

UNIT-V STATISTICAL THERMODYNAMICS

PROBABILITY.

The probability P is defined as the ratio of the number of ways of getting an event (w) ~~to~~ to the total number of possible events (n)

$$P(w) = \frac{w}{n}$$

The probability of not getting the event will be

$$1 - P(w) = (n - w) / n$$

example 1. If a coin is tossed, it will have equal chance of getting a head or a tail. That is the chance of tossing either a head or tail is 1 out two or probability of tossing a head or tail is $\frac{1}{2}$

(ii) If a dice is thrown, the probability of getting any number will be $\frac{1}{6}$.

(iii) From a deck of cards are well shuffled, the probability of drawing say, an ace of spades, will be $\frac{1}{52}$ and the probability of drawing a spades card will be $\frac{13}{52}$.

(iv) Consider two dice say x and y , both having six faces numbered 1 to 6. Total number of combinations would be 6×6 or 36. If these dices are rolled, what is the probability of getting a number 8. These possible number of getting a number 8 are

$$x(6) y(2)$$

$$x(4) y(4)$$

$$x(5) y(3)$$

$$x(2) y(6)$$

$$x(3) y(5)$$

Therefore there are 5 ways of getting number 8 from a pair of dice. Hence the probability of securing number 8 from a pair of dice will be $5/36$. There is only one way of getting number 12, $x(6)y(6)$, therefore the probability of getting number 12 will be $1/36$.

The probability of a given distribution of molecules in various energy states could be defined as the number of ways of realizing a particular distribution divided by the total number of possible distributions. The probability is a fractional number and its value lies between 0 and 1.

Law of addition of Probabilities

The probability that one of the two (or more) mutually exclusive events will occur is the sum of the probability of their separate occurrence, p_1 and p_2 .

$$P_{12} = p_1 + p_2$$

Illustration:

What is the probability that a dice will turn to 5 or an even number?

Solution - The chance of getting 5 are $1/6$ and the chance of getting an even number (2, 4, 6) is $3/6$. Both those events are mutually exclusive, since it is 5, it cannot be even number or vice versa.

$$\text{Hence } p = 1/6 + 3/6 = 2/3.$$

Law of Multiplication of Probabilities.

The probability that two independent events will occur simultaneously is equal to the product of the probability of separate events, or

$$P_{12} = P_1 \cdot P_2$$

where P_{12} is the probability that events 1 and 2 occur simultaneously and P_1 and P_2 are the probabilities of events 1 and 2.

Illustration: A bag contains 10 red balls and 5 white balls. All balls are identical except for the colour. What is the probability that on two independent drawings one ball is red and one is white?

There are two ways of drawing one red and one white ball. One way is in which 1st ball is white and the second ball is red. The other way would be in which 1st ball is red and 2nd white.

In first case the probability of 1st ball being white = $5/15 = 1/3$.

The probability that 2nd is red = $10/15 = 2/3$.

Therefore, the probability that one ball is white and other red would be combined probability p_{12}
 $= \frac{1}{3} \times \frac{2}{3} = \frac{2}{9}$

1. Maxwell-Boltzmann Statistics.

Consider a system of N distinguishable particles occupying energy levels $\epsilon_1, \epsilon_2, \epsilon_3$ etc. The total number of arrangements for placing n_1 particles in the ground state energy level ϵ_1 , n_2 particles in the first excited energy level ϵ_2 , n_3 particles in the second excited energy level ϵ_3 and so on, is known as the thermodynamic probability, W , of the given macrostate. The number of microstates (w) correspond to a given macrostate is given by

$$W = \frac{N!}{n_1! n_2! \dots n_i!} = \frac{N!}{\prod n_i!} \quad \text{--- (1)}$$

where $N = \sum n_i$

In the above eqn (1) N is the total number of particles and the summation is over all the energy levels.

It is possible to realize a given energy level in more than one way, i.e., more than one quantum state.

has the same energy. When this happens, the energy level is said to be degenerate. Let, g_i be the

degeneracy (or multiplicity) of the energy level ϵ_i .

This means that if there is one particle in the i^{th} energy level, there are g_i ways of distributing it.

For two particles in the i^{th} level, there are g_i^2 possible distribution and for n_i particles, there are $g_i^{n_i}$ possible distributions.

Hence, the thermodynamic probability for the system of N particles is given by

$$W = N! \prod_i \frac{g_i^{n_i}}{n_i!} \times \text{constant} \quad \text{--- (2)}$$

If we confine our investigation to a closed system of independent particles, it would meet the following two requirements:

(i) The total number of particles is constant, i.e.

$$N = \sum_i n_i = \text{constant} \quad \text{--- (3)}$$

(ii) The total energy U of the system is constant

$$U = \sum_i n_i \epsilon_i = \text{constant} \quad \text{--- (4)}$$

The constancy of the total number of particles implies that

$$dN = \sum_i dn_i = 0 \quad \text{--- (5)}$$

and the constancy of the total energy implies that

$$dU = \sum_i \epsilon_i dn_i = 0 \quad \text{--- (6)}$$

From eq (2), taking logarithms on both sides, we get

$$\ln W = \ln N! + \sum_i n_i \ln g_i - \sum_i \ln n_i! \times \text{const} \quad \text{--- (7)}$$

Involving the Sterling approximation on eqn (7)

$$\ln W = (N \ln N - N) + \sum_i n_i \ln g_i - \sum_{n_i} n_i \ln n_i + \sum_{n_i} n_i + \text{const.} \quad \text{--- (8)}$$

$$= N \ln N + \sum_i n_i \ln g_i - \sum_{n_i} n_i \ln n_i + \text{const.} \quad \text{--- (9)}$$

Differentiating and bearing in mind that N and g_i are constants, we get

$$d \ln W = \sum_i \ln g_i dn_i - \sum_i \ln n_i dn_i - \sum_i n_i d \ln n_i \quad (10)$$

Now $\sum_i n_i d \ln n_i = \sum_i n_i d \ln n_i = \sum_i n_i \frac{dn_i}{n_i} = \sum_i dn_i = 0 \quad (11)$

Hence at equilibrium

$$d \ln W = \sum_i \ln g_i dn_i - \sum_i \ln n_i dn_i = 0 \quad (12)$$

The above eqn. gives the change in $\ln W$ which results when the number of particles in each energy level is varied.

Since the system is closed, N is constant and the values of dn_i are not independent of one another, the desired solution is obtained by applying the method of Lagrange's Undetermined multipliers. Rewriting eqn. (12) we have

$$\sum_i \ln \frac{g_i}{n_i} dn_i = 0 \quad (13)$$

Multiplying eqns (3) and (4) by arbitrary constants α and β (known as Lagrange's Undetermined multipliers) and subtracting from eqn (13) we get

$$\sum_i \left[\ln \frac{g_i}{n_i} - \alpha - \beta \epsilon_i \right] dn_i = 0 \quad (14)$$

$$\ln(g_i/n_i) - \alpha - \beta \epsilon_i = 0 \quad (1)$$

$$\ln(g_i/n_i) = \alpha + \beta \epsilon_i \quad (2)$$

$$\ln n_i = \ln g_i - \alpha - \beta \epsilon_i$$

$$\text{or } n_i = g_i e^{-\alpha - \beta \epsilon_i} \quad (15)$$

The above equation (15) which is one form of the Boltzmann distribution law, gives the most probable distribution for a macrostate. i.e. it gives the occupation numbers of the molecular energy levels for the most probable distribution in terms of the energies ϵ_i , the degeneracy g_i and the undetermined multipliers α and β .

Bose-Einstein Statistics

Consider a system of N indistinguishable particles such that n_i particles are in the i th energy level with degeneracy g_i . The n_i particles have to be distributed among g_i states. For the sake of simplicity, imagine that the i th energy level has $g_i - 1$ partitions which are sufficient to separate energy level into g_i intervals. Now the possible number of distributions of n_i particles among the g_i states, may be determined by permuting the array of partitions and particles. The total number of permutations of n_i particles and $(g_i - 1)$ partitions is $(n_i + g_i - 1)!$. However the partitions and particles are indistinguishable. This implies that interchanging of two partitions does not alter an arrangement; also interchanging two particles does not alter an arrangement. Hence we must divide $(n_i + g_i - 1)!$ by the number of permutations of the $g_i - 1$ partitions viz, $(g_i - 1)!$ and the number of permutations of n_i particles viz, $n_i!$ to obtain the number of possible arrangements of the n_i particles in the energy level ϵ_i . Thus

$$\text{The number of arrangements} = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

Here also the total number of particles is constant and the total energy of the system also constant i.e.

$$N = \sum_i n_i = \text{Constant} \quad - (1)$$

$$U = \sum_i n_i \epsilon_i = \text{Constant} \quad - (2)$$

Thus the thermodynamic probability W for the system of N particles

$$W = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \times \text{Constant} \quad - (3)$$

Taking logarithms of both sides of eqn 3

$$\ln W = \sum_i \ln (n_i + g_i - 1)! - \ln n_i! - \ln (g_i - 1)! + \text{Const.} \quad (4)$$

Involving Stirling's approximation we get

$$\ln W = \sum_i [(n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i] + \text{Constant} \quad (5)$$

Since, n_i is very large, it can be treated as a continuous variable. Differentiation of eqn (5) w.r.t n_i and setting the differential equal to zero gives for the most probable thermodynamic state of the system.

$$d \ln W = \sum_i [\ln n_i + \ln (n_i + g_i)] dn_i = 0 \quad \text{or} \\ \sum_i \left[\ln \frac{n_i + g_i}{n_i} \right] dn_i = 0 \quad - (6)$$

$$\text{From equation (1) and (2) } dN = \sum_i dn_i = 0 \quad - (7)$$

$$dU = \sum_i \epsilon_i dn_i = 0 \quad - (8)$$

Applying the method of Lagrange's undetermined multipliers to eqns 6, 7 and 8 we get

$$\sum_i \left[\ln \frac{n_i + g_i}{n_i} - \alpha - \beta \epsilon_i \right] dn_i = 0 \quad - (9)$$

Since the variations dn_i are independent of another. Hence $\ln \frac{n_i + g_i}{n_i} - \alpha - \beta \epsilon_i = 0 \quad - (10)$

whence $\ln \left[\frac{g_i}{n_i} + 1 \right] = \alpha + \beta \epsilon_i$

or $\frac{g_i}{n_i} + 1 = e^{\alpha + \beta \epsilon_i}$

$$n_i = g_i / [e^{\alpha + \beta \epsilon_i} - 1]$$

The above eqn. is the expression for the most probable distribution of N particles among the various energy levels according to the Bose-Einstein statistics.

Fermi-Dirac Statistics

Consider that the n_i particles are distributed among the g_i states ($n_i < g_i$) where g_i is the degeneracy of the i th energy level.

Imagine that the particles are distinguishable. This implies that the first particle may be placed in any one of the g_i states and for each one of these choices, the second

particle may be placed in any one of the remaining $g_i - 1$ states and so on.

Thus, the number of arrangements is given by the expression $g_i! / (g_i - n_i)!$

Since, however, the particles are distinguishable, the expression has to be divided by the possible number of permutations of n_i particles, viz, $n_i!$. Hence the number of arrangements of n_i particles in the i th energy level is given by the expression $g_i! / n_i! (g_i - n_i)!$.

Thus, the thermodynamic probability W for the system of N particles (i.e. the number of ways of distributing N particles among the various energy levels) is given by

$$W = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!} \times \text{Constant} \quad \text{--- (1)}$$

Taking logarithms of both sides of eqn (1)

$$\ln W = \sum_i [\ln g_i! - \ln n_i! - \ln (g_i - n_i)!] + \text{Constant} \quad \text{(2)}$$

Assuming that n_i , g_i and $(g_i - n_i)$ are very large we can apply Stirling's approximation, obtaining

$$\ln W = \sum_i -n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i) + g_i \ln g_i + \text{Constant} \quad \text{(3)}$$

Thus for the most probable state

$$d \ln w = \sum [-\ln n_i + \ln(g_i - n_i)] dn_i = 0 \quad \text{or}$$
$$\sum [\ln(g_i - n_i) / n_i] dn_i = 0 \quad (4)$$

Since $N = \sum n_i = \text{constant}$ and $U = \sum n_i \epsilon_i = \text{constant}$
hence $dN = \sum dn_i = 0$ and $dU = \sum \epsilon_i dn_i = 0$ — (5)

Applying Lagrange's method of Undetermined multipliers, we obtain

$$\sum [\ln(g_i - n_i) / n_i - \alpha - \beta \epsilon_i] dn_i = 0 \quad (7)$$

Since the variations are independent of one another, hence

$$\ln(g_i - n_i) / n_i - \alpha - \beta \epsilon_i = 0 \quad \text{or}$$

$$\ln(g_i / n_i - 1) = \alpha + \beta \epsilon_i = 0 \quad \text{or}$$

$$(g_i / n_i) - 1 = e^{\alpha + \beta \epsilon_i} = 0 \quad (8)$$

$$n_i = g_i / \exp(\alpha + \beta \epsilon_i) + 1 \quad (9)$$

The above eqn is the expression for the most probable distribution of N particles among energy levels according to the Fermi-Dirac statistics.

Partition Function

The most general form of Boltzmann distribution law is

$$\frac{n_i}{N} = \frac{g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}} \quad (1)$$

The term β in the above eqn is a measure of temperature of the system, whereas the quantity $\sum_i g_i \exp(-\beta E_i)$ appearing in the denominator is a characteristic of the system. It is called the partition function q . The exponential $g_i \exp(-\beta E_i)$ indicates the occupation number (n_i) as a fraction of total number N of the particles. The sum $\sum g_i e^{-\beta E_i}$ being only a normalizing factor. i.e.

$$q = \sum_i g_i e^{-\beta E_i} = g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2} + g_3 e^{-\beta E_3} + \dots + g_i e^{-\beta E_i} \quad (2)$$

The first term relating to level E_1 , the second to E_2 and so on. The equivalent way of defining q may be, as the sum of terms over all accessible quantum (i.e.) $q = \sum_{\text{quantum states}} e^{-\beta E_i}$ — (3)

The significance of the partition function q is understood by expressing the distribution law as

$$\frac{n_i}{N} = \frac{e^{-\beta E_i}}{q} \quad (4)$$

if i denotes the lowest energy state so that $E_i = 0$, then eqn (4) becomes

$$\frac{n_i}{N} = \frac{1}{q} \quad (5)$$

The partition function is defined as a reciprocal of the fraction of particles occupying the lowest energy state (may be called as ground state). Alternatively, it may be defined as the ratio of the total number of particles in a system to the number of particles in the lowest energy state.

Important aspects of partition function.

- a) It indicates the mode of distribution of particles in various energy states.
- b) It is a pure number, hence dimensionless quantity.
- c) q may ^{also} be considered a measure of the extent to which molecules may escape from the ground state.
- d) It can be applied to ^{any} system of physical states.