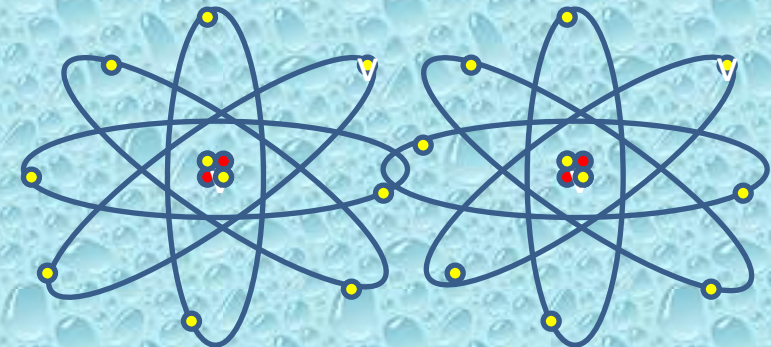
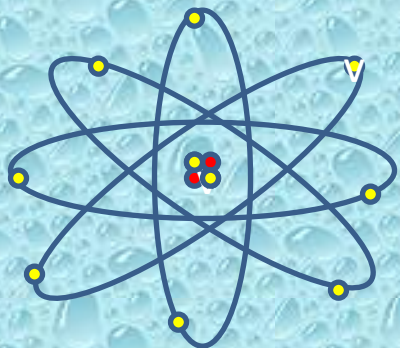


# STATISTICAL THERMODYNAMICS

## Part – B

### ( Module -1: Basic Concepts)

(M.Sc. Sem – II/ Chemistry, Paper III, Unit – II)

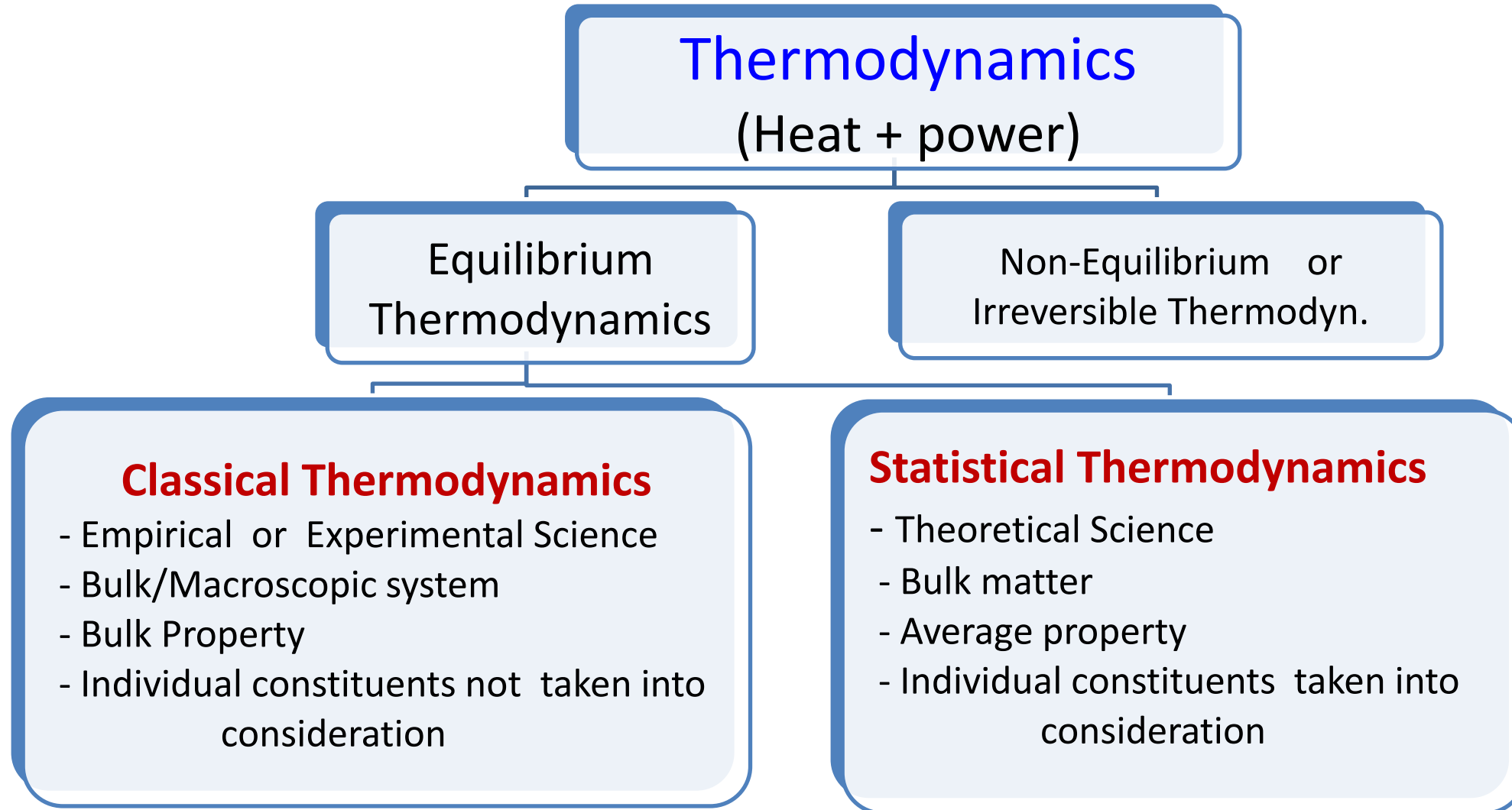


- **Learning Objectives:**
  - To introduce the concepts of Statistical Mechanics
  - To understand its significance in Chemistry
  - To learn about its role in studying the properties of matter
- **Learning Outcomes:**
  - Gain knowledge of concepts of probability and partition function
  - Differentiate between the different statistics applicable to different systems
  - Correlate partition function with various thermodynamic functions and properties of matter

# Contents:

- What is Statistical Thermodynamics?
- System, Assembly, Ensemble
- Important Terms
- Essential Condition for Distribution
- Macrostate and Microstate
- Principle of equal a priori probabilities
- Thermodynamic Probability
- Most Probable Distribution
- Stirling's Approximation

# What is Statistical Thermodynamics?



# MECHANICS

## Classical Mechanics

- Based on Newton's law & Maxwell's EM theory
- Macroscopic matter
- Motion of large objects
- Energy is continuous

## Statistical Mechanics

- Based on Probability theory & Statistical methods
- Bulk Matter
- Average property of the Bulk system

## Quantum Mechanics

- Based on de-Broglie hypothesis
- Heisenberg principle & Planck's quantum theory
- Microscopic matter
- Properties of atomic/subatomic particles
- Energy levels are quantized

Results from  
**Quantum Mechanics**  
(Property of individual Microscopic matter)

Using Probability theory & Statistical  
methods from  
**Statistical Mechanics**

Applied to  
**Classical Thermodynamics**  
(Bulk/ Macroscopic System)

Gives  
Property of Bulk System

**STATISTICAL  
THERMODYNAMICS**

## Correlation between different branches of Science

**Classical Thermodynamics** deals with the macroscopic matter and describes the behaviour of large no. of molecules in terms of properties like P, V, T.

**Quantum Mechanics** deals with matter at microscopic level and the state is described by a wave function.

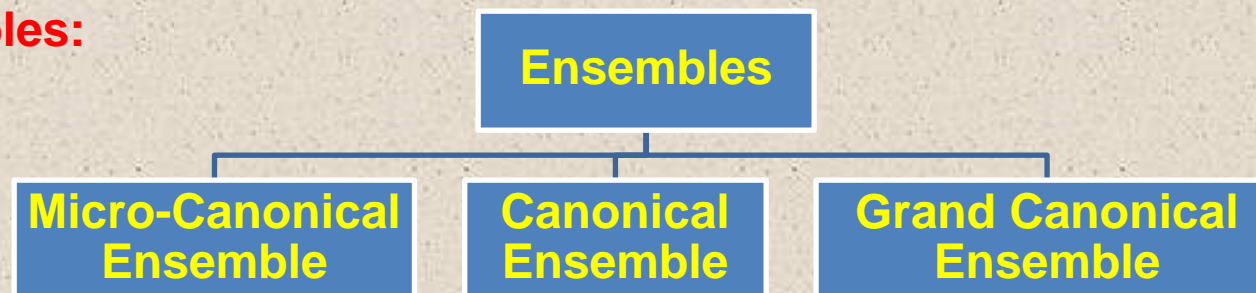
**Statistical Mechanics** provides the link between the microscopic properties of matter and its bulk properties.

**Statistical Thermodynamics** thus links the **microscopic world** with **macroscopic world** i.e. Quantum Mechanics and Classical Thermodynamics

# SYSTEM, ASSEMBLY & ENSEMBLES

- **System:** If there is a collection of particles, each single particle is referred to as **System**  
↓
- **Assembly:** Collection of systems (particles) as a whole forms **Assembly**  
↓
- **Ensemble:** Collection of very large number of assemblies which are independent of each other but which have been made macroscopically as identical as possible is known as **Ensemble**
  - Introduced by **W. Gibbs** in **1902**
  - Time averaging for a system containing molecules of the order of Avogadro number
  - Formed by reproducing distinct units many times
  - Set of imaginary replications
  - Each member subjected to identical thermodynamic constraints

- **Types of Ensembles:**





E, V, N	E, V, N	E, V, N
E, V, N	E, V, N	E, V, N
E, V, N	E, V, N	E, V, N

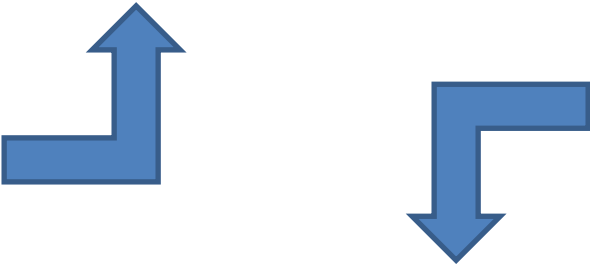
**Micro-Canonical Ensemble:**

- ✓ Independent assemblies with same Energy  $E$ , Volume  $V$ , Number  $N$
- ✓ Rigid, Impermeable, Adiabatic (insulated) Walls

T, V, N	T, V, N	T, V, N
T, V, N	T, V, N	T, V, N
T, V, N	T, V, N	T, V, N

**Canonical Ensemble:**

- ✓ Independent assemblies with same Temperature  $T$ , Volume  $V$ , Number  $N$
- ✓ Rigid, Impermeable, Conducting Walls



T, V, $\mu$	T, V, $\mu$	T, V, $\mu$
T, V, $\mu$	T, V, $\mu$	T, V, $\mu$
T, V, $\mu$	T, V, $\mu$	T, V, $\mu$

**Grand Canonical Ensemble:**

- ✓ Independent assemblies with same Temperature  $T$ , Volume  $V$ , Chemical potential  $\mu$
- ✓ Rigid, Permeable, Conducting Walls

## IMPORTANT TERMS

- **Phase Space:** Six dimensional space with six coordinates  $x, y, z, p_x, p_y, p_z$
- **Cell:** Element of volume in space  $dx dy dz dp_x dp_y dp_z$
- **Phase point:** Cell with minimum volume of the order  $h^3$
- **Occupation number:** No. of particles in a given state
- **Distribution:** Entire set of occupation number or number of particles in each state
- **Configuration :** A given specific distribution of molecules
- **Weight:** The number of ways of achieving a particular configuration
- **Statistical weight factor:** Degree of degeneracy of a particular energy level or no. of energy states of an energy level, denoted by  $g$

## ESSENTIAL CONDITIONS for DISTRIBUTION of MOLECULAR STATES

➤ Consider a system composed of  $N$  molecules, and its total energy  $E$ , then it must satisfy:

$$\sum N_i = N \quad \text{and} \quad \sum N_i \epsilon_i = E \quad (\mathbf{N} \ \& \ \mathbf{E} \ \text{must remain constant})$$

- ✓ These molecules are considered as independent, i.e. no interactions exist among the molecules
- ✓ Infinite collisions take place between these molecules
- ✓ It impossible to keep track of their positions, momenta, and internal energies
- ✓ No. of molecules in each state may keep on changing

# WHAT IS A MACROSTATE ?

**Macrostate:** It is defined by specification of the number of molecules or phase points in each cell of phase space

For example, Consider a system with  $N = 3$  with total energy  $E = 3\varepsilon$  at a particular temperature  $T$  then the following distributions are possible:

	● ● ●	
----- $3\varepsilon$	----- $3\varepsilon$	----- $3\varepsilon$
----- $2\varepsilon$	----- $2\varepsilon$	----- $2\varepsilon$
----- $1\varepsilon$	----- $1\varepsilon$	----- $1\varepsilon$
----- $0\varepsilon$	----- $0\varepsilon$	----- $0\varepsilon$

Thus, there are 3 ways of distribution i.e. 3 Macrostates

✓ Principle of equal a priori probabilities

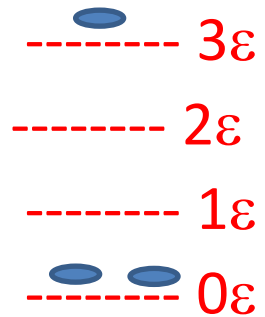
- Provided the number of molecules and the total energy are kept the constant, all possibilities for the distribution of energy are equally probable
- For the system with  $N = 3$  with total energy  $E = 3\varepsilon$  at a particular temperature  $T$  all the three distributions are equally probable

## WHAT IS A MICROSTATE ?

- **Microstate:** Number of possible ways a particular distribution can be achieved if particles are **distinguishable**
  - It is defined by specification of with six coordinates  $x, y, z, p_x, p_y, p_z$  of each molecule of the system within the limits of the dimensions of the cell in which its representative points lies
  - In order to define microstate we must specify the place of each molecule with the limits  $dx, dy, dz$  & magnitude & direction of each molecule with the limits  $dp_x, dp_y, dp_z$
  - We must state to which cell each molecule of the system belongs temporarily

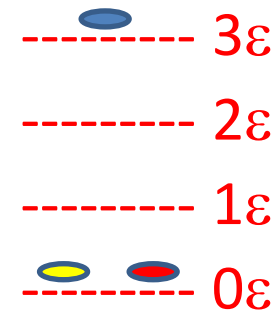
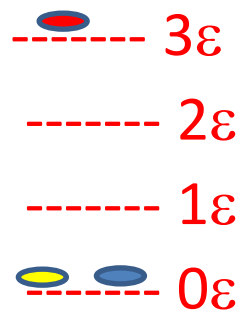
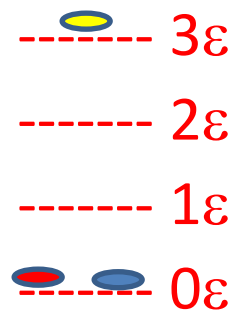
For example: Consider any one of the Macrostate

Macrostate – I:



Possible Microstates:

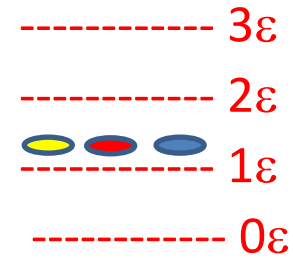
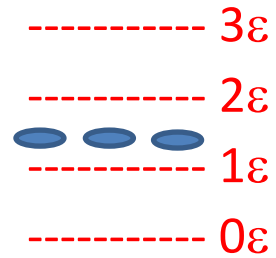
(If particles distinguishable)



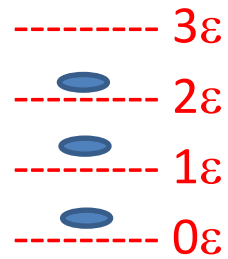
Thus, there are **3 Microstates** for the given Macrostate.  
 Similarly for other configuration there will be **6** and **1** ways of  
 arranging Macrostate – II & III

Possible Microstates: **01 only**

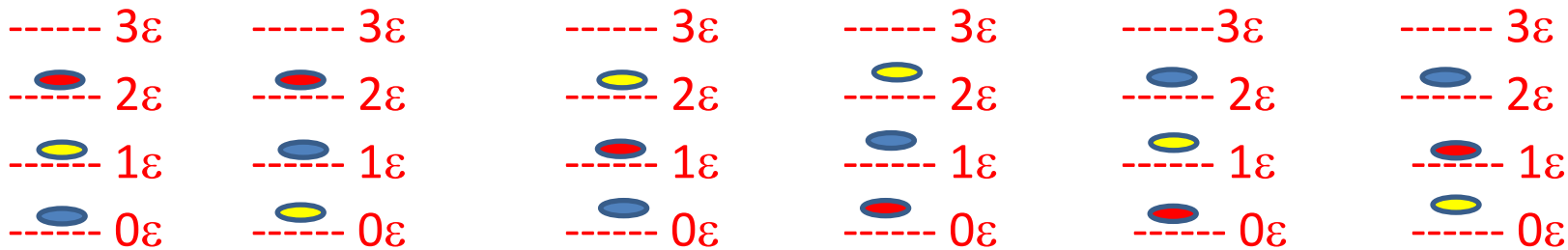
Macrostate – III:



Macrostate – II:



Possible Microstates: **06**



Thus, for **Macrostate – II** there will be **6** ways of arranging and only **1** way of arranging **Macrostate – III**



## WHAT IS THERMODYNAMIC PROBABILITY?

Thermodynamic probability of a macrostate is defined as the number of microstates corresponding to that macrostate and is represented by  $W$

$$W = N! / N_1! N_2! \dots = N! / \prod N_i!$$

where  $N$  = Total number of particles

$N_i$  = Number of particles in  $i^{\text{th}}$  energy level

$N!$  =  $N(N-1)(N-2)\dots\dots 3.2.1$

Thus, for Macrostate – I ;  $W = 3! / 2! 1! = 6/2 = 3$

Macrostate – II ;  $W = 3! / 1!1!1! = 3/1 = 6$

Macrostate – III ;  $W = 3! / 3! = 3/3 = 1$

## MOST PROBABLE DISTRIBUTION

✓  $\sum N_i = N$  and  $\sum N_i \epsilon_i = E$  (N & E must remain constant)

- Ways of achieving :  $W = N! / N_1! N_2! \dots = N! / \prod N_i!$ 
  - If a single particle has that value & others have zero value, then there will be N ways
    - » Macrostate – I ;  $W = 3! / 2! 1! = 6/2 = 3$
  - If equal distribution of energy among all particles, then only one way
    - » Macrostate – III ;  $W = 3! / 3! = 3/3 = 1$
  - If it is arranged in 1:1 configuration, then maximum
    - » Macrostate – II ;  $W = 3! / 1!1!1! = 3/1 = 6$

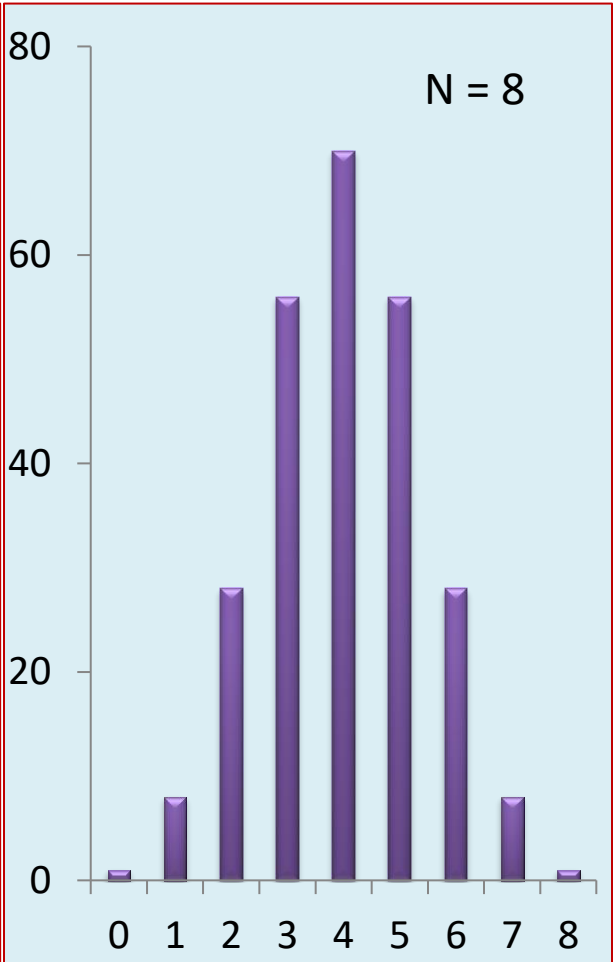
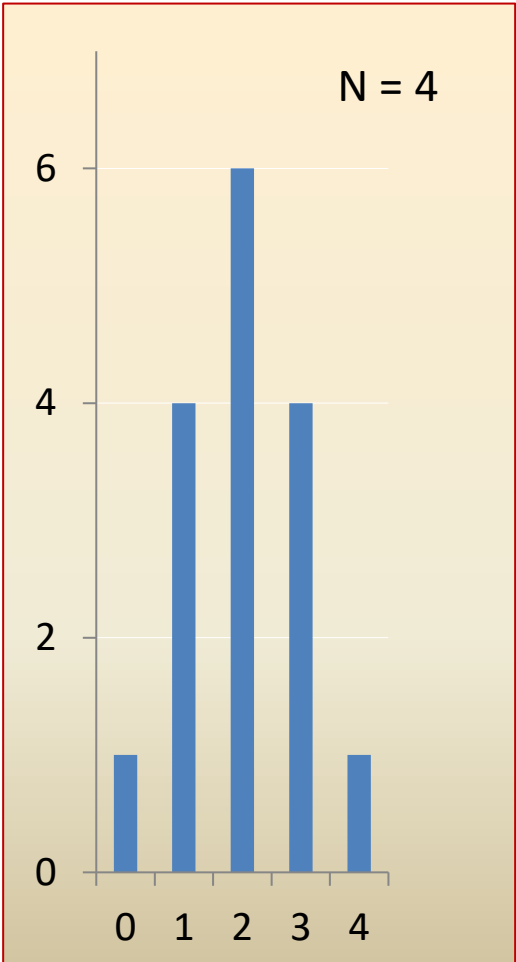
**The Most Probable distribution is the one which can be obtained in the largest no. of ways and the 1:1 configuration is having maximum value of W or maximum frequency of occurrence. Thus, MPD is the distribution with maximum probability .**

# MOST PROBABLE DISTRIBUTION

The most dominating distribution ---- 1:1 configuration

Plot between  $k$  versus  $W$   
when  $\{N, 0\}, \{N-1, 1\}, \dots, \{N-k, k\}, \dots, \{1, N-1\}, \{0, N\}$  are possible configurations

$W$  ↑



$k$  →

## DETERMINATION OF MOST PROBABLE DISTRIBUTION

- No. of ways of getting a distribution of a group of  $N_i$  particles in a given state

$$W = N! / N_1! N_2! \dots = N! / \prod N_i!$$

- Requires a set of numbers  $N_1, N_2, \dots$
- Can be obtained by applying condition of maxima
$$\delta W(N) / \delta N_i = 0 \quad \text{or}$$
$$\delta \ln W(N) / \delta N_i = 0 \quad (\text{to avoid factorial terms})$$
- Gives set of numbers, which corresponds to most probable distribution

✓ **STIRLING'S APPROXIMATION**

When  $N$  is very large, the summation can be approximated by an integral

$$N! = N.(N-1).(N-2).....3.2.1$$

$$\begin{aligned}\ln N! &= \ln N + \ln (N-1) \dots \ln 3 + \ln 2 + \ln 1 \\ &= \sum \ln N \quad (\text{limit } N = 1 \text{ to } N)\end{aligned}$$

Hence  $\ln N! \approx N \ln N - N$

Then  $W = N! / (n_0! n_1! n_2! \dots)$  can be written as

$$\begin{aligned}\ln W &\approx (N \ln N - N) - \sum (n_i \ln n_i - n_i) \\ &= N \ln N - \sum n_i \ln n_i\end{aligned}$$