is the no of different ways that the particles may be redistribute among the small box without changing the number in each small box.

Here the ~~pro~~ priori probability g_i that a particle fall into the ith box is the ratio between the surface area a_i of the small box and the total surface area (A) of the large box i.e

$$g_i = \frac{a_i}{A} \longrightarrow (1)$$

where $A = a_1 + a_2 + \cdots + a_K$ total surface area of the box.

The priori probability for 'n_i' particles to fall in ith box is $g_i^{n_i}$. Total priori probability of any particular distribution of 'N' particles among the 'K' small box is the product of 'K' priori probability i.e

$$G = g_1^{n_1} \times g_2^{n_2} \times \cdots g_K^{n_K}$$

$$= \prod_{i=1}^{K} g_i^{n_i} \longrightarrow (2)$$

where n_1 particles fall into first small box, n_2 particles fall into 2nd and so on.

Since ~~the~~ all distribution of particles among the small box are not equally probable, we have to introduce the concept of thermodynamic probability. The no of ways in which any n_1 particles out of total 'N' particles may fall in the first small box are

$$^{N}C_{n_1} = \frac{N!}{n_1!\,(N-n_1)!}$$

The no of ways in which any n_2 particles out of remaining $(N-n_1)$ particles may fall in the 2nd box are

$$^{N-n_1}C_{n_2} = \frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)!}$$

and so on upto k Th box.

∴ Total thermodynamic Probability

$$\omega = \frac{N!}{n_1!\,(N-n_1)!} \times \frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)} \times \cdots \frac{(N-n_1-n_2-\cdots-n_{k-1})!}{n_k!\,(N-n_1-n_2-\cdots-n_k)}$$

$$= \frac{N!}{n_1!\,n_2!\cdots n_k!}$$

$$= \frac{N!}{\sum_{i=1}^{k} n_i!}$$

$(N-n_1-n_2\cdots-n_k)$
$= 0!$
$= 1$

Thus the total probability P of the distribution is the product of the priori probability and thermodynamic probability.

∴ Total probability

$$P = \omega \times G$$

$$= \frac{N!}{\prod_{i=1}^{k} n_i!} \times \prod_{i=1}^{k} g_i^{n_i}$$

$$= N! \prod_{i=1}^{k} \frac{g_i^{n_i}}{n_i!}$$

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