... capacity etc.) of a system containing a large number of molecules, it is denoted by the symbol Q.

Probability Theorems

(N! = N factoria

The following are the important probability theorems used in statistical thermodynamics.

(i) The number of ways in which N distinguishable particles can be arranged in order will be equal to

(No. of identical sys = N

$$N!$$

(ii) The number of different ways in which n particles can be selected from N distinguishable particles irrespective of the order of selection will be equal to

$$\frac{N!}{(N-n)!\,n!}$$

(iii) The number of different ways in which n distinguishable particles can be arranged in g distinguishable states with not more than one particles in each state will be equal to

$$\frac{g!}{n!(g-n)!}$$

4.3 STIRLING'S APPROXIMATION

The calculation of N! becomes laborious for large values of N. The Stirling's approximation gives the approximation values of log N! when N is very large. According to formula one has,

$$\ln N! = N \ln N - N \qquad \text{(Stirling's approximation)}$$

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

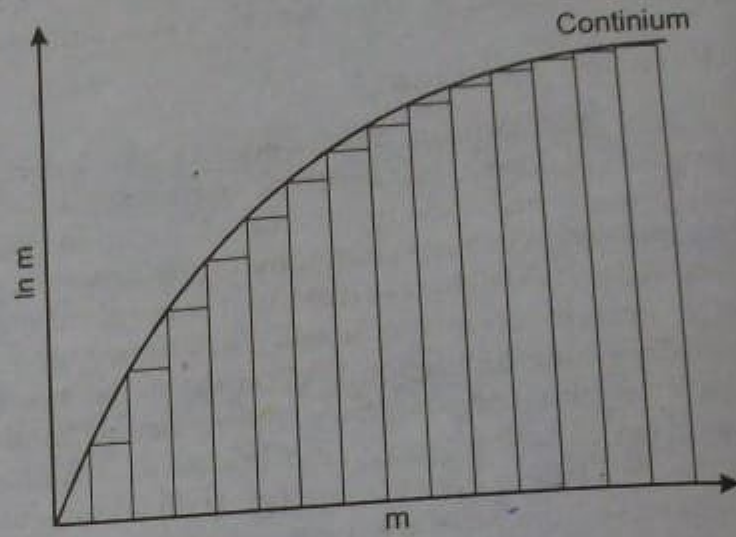

Fig. 4.3 A plot of ln *m* versus *m*

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

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

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

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

4.4 THERMODYNAMIC PROBABILITY

The thermodynamic probability of a macrostate of a system is defined as the total number of different ways (i.e., total number of microstates) by which the given