The Stirling's theorem is an approximation and is only valid when n is very large. For example, let us calculate the value of $\ln 5!$ with and without Stirling's theorem.

$$5! = 5 \times 4 \times 3 \times 2 \times 1 = 120$$

$$\ln 5! = \ln 120 = 2.303 \log 120$$

$$= 4.7883$$

②

$$\boxed{\ln x! = x.\ln x - x}$$

By Stirling's theorem,

$$\ln 5! = 5 \ln 5 - 5$$

$$\ln n! = n.\ln n - n$$

$$= 5 \times 2.303 \log 5 - 5$$

$$= 8.0486 - 5 = 3.0486$$

The above calculations show that Stirling's theorem is valid only when n is very large.

THERMODYNAMIC PROBABILITY

Planck gave the concept of ***thermodynamic probability*** or ***statistical probability*** (denoted by P) to indicate the total number of possible complexions or microstates for any given combination.

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 microstate may be realised. It is denoted by P or W.

$\therefore$ P of a macrostate = Number of microstates corresponding to that macrostate. ①

The thermodynamic probability for different states (macrostates) of molecular systems is a very great number. It is to remember, that *thermodynamic probability is proportional to mathematical probability**.

Consider a system of volume V containing n identical and distinguishable particles; the value of n being very large. Let E_t be the total energy of the system whose temperature is T. It is clear that all the particles will not have the same energy. Suppose n_0 particles are in energy level ε_0 ε_0, n_1 particles are in energy level ε_1 and so on. Then,

$$E_t = n_0\varepsilon_0 + n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots n_i\varepsilon_i + \ldots = \Sigma\, n_i\varepsilon_i$$

Also

$$n = n_0 + n_1 + n_2 + \ldots n_i + \ldots = \Sigma n_i$$

As the occupation numbers, $n_1, n_2, n_3 \ldots$ etc., in different energy levels change, the distribution also changes. There are obviously number of ways of distribution, similar to the arrangement of n boys in p-rooms, so that one room has n_0 boys and the other room has n_1 boys and so on. This number is given by,

$$\boxed{P = \frac{n!}{n_0!\, n_1!\, n_2! \ldots n_p!} = \cancel{\frac{n!}{\Pi n_1!}}} \qquad \ldots (1)$$

The thermodynamic probability of a distribution is thus equal to the number of ways of realising the distribution.

Equation (1) is used to determine the probability for all distributions of all the molecules in a given molecular system in different energy levels at a constant total energy.

Taking the logarithm of both sides of equation (1)

$$\ln P = \ln n! - (\ln n_0! + \ln n_1! + \ln n_2! + \ldots + \ln n_i!)$$

or

$$\ln P = \ln n! - \Sigma \ln n_i! \qquad \ldots (2)$$

---

* The thermodynamic probability (P) is relaed to mathematical probability (W) which is given by :

$$W = \frac{n!}{\Pi_i n_i!} \cdot C^{-n}, \text{ where } C^{-n} \text{ is the total number of possible cases.}$$

②

According to Stirling's theorem,

$$\boxed{\ln n! = n \ln n - n} \quad \dots (3)$$

$$\therefore \quad \Sigma \ln n_i! = \Sigma n_i \ln n_i - \Sigma n_i \quad \dots (4)$$

Putting the values from equations (3) and (4) in equation (2), we get,

$$\ln P = n \ln n - n - (\Sigma n_i \ln n_i - \Sigma n_i)$$

or

$$\ln P = n \ln n - n - \Sigma n_i \ln n_i + \Sigma n_i$$

But

$$n = \Sigma n_i$$

$$\therefore \quad \ln P = n \ln n - \Sigma n_i \ln n_i \quad \dots (5)$$

Condition of maximum probability ($d \ln P = 0$)

The differential form of equation (5) can be written as,

$$d \ln P = d\,(n \ln n) - \Sigma\, d\,(n_i \ln n_i) \quad \dots (6)$$

But the total number of particles (n) is constant. So equation (6) becomes,

$$d \ln P = -\Sigma\, d\,(n_i \ln n_i) \quad \dots (7)$$

Modification of equation (1) : Two modifications have been introduced in equation (1).

(a) First modification : Certain states are energetically so close to each other that they cannot be distinguished from one another, *i.e.*, degeneracy of energy-levels. Regarding this correction, a factor 'g' called *statistical weight factor* for each state is introduced. This factor represents the degeneracy of the given energy state or level. A given energy-level is said to be '*g-degenerate*' if there are g-number of possible distributions (equal distribution) of energy in that energy-level.

(b) Second modification : This modification is based on the fact that molecules are indistinguishable. Therefore, we have to divide the total expression for P by n !.

On the basis of the above two corrections the expression for P can be written as,

$$P = \frac{g_0^{n_0}}{n_0!} \cdot \frac{g_1^{n_1}}{n_1!} \cdot \frac{g_2^{n_2}}{n_2!} \cdots \frac{g_i^{n_i}}{n_i!}$$

This equation is the result of classical statistical treatment modified by ***quantum statistics.***

Problem 1 : ***Calculate the number of ways of distributing distinguishable molecules x, y and z between three energy levels so as to obtain the following sets of occupation number.***
$N_0 = 1, N_1 = 1, N_2 = 1$; i.e., each energy level is occupied by one molecule.

Solution : The probability W is given by

$$W = \frac{N!}{N_0!\,N_1!\,N_2!}$$

Here,

$$N = 3, N_0 = N_1 = N_2 = 1$$

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

There are six ways of distributing the three molecules as required in the problem. The same result may be obtained by considering the following treatment.

Energy state $N_0 = 1, N_1 = 1, N_2 = 1$	Configuration					
	I	II	III	IV	V	VI
ε_0	x	x	y	y	z	z
ε_1	y	z	z	x	x	y
ε_2	z	y	x	z	y	x

There are six possible configurations.

$$\Omega_{total} = 4 + 12 + 4 = 20$$

Problem 5 : ***Calculate the total number of complexions in arranging four distinguishable systems energy level 0, 1ε, 2ε provided these levels are respectively 3–, 2– and 2– fold degenerate.***

Solution : As calculated in the previous problem, we have

$$\Omega_1 = \frac{4\,!\,(3)^3}{(3\,!)\,(1\,!)} = 108$$

$$\Omega_2 = \frac{(4\,!)\,(3^2)\,(2^1)\,(2^1)}{(2\,!)\,(1\,!)\,(1\,!)} = 432$$

$$\Omega = \frac{(4\,!)\,(3^1)\,(2^3)}{(3\,!)\,(1\,!)} = 96$$

$$\Omega_{total} = 108 + 432 + 96 = 636$$

MOST PROBABLE DISTRIBUTION AND MAXWELL-BOLTZMANN DISTRIBUTION LAW OF ENERGY

Consider a system containing n particles having a total energy E_t. All particles are in different energy levels. The allowed energy levels are fixed by quantum mechanical principles.

The thermodynamic probability (P) of this distribution is given by,

$$P = \frac{n\,!}{\Pi n_i\,!} = \frac{n!}{n_0!\, n_1!\, n_2! \ldots n_p!}$$

or

$$\log P = \log n\,! - \Sigma \log n_i\,!$$

Since n, as also n_i are very large, we can apply Stirling's theorem, *viz.*,

$$\log x\,! = x \log x - x$$

Therefore,

$$\log P = \log n\,! - \Sigma \log n_i!$$

$$= n \log n - n - [n_1 \log n_1 - n_1 + n_2 \log n_2 - n_2 \ldots]$$

or

$$\log P = n \log n - \Sigma n_i \log n_i - \cancel{n} + \Sigma \cancel{n_i}$$

$$= n \log n - \Sigma n_i \log n_i \qquad (\text{Since } \Sigma n_i = n) \quad \ldots (1)$$

We can find out the ***most probable distribution***, when the system attains equilibrium. The probability will be maximum when the distribution corresponding to equilibrium is attained. In other words, at equilibrium distribution, the magnitude of P and, therefore, of $\log P$ will be maximum. Hence, at equlibrium, $d \log P = 0$.

At equilibrium, equation (1) can be written as,

$$d \log P = d\,(n \log n) - d\,(\Sigma n_i \log n_i) = 0$$

i.e.,

$$d\,(\Sigma n_i \log n_i) = 0$$

or

$$\Sigma \log n_i\, dn_i + \Sigma\, dn_i = 0$$

Since $\Sigma n_i = n =$ constant, therefore, $\Sigma dn_i = 0$

$$\therefore \quad \Sigma \log n_i\, dn_i = 0 \qquad \ldots (2$$

For the given system, the total energy (E_t) and the total number of particles (n) remai constant, *i.e.*,

$$n = \Sigma n_i \quad \text{or} \quad dn = \Sigma\, dn_i = 0 \qquad \ldots (3$$

$$E_t = \Sigma n_i \varepsilon_i \quad \text{or} \quad dE_t = \Sigma \varepsilon_i\, dn_i = 0 \qquad \ldots ($$

agrange's Method of Undetermined Multiples

Multiply equations (3) and (4) by arbitrary undetermined multipliers α and β, respectively and add equation (2), we get,

④

$$\Sigma \log n_i\, dn_i + \alpha\, \Sigma\, dn_i + \beta\, \Sigma\, \varepsilon_i\, dn_i = 0$$

or

$$dn_i\, (\Sigma \log n_i + \alpha + \beta\, \Sigma\, \varepsilon_i) = 0$$

Since α and β are independent, the restraining conditions are removed, and $dn_i \neq 0$, so this relation will hold good for any energy level or cell. Thus,

$$\log n_i + \alpha + \beta\varepsilon_i = 0$$

or

$$\log n_i = -\alpha - \beta\varepsilon_i$$

or

$$n_i = e^{-\alpha} \cdot e^{-\beta\varepsilon_i} \qquad \text{... (5)}$$

Equation (5) gives the number of particles in each energy level (α, β are unknown arbitrary constants). It is one form of the celebrated ***Boltmann distribution law.***

$$n = \Sigma n_i = e^{-\alpha} \cdot \Sigma e^{-\beta\varepsilon_i} \qquad \text{... (6)}$$

$$\frac{n_i}{n} = \frac{e^{-\beta\varepsilon_i}}{\Sigma e^{-\beta\varepsilon_i}} \qquad \text{... (7)}$$

Equation (6) is known as ***Maxwell-Boltzmann distribution law*** : This law gives at a temperature T, the fraction of the total number of molecules which at equilibrium or most probable state would possess energy ε_i. Equation (7) gives the populations of the most probable configuration of the ensemble. This is known as ***canonical distribution.***

A new factor may, however, be introduced at this point. In a given cell or energy level i, all the particles may have the same energy ε_i, but the energy may be arrayed in different ways for different particles. So, such a state in which there are different ways of array is known as *'degenerate'*. If there are g_i number of possible distributions of energy in a given energy level i, then the state is said to be *"g_i-degenerate"*, *where* g_i is called the *statistical weight factor.*

Thus, equations (5) and (6) become :

$$n_i = e^{-\alpha} \cdot g_i\, e^{-\beta\varepsilon_i} \qquad \text{... (8)}$$

and

$$n_i = e^{-\alpha} \cdot \Sigma g_i\, e^{-\beta\varepsilon_i} \qquad \text{... (9)}$$

∴

$$\frac{n_i}{n} = \frac{g_i e^{-\beta\varepsilon_i}}{\Sigma g_i e^{-\beta\varepsilon_i}} \qquad \text{... (10)}$$

PARTITION FUNCTION

In equation (7), the factor $\Sigma e^{-\beta\varepsilon_i}$ represents the sum of the factor $e^{-\beta\varepsilon_i}$ over all the energy levels. It is called the ***partition function*** and is denoted by f. Therefore,

$$f = \Sigma e^{-\beta\varepsilon_i}$$

The factor β is called the modulus of distribution.

Evaluation of β. The Boltzmann law can be written in terms of partition function as :

$$n_i = \frac{n}{f} \cdot e^{-\beta\varepsilon_i}$$

$$-d\, \Sigma n_i \cdot \ln n_i = 0$$

or

$$\log n_i = \log n - \log f - \beta\varepsilon_i \qquad \text{... (11)}$$

$$\Sigma dn_i + \Sigma \ln n_i\, dn_i$$

$$d\, \Sigma n_i \cdot d \ln n_i = 0$$

$$(\Sigma dn_i)\, d \ln n_i + (\Sigma \ln n_i)\, dn_i$$

$$\Sigma n_i (d \ln n_i) + \Sigma \ln n_i\, dn_i$$

function $f = \Sigma e$

Subst. $\beta \to \frac{1}{kT}$ $n_i = n/f\, e^{-\beta\varepsilon_i} \Rightarrow \log n_i = \log n - \log f - \beta\varepsilon_i$

⑤ We know that both entropy and probability attain maximum value at equilibrium. The relation between entropy (S) and probability (W) is given by,

$$S = k \log W$$

Since probability (W) is proportional to the thermodynamic probability (P), we have,

$$S - B = k \log P$$

where, B is a constant and has been taken as zero by Planck.

Substituting the value of P from equation (1) in the last equation, we have,

$$\frac{S-B}{k} = n \log n - \Sigma n_i (\log n - \log f - \beta\varepsilon_i) \quad \text{[From equation (11)]}$$

$$= n \log n - \log n \,\Sigma n_i + \log f \,\Sigma n_i + \beta \,\Sigma n_i \varepsilon_i$$

$$= n \log n - n \log n + n \log f + \beta\varepsilon_i\, n$$

or

$$\frac{S-B}{k} = n \log f + \beta E_t \quad (\text{where } E_t = \varepsilon_i n) \quad \text{...(12)}$$

or

$$S - B = nk \log f + \beta\, E_t k \quad \text{...(13)}$$

Differentiating this equation with respect to E_t at constant volume, we get,

$$\left(\frac{dS}{dE_t}\right)_V = \frac{nk}{f} \cdot \frac{df}{d\beta}\left(\frac{d\beta}{dE_t}\right)_V + k\beta + kE_t\left(\frac{d\beta}{dE_t}\right)_V$$

Since,

$$f = \Sigma e^{-\beta\varepsilon_i}$$

∴

$$\frac{df}{d\beta} = -\Sigma\varepsilon_i e^{-\beta\varepsilon_i} = \frac{-E_t}{n} \cdot f$$

∴

$$\left(\frac{dS}{dE_t}\right)_V = -\frac{nk}{f} \cdot \left(\frac{E_t \cdot f}{n}\right)\left(\frac{d\beta}{dE_t}\right)_V + k\beta + kE_t\left(\frac{d\beta}{dE_t}\right)$$

$$= k\beta$$

When the energy (E_t) is purely the internal energy (E), then,

$$\left(\frac{dS}{dE}\right)_V = k\beta \quad \text{...(14)}$$

From first and second law of thermodynamics, we have

$$dE + PdV = dQ = TdS$$

or

$$\left(\frac{dS}{dE}\right)_V = \frac{1}{T} \quad \text{...(15)}$$

From equations (14) and (15), we have

$$k\beta = \frac{1}{T}$$

So, undetermined multuplier, $\beta = \frac{1}{kT}$

Therefore, partition function, $f = \Sigma e^{-\varepsilon_i/kT}$

and

$$n_i = \frac{n}{f} e^{-\varepsilon_i/kT} \quad \text{...(16)}$$

If we consider the degenerate state of a system, then,

$f = \Sigma g_i e^{-\varepsilon_i/kT}$ & $n_i = n/f\, g_i e^{-\varepsilon_i/kT}$

⑥

$$f = \Sigma g_i e^{-\varepsilon_i/kT}$$

$$n_i = \frac{n}{f} g_i e^{-\varepsilon_i/kT} \qquad ...(17)$$

ysical Significance of *f*

(i) Qualitatively speaking, the partition function indicates how the particles are distributed among the various energy states (levels or cells). It is a measure of available energy-levels.

(ii) Partition function is a quantity, characteristic of every substance (and also of a mixture of substances or a system). It reflects the diversity of energy states of the molecules of a system and relative probability of these states (in comparison to the lowest energy-level, ε_0). In other words, the relative population of any two quantum states *p* and *q* is given by the ratio n_p/n_q obtained by the application of equation (17),

$$n_p = n g_p \frac{e^{-\varepsilon_p/kT}}{f}$$

and

$$n_q = n g_q \frac{e^{-\varepsilon_q/kT}}{f}$$

∴

$$\frac{p_p}{p_q} = \frac{n_p}{n_q} = \left(\frac{g_p}{g_q}\right) e^{-(\varepsilon_p - \varepsilon_q)/kT}$$

Here 'p' terms denote the probability at a particular level. The second form of distribution law gives the population in two different levels.

Case 1. If these two states are degenerate, *i.e.*, $\varepsilon_p = \varepsilon_q$, it follows that they are equally populated.

Case 2. If $\varepsilon_p > \varepsilon_q$, then $n_p < n_q$, *i.e.*, states are equally populated.

Case 3. As long as $(\varepsilon_p - \varepsilon_q) < kT$, the population will be of the same order of magnitude. If there are many low lying states of energy, substantially lower than *kT*, they all will be well populated, relative to ground state (*i.e.*, ε_0). A further consequence of such uniform distribution is that no one state is heavily populated. Such a distribution corresponds to a large value of *Q*. In contrast, widely spaced energy-levels result in very uneven distributions of molecules among states and value of *f* approaching unity. These situations are illustrated in fig. (3).

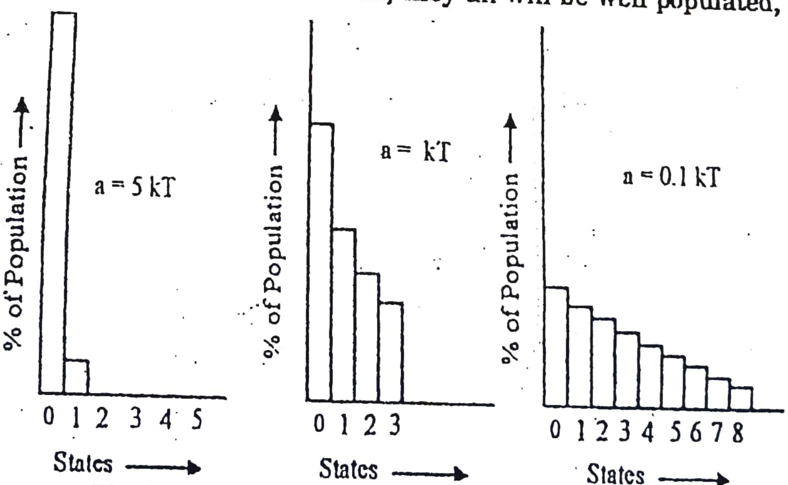

Fig. 3. Effect of quantum size on population of states.

The Boltzmann distribution in the diagram shows that *molecules are largely confined to their lowest energy-levels,* when $\varepsilon >>> kT$. Conversely, small energy gradations from level to level result in more nearly uniform distribution of molecules among the available states.

(iii) According to Maxwell-Boltzmann's law

$$\frac{n_i}{n_0} = \left(\frac{g_i}{g_0}\right) e^{-\varepsilon_i/kT}$$

where n_i = Number of molecules in the energy state 'i'.

n_0 = Number of molecules in the energy state denoted by 'zero'.

g_i and g_0 = Degeneracy of levels (state 'i' and 'zero'), respectively.

When ε_0 = energy of zeroth level = 0, then $g_0 = 1$

$$\therefore \quad n_i = n_0 \cdot g_i \cdot e^{-\varepsilon_i/kT}$$

Taking summation of the above equation, we get,

$$\Sigma n_i = n_0 \Sigma g_i \, e^{-\varepsilon_i/kT}$$

But $\Sigma g_i \, e^{-\varepsilon_i/kT} = f$

Hence, $\Sigma n_i = n_0 f$

Since, $\Sigma n_i = n$,

hence $n = n_0 f$

or $f = \dfrac{n}{n_0}$

The equation states that partition function is the ratio of total number of molecules to the number of molecules in zeroth level. At absolute zero ($T = 0$K) or $t = 273$°C, all the molecules tend to go in zeroth level. So,

As $T \rightarrow 0; n \rightarrow n_0 \qquad \therefore f = \dfrac{n}{n_0} \rightarrow 1$

Thus, the value of partition function is unity at absolute zero. As the temperature rises, more and more molecules go to higher energy levels and lesser molecules remain in zeroth level. Hence, according to equation,

$$f = \frac{n}{n_0}$$

f will increase. In other words, ***higher the temperature, larger is the value of partition function.***

(iv) Partition function was introduced by Fowler and is a dimensionless quantity. Its value depends on the molecular weight, molar volume, temperature etc. It provides a link between microscopic properties of individual molecules (such as their discrete energy-levels, dipole moment etc.) and macroscopic properties of the system (such as entropy, polarization, molar heat etc.). It may be defined as, ***'the sum of the probability factors for the various energy levels or the ways in which the energy of the system is partitioned amongst the molecules constituting the system.'*** In other words, partition function may be defined as, ***'the reciprocal of the mole fraction of the molecules occupying the ground state*** ($\varepsilon_0 = 0$).***'*** It is also the ***ratio of the total number of molecules to the number of molecules in the ground state.***

ENTROPY AND PROBABILITY

Boltzmann said that the thermodynamical entropy is related to the probability of the dynamical equilibrium state. If S and W represent the entropy of an isolated system and the probability of a particular state, then according to Boltzmann,

$$S = f(W)$$

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order to understand the nature of this function, consider two separate systems, having ies S_1 and S_2 and thermodynamic probabilities W_1 and W_2. Then, we have for the two ms,

⑧

$$S_1 = f(W_1) \quad \text{...(18)}$$

$$S_2 = f(W_2) \quad \text{...(19)}$$

If the two systems are combined, the probability of the resulting system is the product $W_1 \times W_2$, whereas the entropy being additive is $S_1 + S_2$. Hence,

$$S_{1,2} = S_1 + S_2 = f(W_1 \times W_2) \quad \text{...(20)}$$

Combining equations (18), (19) and (20), we get,

$$f(W_1) + f(W_2) = f(W_1 \times W_2) \quad \text{...(21)}$$

Differentiating equation (21) with respect to W_1, keeping W_2 constant, we get,

$$W_2 \, . \, f'(W_1 \times W_2) = f'(W_1) \quad \text{...(22)}$$

Now differentiating equation (22) again with respect to W_2, keeping W_1 constant, we get,

$$W_1 W_2 \, . \, f''(W_1 \times W_2) + f'(W_1 \times W_2) = 0$$

or $$Wf''(W) + f'(W) = 0 \qquad [\text{As } W = W_1 \times W_2]$$

Put $$f'(W) = X$$

then $$\frac{dX}{dW} = f''(W)$$

Thus, $$W \frac{dX}{dW} + X = 0$$

or $$WdX + XdW = 0$$

or $$d(W \, . \, X) = 0$$

On integration, we get,

$$W \, . \, X = k$$

where, k is a constant having the same value as Boltzmann constant (R/N).

Alternatively, $$W \, . \, f'(W) = k$$

or $$W \frac{d}{dW} [f(W)] = k$$

or $$df(W) \, k = \frac{dW}{W}$$

On integration, $$f(W) = k \log W + I_c \quad \text{...(23)}$$

where, I_c is an integration constant.

Equation (23) is known as ***Boltzmann equation.*** Planck found the value of $I_c = 0$, so Boltzmann equation becomes,

$$S = k \log W \quad \text{...(24)}$$

Equation (24) is known as ***Boltzmann-Planck equation.***

Problem 1 : *10 molecules of a gas are present in a container maintained at 298K. What is the probability that all ten molecules will be found simultaneously, in one half of the container?*

Solution : $N = 10$ molecules