By definition of N! one has

$$N! = 1 \times 2 \times 3 \times \ldots \times (N-2) \times (N-1) \times N$$

Therefore,

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \ldots + \ln(N-2) + \ln(N-1) + \ln N$$

$$= \sum_{m=1}^{N} \ln m$$

In this summation, except for the first few terms whose values are small, as m increases and attains large values, the increase in the value of m by unity is very small. Hence in the above summation lnm can be approximately treated as continuous so that it gives the area under the curve from m = 1 to m = N obtained by plotting lnm vs m (Fig. 4.3). This is a turn and is equal to the integration of ln x dx between limits x = 1 and x = N. Hence above equation can be approximated to

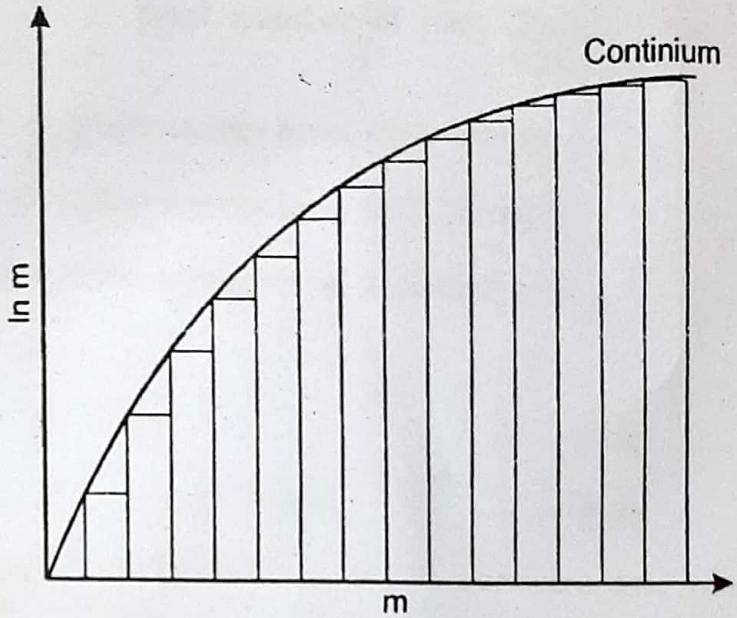

Fig. 4.3 A plot of ln *m* versus *m*

$$\ln N! = \int_1^N 1 \ln x \, dx$$

$$\ln N! = [x \ln x]_1^N - \int_1^N x \cdot \frac{1}{x} dx$$

$$= N \ln N - 1 \ln 1 - \int_1^N dx$$

To solve this integral use integration by parts.

$$\int u \, dv = uv - \int v \, du$$

Here u = ln x and dv = dx

Then v = x and $du = \frac{dx}{x}$

$$= N \ln N - 0 - \int_1^N dx$$

$$= N \ln N - [x]_1^N$$

$$= N \ln N - [N - 1]$$

$$= N \ln N - N + 1$$

Here we can neglect 1 in comparison with the large quantity N, then

$$\ln N! = N \ln N - N$$

This is simplified as Stirling's theorem macrostate may be realized. It is denoted by W. This definition was introduced by Boltzmann and is not equivalent to probability since the former is always greater or equal to unity whereas the latter is always less than one.

Consider a system composed of N identical and distinguishable particles, such as gas molecules, at temperature T, volume, V and total energy E. Now all the particles will not have the same energy. Each molecule or particle may exist in a number of allowable energy levels. Hence total number of particles (N) may be assigned to different energy levels. Suppose

n_0 = Number of particles in the energy level with energy ϵ_0

n_1 = Number of particles in the energy level with energy ϵ_1

n_2 = Number of particles in the energy level with energy ϵ_2

and so on.

Then $N = n_0 + n_1 + n_2 + \ldots\ldots n_i = \Sigma n_i$ ...... (4.2)

and $E = n_0\epsilon_0 + n_1\epsilon_1 + n_2\epsilon_2 + \ldots\ldots n_i\epsilon_i = \Sigma n_i\epsilon_i$ ...... (4.3)

Equation (4.2) and (4.3) represent the total number of particles and total energy of the system. Since the numbers n_0, n_1, n_2 ... etc. in different energy levels change, the distribution also changes. It means there will be various ways of distribution. The total number of distributions (i.e., total number of microscopic states) can be determined by statistical method. According to classical statistics, the total number of ways (i.e., distribution of microstates) in which N particles can be arranged in these energy levels, is equal to the number of permutations of N things in groups n_0, n_1, n_2 ... n_i. Thus the probability is expressed as

$$W = \frac{N!}{n_0!\, n_1!\, n_2! \ldots ni!} \quad \ldots\ldots (4.4)$$

Here N! is N factorial as in written as

$$N! = N \times (N-1)(N-2) \times \ldots \times 4 \times 3 \times 2 \times 1$$

Similarly the terms in the denominator are different. The quantity W is called thermodynamic probability for a system of distinguishable particles. On taking logarithms of both sides equation (4.4) becomes

$$\ln W = \ln N! - [\ln n_0! + \ln n_1! + \ln n_2! + \ldots + \ln n_i!]$$

$$\ln W = \ln N! - \Sigma \ln n_i! \quad \ldots\ldots (4.5)$$

When N is large, then ln N! can be approximated by Stirling's formula

$$\ln N! = N \ln N - N$$

Under these conditions n! is also large, and hence,

$$\Sigma \ln n_i! = \Sigma n_i \ln n_i - \Sigma n_i$$

$$= \Sigma n_i \ln n_i - N \quad \ldots\ldots (4.6)$$

On substituting these values in equation (4.5)

$$\ln W = N \ln N - N - \Sigma n_i \ln n_i + N$$

$$\ln W = N \ln N - \Sigma n_i \ln n_i \quad \text{...... (4.7)}$$

Equation (4.7) is the expression for thermodynamic probability.

Example 4.1

Calculate the number of ways of distributing distinguishable molecules *a*, b, c, between these energy levels so as to obtain the following set of occupation number

$n_0 = 1, n_1 = 1, n_2 = 1$ i.e., each energy level is occupied by one solution.

Solution

The probability W is given by

$$W = \frac{N!}{n_0!\, n_1!\, n_2!} \quad (\because N = 3)$$

$$\therefore \quad W = \frac{3!}{1!\, 1!\, 1!} = \frac{3 \times 2 \times 1}{1 \times 1 \times 1} = 6$$

These are six ways of distributing the three molecules as required.