

STATISTICAL THERMODYNAMICS

4.1 INTRODUCTION

In chemical or classical thermodynamics one deals with macroscopic properties of the system without regarding the contribution of individual particles (atoms, ions, molecules). Typical macroscopic properties are entropy, internal energy, heat capacity, surface tension, viscosity, dielectric constant, electrical conductivity and chemical reaction rate. In quantum mechanics one deals with microscopic properties like position, velocity, orientation, distribution, energy, intermolecular forces, molecular masses, intramolecular forces etc. of microsystems, associated with microscopic particles like electrons, protons, neutrons etc.

In classical thermodynamics one discusses thermodynamic principles without considering any model or theory on microscopic level. This treatment has both advantages and disadvantages. The advantage includes is that its prediction can be extended to as complex systems as biological process even though the exact mechanism may not be known. The disadvantage of classical thermodynamics is that we are not certain about the rate and mechanism of the process under investigation. The relevant information can be provided if we know the link between classical thermodynamics and quantum mechanics.

The link between classical thermodynamics and quantum mechanics is provided by the statistical thermodynamics or statistical mechanics or chemical statistics, who aim is to deduce the macroscopic properties of matter from the properties of the molecules composing the system. Thus, the subject of study of link between thermodynamics and quantum mechanics is called statistical thermodynamics or statistical mechanics. Quantum mechanics provides information about the energy of a molecular system, statistical mechanics tells us about the possible arrangement of the energy among various molecules of the system and introduces the concept of probability and partition functions. Statistical thermodynamics deals with the relationship between the probability, partition and thermodynamics properties. This chapter is restricted to equilibrium statistical thermodynamics which deals with systems in thermodynamic equilibrium. Nonequilibrium statistical thermodynamics deals with transport properties and chemical reaction rates. The methods of statistical mechanics were first developed by Maxwell and Boltzmann (1860 - 1900). Major advances in the theory and calculation were made by Gibbs (1902) and Einstein (1902 - 1904). With the development of methods of quantum theory some modification in Boltzmann original ideas were introduced by Bose (Indian physicist) and Einstein (Germany) and Fermi (Italian Physicist) and Dirac (English Physicist)

Statistical thermodynamics has been applied successfully to relate the microscopic properties of the individual molecules (i.e. moment of inertia, dipole moment etc) with macroscopic properties (molar heat capacity, polarization etc.) of a system having a large number of molecules. In statistical thermodynamic approach, the matter is pictured as composed of innumerable particles in motion. The motion of the particles is governed by the laws of dynamics and, in fact, subject to quantum mechanical principles. Even in the smallest system taken, the number of particles is so large that it is impossible to follow the behaviour of the system, particular, to ascertain what fraction of the molecules has a given energy. This chapter presents statistical methods are utilized to find out the properties of the system, particular, to ascertain what fraction of the molecules has a given energy. This chapter presents statistical mechanics using quantum mechanics and in a general form applicable to all forms of matter, not just gases. Most of this chapter is restricted to statistical mechanics of ideal gases.

Statistical thermodynamics, unlike kinetic theory, does not concern itself with detailed considerations of such things as collisions of molecules with one another or with a surface. Instead it takes advantage of the fact that molecules are very numerous and average properties of a large number of molecules can be calculated even in the absence of any information about specific molecules. Statistical methods can be applied not only to molecules, but to photons, to elastic waves of solids, and to more abstract entities of quantum mechanics called wave functions. We shall use the neutral term "particle" to designate any of these.

4.2 TERMINOLOGY USED IN STATISTICAL THERMODYNAMICS

Statistical thermodynamics deals with both the microscopic (molecular) and macroscopic level, and it is important to define basic terminology very clearly.

System and Particles

The world system in this chapter refers only to a macroscopic thermodynamic system. The fundamental microscopic entities that compose a system are called molecules or particles. Suppose we have a collection of particles, then each particle is termed as a system. However, in some cases, these entities are not actually molecules. For example, one can apply statistical methods to the conduction electrons in a metal or to the photons in electromagnetic radiation.

Phase Space

The state of a gas can be specified if we define the state of each molecule of the gas. The state of each molecule can be specified by defining its position and velocity, i.e., we must specify f -positional and f -velocity coordinates, when f is the number of degrees of freedom of molecule. Total degrees of freedom of the molecules are

$$f = 3 \times \text{No. of atoms in a molecule}$$

A phase space is a hypothetical space and can be imagined with $2f$ -axes. The state of a molecule can be represented by a point in this imaginary space.

$$\text{Minimum number of atoms in a molecule} = 1$$

$$\therefore \text{Minimum } f = 3$$

Then minimum axes = $2f = 2 \times 3 = 6$

Out of six coordinates, three will be position coordinates (x, y, z) and three will be velocity coordinates (v_x, v_y and v_z). Thus we may imagine a six dimensional space in which $d_x, d_y, d_z, dv_x, dv_y, dv_z$ is an element of the volume and the position of a point (molecule) in this imaginary space will be defined by a set of six coordinates namely, x, y, z, v_x, v_y and v_z . Here phase space is an imaginary six-dimensional space.

Unit Cell or Cell

The entire phase space is divided into a number of very small elements of volume. An element of volume in phase space is termed as a cell or unit cell. In the cell the points represent the molecules. All cells have virtually same internal and external configurations and same energy.

Occupation Number

It is the number of systems in that particular state. The set of occupation number is called a distribution.

Microstate and Macrostate

Let us divide the phase space into cells numbered 1, 2, 3 etc. A microstate of the system may be defined by the specification of six coordinates x, y, z, v_x, v_y, v_z of each molecule of the system within the limits of the dimensions of the cell in which its reproductive point lies. This means that in order to define a microstate we must specify the place of each molecule within the limits d_x, d_y and d_z and the magnitude and direction of each molecule within the limits dv_x, dv_y and dv_z . In other words we may say that, in order to define microstate we must state to which cell each molecule of the system belongs temporarily. Hence we can say that each distribution of the molecules among the permissible unit cells corresponding to the same macroscopic state of the system, is called a microscopic state.

Cell 1	a, b, c	$N_1 = 3$
Cell 2	d, e	$N_2 = 2$
Cell 3	f	$N_3 = 1$
Cell 4	g, h	$N_4 = 2$

Fig. 4.1 Distribution between microstate and macrostate

A macroscopic state of a system may be defined by the specification of the number of molecules or phase points in each cell of the phase space, such as n_1 molecules in cell 1, n_2 molecules in cell 2 and n_3 molecules in cell 3. The distribution between microstate and macrostate is illustrated in Fig.4.1. The cells in the phase are numbered 1, 2, 3 etc., and the phase points are lettered, a, b, c etc. A particular

microstate is specified by stating that phase points a, b, c are in cell 1, phase points d, e are in cell 2 and so on. The corresponding macrostate is specified by giving the total number N_1 of the phase points in cell 1, the number N_2 in cell 2 and so on.

The term macrostate means the thermodynamic state of a system. The term microstate means the quantum state of a system. Because of any large number of particles in a system, there are a huge number of different microstates that are compatible with a given macrostate.

Assembly and Ensemble

A number of N identical entities is called an assembly. An ensemble is defined as a collection of a very large number of assemblies which are independent of each other but which have been made macroscopically as identical as possible. By being independent of one another, it means that in calculating the possible energy states of an assembly, one should not take into account interaction between the assembly of interest and any of other assemblies. By macroscopically identical, it means that each assembly is characterized by the same value of same set of macroscopic parameters which uniquely define the equilibrium state of the assembly.

The Canonical Ensemble

It is defined as a collection of a large number of independent assemblies, having the same temperature, T , volume V , and number of identical system N . As all the assemblies possess the same temperature, T , it means that one could bring them in thermal contact with each other and also a large heat reservoir at the same temperature, T . Thus, in canonical ensemble, systems can exchange energy but not particles. Fig. 4.2 illustrates the canonical ensemble in which the individual assemblies are separated by rigid, impermeable but conducting 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

Fig. 4.2 Illustration of the canonical ensemble

Probability

The probability of a state of a system is defined as the number of configurations leading to that particular state divided by the total number of configurations possibly available to the system. For example, tossing of a coin. It can either show head or tail. Thus, total number of possible configurations of the state of the coin is two, i.e., one head and one tail. The probability of showing head in one out of two configurations is, i.e. $1/2$, similarly the probability of showing tail is $1/2$.

Thermodynamic Probability

The thermodynamic probability of a system is equal to the number of ways of realizing the distribution. The symbol of thermodynamic probability is W . Here, it is

to be noted that thermodynamic probability is not equivalent to probability since former is always equal to or greater than unity whereas the latter is always less than one.

Statistical Weight Factor

It is the degree of degeneracy of a particular energy level, and is equal to energy states of an energy level. It is usually denoted by 'g'.

Partition Function

In quantum mechanics, all the information about microscopic system i.e., position, velocity, momentum, energy etc. is stored in wave function Ψ . In statistical mechanics also, there, exists a function which contains all information about macroscopic system, that function is known as *partition function*. It is a dimensionless quantity. It summarizes in a convenient mathematical form as to how the energy of a system of molecules is partitioned among the molecules. The value of the partition function depends upon the molar mass, the temperature, the molar volume, the inter nuclear distance, the molecular motion and the inter nuclear forces. The partition function provides a bridge to link the microscopic properties of individual molecules (their discrete energy levels, moment of inertia etc.) with the macroscopic properties (like entropy, heat capacity etc.) of a system containing a large number of molecules. it is denoted by the symbol Q .

Probability Theorems

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

$$N!$$

- (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,

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

By definition of $N!$ one has

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

Therefore,

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

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

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

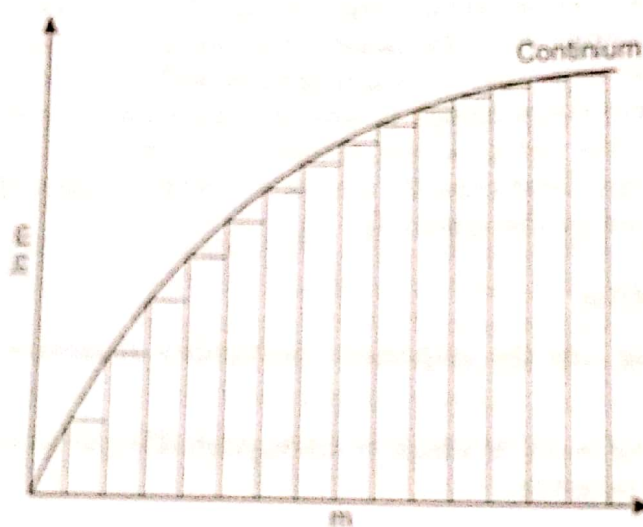


Fig. 4.3 A plot of $\ln m$ versus m

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

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

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

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

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

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

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

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 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 $N = n_0 + n_1 + n_2 + \dots + n_i = \sum n_i$ (4.2)

and $E = n_0\epsilon_0 + n_1\epsilon_1 + n_2\epsilon_2 + \dots + n_i\epsilon_i = \sum n_i\epsilon_i$ (4.3)

Equation (4.2) and (4.3) represent the total number of particles and total energy of the system. Since the numbers $n_0, n_1, n_2 \dots$ 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 microstates) in which N particles can be arranged in these energy levels, is equal to the number of permutations of N things in groups $n_0, n_1, n_2 \dots n_i$. Thus the probability is expressed as

$$W = \frac{N!}{n_0! n_1! n_2! \dots n_i!}$$
 (4.4)

Here $N!$ is N factorial as in written as

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

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

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

$$\ln W = \ln N! - \sum \ln n_i!$$
 (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 $n_i!$ is also large, and here,

$$\begin{aligned} \sum \ln n_i! &= \sum n_i \ln n_i - \sum n_i \\ &= \sum n_i \ln n_i - N \end{aligned} \quad \dots (4.6)$$

On substituting these values in equation (4.5)

$$\begin{aligned} \ln W &= N \ln N - N - \sum n_i \ln n_i + N \\ \ln W &= N \ln N - \sum n_i \ln n_i \end{aligned} \quad \dots (4.7)$$

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

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

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

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

Example 4.2

Calculate the number of ways of distributing four molecules in four energy levels so as there are 2 molecules in the level ϵ_0 , 1 molecules in the ϵ_1 level, 1 molecule in ϵ_2 level and zero molecule in the ϵ_3 energy level i.e.,

$$n_0 = 2, n_1 = 1, n_2 = 1, n_3 = 0$$

Solution

The probability equation gives

$$W = \frac{4!}{2! 1! 1! 0!} \quad (\because N = 4)$$

$$= \frac{4 \times 3 \times 2 \times 1}{(2 \times 1) \times 1 \times 1 \times 1} = 12$$

4.3 THE BOLZMANN DISTRIBUTION LAW

The Boltzmann distribution law or Maxwell-Boltzmann distribution law (also known as the most probable distribution) is very important in statistical thermodynamics. It deals with the probability distribution of the total energy among the particles or molecules of the system, and leads to the introduction of the concept of partition function, a very important quantity used in statistical thermodynamics. This law fails, however, to harmonize with quantum theory and to account for the behaviour of the particles at high densities.

Consider a system of constant energy E composed of N identical particles at temperature T and possess the following characteristics.

- (i) Each particle is distinguishable from the other.
- (ii) Particles do not attract or repel each other.
- (iii) No restriction on assigning various energy levels to the particles is being imposed.
- (iv) The particles are localized.

These assumption lead to the classical Boltzmann distribution law. Now we shall consider the distribution of the total energy E among the various energy levels say $\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_n$ of the N particles. As we know that each possible may exist in a number of allowable energy levels, the total number of particles N may be assigned to the energy levels in such a way that n_1 particles be present in energy level ϵ_1, n_2 in the level with ϵ_2, n_3 in the level with ϵ_3 and so on. Irrespective of this distribution, the total number of particles and the energy of the system remain constant i.e.,

$$N = \sum n_i \quad \text{and} \quad \sum n_i \epsilon_i$$

Such summations are to be carried over all energy levels. The number of ways in which N particles can be put in these energy level is the number of permutations of N things in groups of n_1, n_2, n_3, \dots , i.e.,

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

On taking logarithm of both sides of above equation

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

$$\ln W = \ln N! - \sum \ln n_i! \quad \dots (4.5)$$

Stirling's approximation can be used for factorials of large number as N is also very large

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

Under these conditions n_i is also large, and have

$$\begin{aligned} \sum \ln n_i! &= \sum n_i \ln n_i - \sum n_i \\ &= \sum n_i \ln n_i - N \end{aligned} \quad \dots (4.6)$$

On substituting these values in equation (4.5)

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

$$\ln W = N \ln N - \sum n_i \ln n_i \quad \dots (4.7)$$

The most probable distribution of particles or molecules in a system is the one for which W is maximum. Hence for these condition δW and $\delta \ln W$ will have to be zero

$$\delta W = \delta \ln W = 0 \quad \dots (4.8)$$

On differentiating equation (4.7), the result is

$$\delta \ln W = - \delta \sum n_i \ln n_i \quad [\delta(N) = \delta(\text{constant}) = 0]$$

and now placing the condition of equation (4.8), we get

$$\delta[\sum n_i \ln n_i] = 0 \quad \dots (4.9)$$

$$\text{or} \quad \sum \left[n_i \cdot \frac{\delta n_i}{n_i} + \ln n_i \delta n_i \right] = 0 \quad \left(\because \delta \ln n_i = \frac{1}{n_i} \delta n_i \right)$$

$$\text{or} \quad \sum [\delta n_i + \ln n_i \delta n_i] = 0$$

$$\text{or} \quad \sum [1 + \ln n_i] \delta n_i = 0 \quad \dots (4.10)$$

We must remember that for the given molecular system, the total energy E and number of particles N remains constant.

$$N = \sum n_i = \text{constant} \quad \therefore \delta N = \sum \delta n_i = 0 \quad \dots (4.11)$$

$$E = \sum n_i \epsilon_i = \text{constant} \quad \therefore \delta E = \sum \epsilon_i \delta n_i = 0 \quad \dots (4.12)$$

Multiplying equations (4.11) and (4.12) by two arbitrary constant α' and β respectively and adding to equation (4.10), we get

$$\sum [(1 + \ln n_i) \delta n_i + \delta n_i \alpha' + \epsilon_i \delta n_i \beta] = 0$$

$$\text{or} \quad \sum [(1 + \ln n_i) + \alpha' + \epsilon_i \beta] \delta n_i = 0$$

$$\text{let} \quad 1 + \alpha' = \alpha$$

$$\sum [\ln n_i + \alpha + \beta \epsilon_i] \delta n_i = 0 \quad \dots (4.13)$$

As the variables $\delta n_1, \delta n_2, \delta n_3 \dots$, are independent of each other so that the equation (4.13) is to hold good, then each term in the summation must be zero

$$\ln n_i + \alpha + \beta \epsilon_i = 0 \quad (\because \delta \neq 0)$$

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

$$\text{or} \quad n_i = e^{-(\alpha + \beta \epsilon_i)} \quad \dots (4.14)$$

$$\text{or} \quad n_i = e^{-\alpha} \cdot e^{-\beta \epsilon_i} \quad \dots (4.15)$$

This is one form of celebrated Boltzmann distribution law. The value of $e^{-\alpha}$ can be found by using the following equation

$$N = \sum n_i = e^{-\alpha} \cdot \sum e^{-\beta \epsilon_i}$$

$$e^{-\alpha} = \frac{N}{\sum e^{-\beta \epsilon_i}} \quad \dots\dots (4.16)$$

Substitute this value in equation (4.15)

$$n_i = \frac{N}{\sum e^{-\beta \epsilon_i}} e^{-\beta \epsilon_i} \quad \dots\dots (4.17)$$

The constant β can be identified by equating the internal energy of a monatomic gas with that obtained from the kinetic theory of gases.

We may express the distribution law in terms of quantum energy levels instead of energy states. For an ideal gas it can be shown that

$$\beta = \frac{1}{kT} \quad \dots\dots (4.18)$$

where k is the Boltzmann constant. Inserting equation (4.18) into equation (4.17), one can have

$$n_i = \frac{N e^{-\epsilon_i/kT}}{\sum e^{-\epsilon_i/kT}}$$

or

$$\frac{n_i}{N} = \frac{e^{-\epsilon_i/kT}}{\sum e^{-\epsilon_i/kT}} \quad \dots\dots (4.19)$$

In equation (4.19) it is assumed that each energy level is non-degenerate, i.e., it is composed of only a single level. However, when such is not the case, then each level must be assigned a statistical g_i and Eq. (4.19) becomes

$$\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}} \quad \dots\dots (4.20)$$

or

$$\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{Q} \quad \dots\dots (4.21)$$

where $Q = \sum g_i e^{-\epsilon_i/kT}$ is called the partition function of the system. Equation (4.21) is known as Boltzmann distribution law and it gives at any temperature T , the fraction of total number of particles in a system which in the most probable or equilibrium state will possess the energy ϵ_i . Hence this equation gives the most probable distribution of the particles in a system among all the allowable energy levels. Equation (4.21) is also known as Boltzmann statistics.

Limitations

Boltzmann distribution law gives the most probable distribution of molecules or particles in a system among all allowable energy levels. However, this law has the following limitations.

- (i) This law is only an approximation and is valid for gases at comparatively low density.
- (ii) In the metallic conductors electrons are confined within the volume of the metal just as gaseous molecules are confined within the containing vessel. When Boltzmann law is applied to an electron gas, discrepancies appear between these and observations.
- (iii) In a similar manner as in (ii), the photon gas presents another difficulty. This law predicts a continuous number of photons per unit range of frequency as the latter increases, whereas the actual distribution is given by the well known law of Planck, exhibits a minimum.

4.6 PARTITION FUNCTION

Statistical thermodynamic analysis is facilitated through the use of partition function. This great analytical tool is defined as

$$Q = \sum g_i e^{-\epsilon_i/kT} \quad \dots (4.22)$$

where g_i is the statistical weight factor and is equal to the degree of degeneracy, i.e., the number of super-imposed energy levels, k is the Boltzmann constant, ϵ_i is the energy of quantum state in excess of the lowest possible value and T is the absolute temperature. In equation (4.22) summation is taken over all integral of i from zero to infinity corresponding to all possible energy states of the molecules. For general purpose, it is required to measure energy level, relative to the ground state. Therefore, equation (4.22) becomes

$$Q = \sum_{i=0}^{\infty} g_i e^{-\epsilon_i/kT} \quad \dots (4.23)$$

Equation (4.23) gives the definition of partition function. It is defined as the sum of the probability factors for different energy states or levels. It can also be stated as the way in which the energy of a system is partitioned among the molecules constituting the system.

Physical Significance of Partition Function

Partition function is a dimensionless quantity and summarizes in convenient mathematical form, the way in which the energy of a system of molecules is partitioned among the different energy states. Its value depends on the molecular weight, the temperature, the molecular volume, the inter nuclear distances, the molecular motion, and the intermolecular forces. The partition function provides the most convenient way for linking the microscopic properties of individual molecules (e.g., their discrete energy levels, moment of inertia, dipole moments) with macroscopic properties (such as molar heat capacity, entropy and polarization). It reflects the diversity of energy states of molecules of a system.

According to Boltzmann distribution law

$$\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}}$$

The ratio of number of particles in any state of energy ϵ_i relative to that in state of energy ϵ_0 follows from above equation.

$$\frac{n_i}{n_0} = \frac{g_i e^{-\epsilon_i/kT}}{g_0 e^{-\epsilon_0/kT}}$$

or
$$\frac{n_i}{n_0} = \frac{g_i}{g_0} e^{-(\epsilon_i - \epsilon_0)/kT} \dots\dots (4.24)$$

For computational purposes, it is convenient to consider $\epsilon_0 = 0$ and to take all ϵ_i values relative to this ground state. On this basis equation (4.24) becomes-

$$\frac{n_i}{n_0} = \frac{g_i}{g_0} e^{-\epsilon_i/kT}$$

or
$$n_i = \frac{n_0}{g_0} g_i e^{-\epsilon_i/kT} \dots\dots (4.25)$$

where n_i is the number of molecules in the i th state, n_0 , the number of molecules in the zero energy level, g_i and g_0 represent the degeneracies in the i th and zero levels respectively.

Where $\epsilon_0 = 0$, then $g_0 = 1$, therefore one can write

$$\frac{n_i}{n_0} = g_i e^{-\epsilon_i/kT}$$

or
$$n_i = n_0 g_i e^{-\epsilon_i/kT} \dots\dots (4.26)$$

Now
$$N = \sum n_i$$

Substituting the value of n_i from equation (4.26) in above equation, we get

$$N = \sum n_0 g_i e^{-\epsilon_i/kT}$$

or
$$N = n_0 g_0 e^0 + n_0 g_1 e^{-\epsilon_1/kT} + n_0 g_2 e^{-\epsilon_2/kT} + \dots$$

or
$$N = n_0 [g_0 + g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT}]$$

or
$$N = n_0 \sum g_i e^{-\epsilon_i/kT} \quad (g_0 = 1)$$

or
$$N = n_0 Q$$

or
$$Q = N/n_0 \dots\dots (4.27)$$

From equation (4.27) it follows that the partition function (Q) may be defined as the ratio of the number of particles or molecules in the i th levels to that of zero level. At absolute zero,

$$N \rightarrow n_0 \quad \text{and} \quad Q \rightarrow 1 \quad \text{as} \quad T \rightarrow 0$$

Hence the value of partition function increases with temperature. As the temperature is raised, there are more molecules in the highest energy levels and few number of molecules in zero energy level. Therefore, the partition function is larger at higher temperature.

Factorization of Partition Function

Partition function is defined as

$$Q = \sum g_i e^{-\epsilon_i/kT} \quad \dots\dots (4.28)$$

The energy ϵ of a molecule is the sum of contribution from the different modes of motion like translational, rotational, vibrational, electronic, etc. If we assume that energy associated with any one mode of behaviour is independent of all other modes, then we can define energy by

$$E = E_T + E_r + E_v + E_c$$

and $g_i = g_T + g_r + g_v + g_c$

where E_T , E_r , E_v and E_c are translation, rotational, vibrational and electronic contribution, respectively and g_T , g_r , g_v and g_c are degeneracy of translational, vibrational, rotational and electronic energy level, respectively. So equation (4.28) can be written as

$$Q = \sum (g_T g_r g_v g_c) e^{-(\epsilon_t + \epsilon_r + \epsilon_v + \epsilon_c)/kT}$$

or $Q = \sum g_T e^{-\epsilon_t/kT} + \sum g_r e^{-\epsilon_r/kT} + \sum g_v e^{-\epsilon_v/kT} + \sum g_c e^{-\epsilon_c/kT}$

or $Q = Q_T \cdot Q_r \cdot Q_v \cdot Q_c \quad \dots\dots (4.29)$

Equation (4.29) is known as *multiplication theorem* or *factorization of partition function*. This factorization means that we can investigate each contribution separately. From equation (4.29), it follows that the net partition function is equal to be the product of the separate partition functions in respect of different types of energy independently associated with molecules.

4.7 TRANSLATIONAL PARTITION FUNCTION

By definition partition function is given by,

$$Q = \sum g_i e^{-\epsilon_i/kT}$$

For translational energy, as the translational energy levels are non-degenerate, e.g., $g_i = 1$, translational partition function can be written as

$$Q_t = \sum e^{-\epsilon_t/kT} \quad \dots\dots (4.30)$$

The Schrodinger wave equation when solved for the particle moving in a rectangular box of dimension a , b , and c gives the expression for translational energy as

$$E_t = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad \dots (4.31)$$

where n_x , n_y and n_z are principal quantum numbers determining the possible value of translational energy of particle along x , y and z directions, respectively.

From equations (4.30) and (4.31) we can write

$$Q_t = \sum e^{-n_x^2 h^2/8ma^2kT} \cdot e^{-n_y^2 h^2/8mb^2kT} \cdot e^{-n_z^2 h^2/8mc^2kT}$$

$$Q_t = Q_x \cdot Q_y \cdot Q_z \quad \dots (4.32)$$

If we consider the motion in x -axis only, then corresponding partition function (Q_x) can be written as

$$Q_x = \sum e^{-n_x^2 h^2/8ma^2kT} \quad \dots (4.33)$$

From equation (4.33), the Q_x can be evaluated. The increment of energy between adjacent energy levels of translation is so small that the translational partition function can be evaluated by integration over all quantum states (from 0 to ∞). In other words, the translational energy levels are closely spaced that the variation of energy may be taken to be continuous and the summation in equation (4.33) is replaced by integration.

Here

$$Q_x = \int_0^{\infty} e^{-n_x^2 h^2/8ma^2kT} \quad \dots (4.34)$$

Putting $l = \frac{h^2}{8ma^2kT}$

$$Q_x = \int_0^{\infty} e^{-ln_x^2} \cdot dn_x \quad \dots (4.35)$$

Using standard integrals

$$\int_0^{\infty} e^{-lx^2} \cdot dx = \frac{1}{2} \sqrt{\frac{\pi}{l}}$$

Equation (4.35) reduces to

$$Q_x = \frac{1}{2} \pi^{1/2} \left(\frac{8ma^2kT}{h^2} \right)^{1/2} \quad \therefore \sqrt{8} = 2\sqrt{2}$$

$$Q_x = (2 \pi m kT)^{1/2} \cdot \frac{a}{h} \quad \dots (4.36)$$

Similarly, for motion along y and z directions, we have

$$Q_y = (2\pi mkT)^{1/2} \cdot \frac{b}{h} \quad \dots (4.37)$$

$$Q_z = (2\pi mkT)^{1/2} \cdot \frac{c}{h} \quad \dots (4.38)$$

Substituting the value of Q_x , Q_y and Q_z into equation (4.32), we can write

$$Q_t = Q_x \cdot Q_y \cdot Q_z = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot abc$$

$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot V \quad \dots (4.39)$$

or
$$Q_t = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V \quad \dots (4.40)$$

where V is the volume of the container. Equations (4.39) and (4.40) give the expression for the translational partition function of a single molecule.

Example 4.3

Calculate the translational partition function of H_2 confined to a 100 cm^3 vessel at 298 K .

Solution

$$\text{Mass of } H_2 \text{ molecule} = \frac{2.016 \times 10^{-3} \text{ kg}}{6.02 \times 10^{23}} = 3.348 \times 10^{-27}$$

$$V = 100 \text{ cm}^3 = 10^{-4} \text{ m}^3$$

$$k = 1.381 \times 10^{-27} \text{ Jk}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$Q_t = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V$$

$$Q_L = \left(\frac{2 \times 3.14 \times (3.348 \times 10^{-27}) \times (1.381 \times 10^{-23}) \times 298}{(6.626 \times 10^{-34})^2} \right)^{3/2} \times 10^{-4}$$

$$Q_t = (1.97 \times 10^{20})^{3/2} \times 10^{-4}$$

$$Q_t = 2.769 \times 10^{26}$$

Thus about 10^{26} quantum states or levels are thermally accessible even at room temperature for H_2 molecule.

4.8 ROTATIONAL PARTITION FUNCTION

From quantum mechanical principles, the rotational energy for a diatomic molecule in the J^{th} state is given by

$$E_r = J(J + 1) \frac{h^2}{8\pi^2 I} \quad \dots (4.41)$$

where I is the moment of inertia of the diatomic molecule and J is the rotational quantum number, $J = 0, 1, 2, 3, \dots$. As we know that the rotational energy at the J^{th} level is degenerate in $(2J + 1)$ ways, the value of statistical weight is given by

$$g_r = (2J + 1)$$

The expression for rotational partition function for a single molecule is

$$Q_r = \sum g_r e^{-\epsilon_r/kT}$$

$$Q_r = \sum (2J + 1) e^{-J(J+1)h^2/8\pi^2IkT} \quad \dots (4.42)$$

Rotational energy levels are sufficiently closely spaced, i.e., variation in energy between two adjacent rotational energy levels can be taken as continuous. Hence, it is possible to replace summation in quantum (4.42) by integration from $J = 0$ to $J = \alpha$, giving

$$Q_r = \int_0^\alpha (2J + 1) \cdot e^{-J(J+1)h^2/8\pi^2IkT} \cdot dJ \quad \dots (4.43)$$

or
$$Q_r = \int_0^\alpha (2J + 1) e^{-J(J+1)\alpha} \cdot dJ \quad \dots (4.44)$$

where
$$\alpha = \frac{h^2}{8\pi^2 IkT}$$

Again put $Z = J(J + 1)$

$$\therefore dZ = (2J + 1) dJ \quad \dots (4.45)$$

Combining equation (4.44) and (4.45)

$$Q_r = \int_0^\infty e^{-z\alpha} dz = \frac{1}{\alpha} \quad \dots (4.46)$$

Putting value of α into equation (4.46) we get

$$Q_r = \frac{8\pi^2 IkT}{h^2} \quad \dots (4.47)$$

The equation (4.47) is only true for heteronuclear diatomic molecules like NO, HCl etc. But in case of homonuclear linear molecules like O_2 , N_2 and also $O=C=O$, $H-C \equiv C-H$, only one half of the rotational terms will be present. This effect reduces Q_r to one half of the value in equation (4.47). In order to avoid

these complications, a symmetry number (σ) is introduced. It is the number of equivalent (or indistinguishable) molecular orientations. Thus the rotational position function for any linear molecule, becomes

$$Q_r = \frac{8\pi^2 I kT}{\sigma h^2} \quad \dots (4.48)$$

This is general equation for rotational position function of a linear (homonuclear or heteronuclear) diatomic molecule. The value of σ for homo nuclear (or symmetrical) linear molecule is 2 because end to end rotation yields an equivalent orientation. On the other hand, the value of σ for heteronuclear (or unsymmetrical) linear molecule such as $O=C=O$, $O=C=S$ etc. is 1.

Example 4.4

Calculate the rotational partition function for H_2 at 300 K. Moment of inertia for H_2 is $4.59 \times 10^{-47} \text{ kg} \cdot \text{m}^2$, symmetry number $\sigma = 2$.

Solution

$$Q_r = \frac{8\pi^2 I kT}{\sigma h^2}$$

$$Q_r = \frac{8 \times (3.1416)^2 \times 4.59 \times 10^{-47} \times 1.38 \times 10^{-23} \times 300}{2 \times (6.62 \times 10^{-34})^2}$$

$$= 1.71$$

4.9 VIBRATIONAL PARTITION FUNCTION

The partition function for vibrational energy of a diatomic molecule is given by

$$Q_v = \sum g_v e^{-\epsilon_v / kT} \quad \dots (4.49)$$

As the statistical weight of each vibrational level is unity, equation (4.49) becomes

$$Q_v = \sum e^{-\epsilon_v / kT} \quad \dots (4.50)$$

According to wave mechanics, the vibrational energy of an harmonic oscillator is given by

$$\epsilon_v = \left(v + \frac{1}{2} \right) h\nu \quad \dots (4.51)$$

where ν is the fundamental frequency of oscillation and v is the vibrational quantum number having value 0, 1, 2, 3, In the expression for partition function, ϵ_v refers to the energy of vibrational state in excess to the ground state energy. For the present case the lowest or ground state energy corresponds to $v = 0$ and is given as

$$\epsilon_{v=0} = \frac{1}{2} h\nu \quad \dots\dots (4.52)$$

Therefore, the expression for energy appearing in the position function is

$$\epsilon_v = \left(v + \frac{1}{2} \right) h\nu - \frac{1}{2} h\nu = v h\nu \quad \dots\dots (4.53)$$

$$Q_v = \sum e^{-v h\nu / kT}$$

Putting $x = h\nu / kT$

$$Q_v = \sum e^{-vx} \quad \dots\dots (4.54)$$

vibrational energy levels are not closely spaced, so summation is not replaced by integration. Since v can take values from 0, 1, 2, 3, ..., so

$$Q_v = 1 + e^{-x} + e^{-2x} + \dots$$

$$Q_v = 1 + e^{-x} + e^{-2x} + \dots$$

$$Q_v = 1 + (e^{-x})^1 + (e^{-x})^2 + \dots$$

This series can be recognized as the geometrical series of common ratio $r = e^{-x}$. Thus we have

$$Q_v = \frac{1}{1 - e^{-x}} \cdot \frac{1}{1 - e^{-h\nu/kT}}$$

$$\text{or } Q_v = (1 - e^{-h\nu/kT})^{-1} \quad \dots\dots (4.55)$$

For most diatomic molecules, at ordinary temperatures, the value of Q_v is nearly unity, because $h\nu$ is appreciably greater than kT .

4.10 ELECTRONIC PARTITION FUNCTION

Many monatomic substances as well as a few polyatomic molecules, possess multiple electronic ground state. In most of these cases in their normal state, there are two or more different electronic levels whose energies are so close that they may be assigned a single energy level with a statistical weight factor greater than unity. In addition to such levels, there may be excited electronic states whose energies may be much greater than that of the ground state. As we increase the temperature, such excited states become more and more occupied. In such cases the electronic partition function is greater than unity and varies with the temperature. The electronic partition function is given by

$$Q_e = \sum g_e e^{-\epsilon_e / kT} \quad \dots\dots (4.56)$$

where g_e is the statistical weight factor of each electronic level, normal or excited and is equal to $(2J + 1)$, where J is the total angular momentum number in the given state and ϵ_e is the energy in the electronic state, in excess of the lowest state. Thus,

$$Q_e = \sum (2J + 1) e^{-\epsilon_e/kT} \quad \dots (4.57)$$

In the general state, the energy is zero, i.e., $\epsilon_e = 0$, thus equation (4.57) becomes

$$Q_e = \sum (2J + 1)^0 = \sum 2J + 1 \quad \dots (4.58)$$

From equation (4.58), it follows that contribution of this state to the electronic partition function is thus $(2J + 1)$. The degeneracy of electronic ground state of atoms is given in Table 4.1.

Table 4.1 Ground State Electronic Degeneracy

Atom	H	He	Na	Ca
Term/Symbol	$^2S_{1/2}$	1S_0	$^2S_{1/2}$	1S_0
$g_0 = 2J + 1$	2	1	2	1

The term symbol $^{2s+1}L_J$ is a short hand notation for all angular momenta of an atom, viz., the spin angular momentum S , the orbital angular momentum L , and the total angular momentum J . Mathematically

$$S = \sum S_i; L = \sum L_i \text{ and } J = L + S \text{ (for atoms with } z \leq 30)$$

where S_i and L_i are the spins and the orbital angular momenta of individual electrons in the atom respectively. The ground state of electronic states of free atoms are generally degenerate-for hydrogen atom with electronic configuration $1S^1$, spin $S = 1/2$ and $L = 0$ so $J = L + S = 1/2$ and $g_0 = 2 \times 1/2 + 1 = 2$. For helium atom with electronic configuration $1S^2$, spin $S = 1/2 - 1/2 = 0$ and $L = 0$, so $J = 0$ and hence $g_0 = 1$. Thus for H-atom, $Q_e = 2$ and for He atom $Q_e = 1$.

4.11 PARTITION FUNCTION AND THERMODYNAMIC FUNCTIONS

We will now utilize the partition function and the distribution law to evaluate various thermodynamic functions including the equilibrium constant in chemical reactions.

(i) Internal Energy

Consider a system consisting of non-interacting molecules (e.g., ideal gas), the total energy of the system is given by

$$E = \sum n_i \epsilon_i \quad \dots (4.3)$$

According to Maxwell-Boltzmann law

$$n_i = g_i e^{-\alpha} e^{-\epsilon_i/kT}$$

Taking summation on both sides

$$\sum n_i = e^{-\alpha} \sum g_i e^{-\epsilon_i/kT} \quad \dots (4.59)$$

$$N = e^{-\alpha} Q$$

$$e^{-\alpha} = \frac{N}{Q}$$

..... (4.60)

Putting the value of Σn_i from equation (4.59) into equation (4.3)

$$E = e^{-\alpha} \Sigma g_i e^{-\epsilon_i/kT} \epsilon_i$$

..... (4.61)

Putting the value of $e^{-\alpha}$ from equation (4.60) into equation (4.61) we get

$$E = \frac{N}{Q} \Sigma g_i e^{-\epsilon_i/kT} \epsilon_i$$

$$\frac{EQ}{N} = \Sigma g_i e^{-\epsilon_i/kT} \epsilon_i$$

..... (4.62)

Now $Q = \Sigma g_i e^{-\epsilon_i/kT}$

Differentiate the above equation with respect to T at constant V, we get

$$\left(\frac{\partial Q}{\partial T} \right)_v = \frac{1}{kT^2} \Sigma g_i e^{-\epsilon_i/kT} \epsilon_i$$

or $kT^2 \left(\frac{\partial Q}{\partial T} \right)_v = \Sigma g_i e^{-\epsilon_i/kT} \epsilon_i$ (4.63)

Comparing equation (4.62) and (4.63)

$$\frac{EQ}{N} = kT^2 \left(\frac{\partial Q}{\partial T} \right)_v$$

$$E = \frac{NkT^2}{Q} \left(\frac{\partial Q}{\partial T} \right)_v$$

$$E = NkT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v$$

$$\therefore \frac{1}{Q} \left(\frac{\partial Q}{\partial T} \right)_v = \left(\frac{\partial \ln Q}{\partial T} \right)_v$$

For one mole of a gas $N = N_A =$ Avogadro number

$$E = N_A k T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v$$

or $E = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v$ (4.64)

$$\therefore R = N_A k$$

Thus, equation (4.64) is the relation between energy (E) and partition function of the system.

(ii) Heat Capacity

Heat capacity at constant volume is given by

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v \quad \dots (4.65)$$

and $E = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v$

Putting the value of E in equation (4.65), we get

$$C_v = \frac{\partial}{\partial T} \left[RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v \right]$$

$$C_v = R \left[2T \left(\frac{\partial \ln Q}{\partial T} \right)_v + T^2 \left(\frac{\partial^2 \ln Q}{\partial T^2} \right)_v \right] \quad \dots (4.66)$$

Equation (4.66) is the relation between the molar heat capacity (C_v) at constant volume of an ideal gas and partition function.

We also know

$$C_p = C_v + R$$

$$\therefore C_p = R + \frac{\partial}{\partial T} \left[RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v \right] \quad \dots (4.67)$$

Equation (4.67) is the relation between molar heat capacity (C_p) at constant pressure of an ideal gas and partition function.

(iii) Entropy

According to Boltzmann distribution law

$$\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{Q} \quad \dots (4.21)$$

where n_i = Number of molecules having energy ϵ_i

N = Total number of molecules in the system

g_i = Statistical weight factor for energy level i

Taking logarithm of above equation on both sides

$$\ln n_i = \ln N + \ln g_i - \epsilon_i/kT - \ln Q$$

Multiplying the above equation by n_i both sides, we get

$$n_i \ln n_i = n_i \ln N + n_i \ln g_i - \frac{n_i \epsilon_i}{kT} - n_i \ln Q$$

or $n_i \ln n_i = (n_i \ln N - n_i \ln Q) + n_i \ln g_i - \frac{n_i \epsilon_i}{kT}$

$$\text{or } n_i \ln n_i = n_i \ln \left(\frac{N}{Q} \right) + n_i \ln g_i - \frac{n_i \epsilon_i}{kT}$$

By taking summation over all the energy-level (or quantum states) we get

$$\sum n_i \ln n_i = \sum n_i \ln \left(\frac{N}{Q} \right) + \sum n_i \ln g_i - \frac{\sum n_i \epsilon_i}{kT}$$

$$\text{or } \sum n_i \ln n_i = - \sum n_i \ln \left(\frac{Q}{N} \right) + \sum n_i \ln g_i - \frac{\sum n_i \epsilon_i}{kT} \quad \dots (4.68)$$

But according to modified definition of probability

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

Taking logarithm on both sides of the equation

$$\ln W = (n_0 \ln g_0 - \ln n_0!) + (n_1 \ln g_1 - \ln n_1!) + \dots + (n_i \ln g_i - \ln n_i!)$$

$$\ln W = (n_0 \ln g_0 + n_1 \ln g_1 + \dots + n_i \ln g_i) - (\ln n_0! + \ln n_1! + \dots + \ln n_i!)$$

$$\ln W = \sum n_i \ln g_i - \sum \ln n_i! \quad \dots (4.69)$$

For any large values of n_i , as in the case with molecules, Stirling's formula may be used

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

$$\therefore \sum \ln n_i! = \sum n_i \ln n_i - \sum n_i$$

$$\text{Here } \sum \ln n_i! = \sum n_i \ln n_i - N \quad \dots (4.70)$$

From equation (4.69) and (4.70)

$$\ln W = \sum n_i \ln g_i - \sum n_i \ln n_i + N$$

$$\text{or } \sum n_i \ln n_i = - \ln W + \sum n_i \ln g_i + N \quad \dots (4.71)$$

From equations (4.68) and (4.71)

$$- \ln W + \sum n_i \ln g_i + N = - \sum n_i \ln \left(\frac{Q}{N} \right) + \sum n_i \ln g_i - \frac{\sum n_i \epsilon_i}{kT}$$

$$\ln W = \sum n_i \ln \left(\frac{Q}{N} \right) + \frac{\sum n_i \epsilon_i}{kT} + N \quad \dots (4.72)$$

Since in the summation $\sum n_i \ln \left(\frac{Q}{N} \right)$, the factor $\ln \left(\frac{Q}{N} \right)$ will come with each term

$$\text{hence } \sum n_i \ln \left(\frac{Q}{N} \right) = \ln \left(\frac{Q}{N} \right) \sum n_i$$

$$\text{But } N = \sum n_i$$

$$\text{Hence } \sum n_i \ln \left(\frac{Q}{N} \right) = N \ln \left(\frac{Q}{N} \right) \quad \dots\dots (4.73)$$

Similarly

$$\sum \left(\frac{n_i \epsilon_i}{kT} \right) = \frac{1}{kT} \sum n_i \epsilon_i \quad \dots\dots (4.74)$$

From equation (4.72), (4.73) and (4.74), we get

$$\ln W = N \ln \left(\frac{Q}{N} \right) + \frac{1}{kT} \sum n_i \epsilon_i + N \quad \dots\dots (4.75)$$

$$\text{But } E = NkT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v \quad \therefore \sum n_i \epsilon_i = E$$

$$\ln W = N \ln \left(\frac{Q}{N} \right) + \frac{NkT^2}{kT} \left(\frac{\partial \ln Q}{\partial T} \right)_v + N$$

$$\ln W = N \ln \left(\frac{Q}{N} \right) + NT \left(\frac{\partial \ln Q}{\partial T} \right)_v + N$$

Taking N s common

$$\ln W = N \left[\ln \left(\frac{Q}{N} \right) + T \left(\frac{\partial \ln Q}{\partial T} \right)_v + 1 \right] \quad \dots\dots (4.76)$$

According to Boltzmann-Planck's equation

$$S = k \ln W$$

$$\ln W = \frac{S}{k}$$

Here equation (4.76) becomes

$$\frac{S}{k} = N \left[\ln \left(\frac{Q}{N} \right) + T \left(\frac{\partial \ln Q}{\partial T} \right)_v + 1 \right]$$

$$S = kN \left[\ln \left(\frac{Q}{N} \right) + T \left(\frac{\partial \ln Q}{\partial T} \right)_v + 1 \right] \quad \dots\dots (4.77)$$

Equation (4.77) is the relation between entropy and partition function for any number of molecules in the system. For one mole of an ideal gas; i.e., $N = N_A$, we get

$$S = kN_A \left[\ln \left(\frac{Q}{N} \right) + T \left(\frac{\partial \ln Q}{\partial T} \right)_v + 1 \right]$$

$$S = R \left[\ln \left(\frac{Q}{N} \right) + T \left(\frac{\partial \ln Q}{\partial T} \right)_v + 1 \right]$$

$$S = R \ln \left(\frac{Q}{N} \right) + RT \left(\frac{\partial \ln Q}{\partial T} \right)_v + R \quad \dots\dots (4.78)$$

$\therefore R = kN_A$, where N_A is the Avogadro number. Equation (4.78) applies to one mole of an ideal gas.

(iv) Work Function

We know that,

$$\Lambda = E - TS$$

Substituting the value of E and S in equation (4.79), we get

$$\Lambda = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v - RT \left[\ln \left(\frac{Q}{N} \right) + T \left(\frac{\partial \ln Q}{\partial T} \right)_v + 1 \right]$$

$$\Lambda = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v - RT \ln \left(\frac{Q}{N} \right) - RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v - RT$$

$$\Lambda = -RT \ln \left(\frac{Q}{N} \right) - RT$$

$$\Lambda = -RT \left[\ln \left(\frac{Q}{N} \right) + 1 \right] \quad \dots (4.80)$$

Equation (4.80) is the relation between work function and partition function.

(v) Pressure

Rearranging equation (4.80)

$$\Lambda = -RT \left[\ln \left(\frac{Q}{N} \right) + 1 \right]$$

$$\Lambda = -RT [\ln Q - \ln N + 1]$$

$$\Lambda = -RT \ln Q + RT \ln N - RT$$

which on differentiation w.r.t. V at constant temperature T , yields

$$\left(\frac{\partial \Lambda}{\partial V} \right)_T = -RT \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad \dots (4.81)$$

We also know that $d\Lambda = -Pdv - SdT$. Differentiate it w.r.t. at constant T , we get

$$\therefore \left(\frac{\partial \Lambda}{\partial V} \right)_T = -P \quad \dots (4.82)$$

$$\therefore -P = -RT \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

$$\text{or } P = RT \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad \dots (4.83)$$

Equation (4.83) is the relation between pressure and partition function.

(vi) Gibb's Free Energy

$$F = H - TS$$

$$F = E + PV - TS$$

$$F = A + PV \quad \dots (4.84)$$

$$F = -kT^2 \left[\ln \left(\frac{Q}{N} \right) + 1 \right] + kT^2 V \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

$$F = -kT^2 \ln \left(\frac{Q}{N} \right) - kT^2 + kT^2 V \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

$$F = -kT^2 \left[\ln \left(\frac{Q}{N} \right) + 1 - V \left(\frac{\partial \ln Q}{\partial V} \right)_T \right]$$

$$F = -kT^2 \left[\ln \left(\frac{Q}{N} \right) + 1 - V \left(\frac{\partial \ln Q}{\partial V} \right)_T \right] \quad \dots\dots (4.85)$$

Equation (4.85) is the relation between Gibbs's free energy and partition function.

(vii) Heat Content

We know that

$$H = E + PV \quad \dots\dots (4.84)$$

Substituting the value of E and P into equation (4.84), we get

$$H = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V + VRT^2 \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

$$H = RT^2 \left[T \left(\frac{\partial \ln Q}{\partial T} \right)_V + V \left(\frac{\partial \ln Q}{\partial V} \right)_T \right]$$

$$H = RT^2 \left[T \left(\frac{\partial \ln Q}{\partial T} \right)_V + \left(\frac{\partial \ln Q}{\partial V} \right)_T \right] \quad \dots\dots (4.85)$$

Equation (4.85) is the relation between heat constant and partition function.

4.12 ENTROPY AND PROBABILITY (STATISTICAL TREATMENT OF ENTROPY)

Second law of thermodynamics has a statistical nature. At constant energy and volume a system is in the equilibrium when its entropy is maximum. Again, the thermodynamic probability is also a maximum. It means that the exist some relationship between entropy and thermodynamic probability of the system. Boltzmann showed that entropy and thermodynamic probability are related by

$$S = k \ln W \quad \dots\dots (4.86)$$

where k is a Boltzmann constant $= k = R/N_A$. R is the gas constant and N_A is the Avogadro number. Entropy is an additive property, where as probability is multiplicative.

Consider two systems of identical particles for which the entropies are S_1 and S_2 and probabilities W_1 and W_2 . When these systems are combined the total entropy is $S = S_1 + S_2$, while the total probability becomes $W_1 W_2$ and this

$$S = k(W_1 W_2)$$

$$S = k \ln W = k \ln W_1 + k \ln W_2$$

The function which satisfies this relation must be logarithmic, namely:

$$S = K_1 \ln W + K_2 \tag{4.67}$$

where K_1 and K_2 are the constants to be evaluated. If equation (4.67) has general validity it should also apply to a perfect crystal at 0K. For such a crystal $S = 0$ by arrangement for it and $W = 1$. On inserting these values in equation (4.67), we see that $K_2 = 0$, and here

$$S = K_1 \ln W \tag{4.68}$$

The nature of K_1 can be found by using equation (4.68) to calculate the translational entropy of an ideal gas. Using equation for thermodynamic probability (W) with modification like insertion of statistical weights and quantum statistical recognition that identical particles are actually indistinguishable

$$W = \frac{(g_0)^{n_0}}{n_0!} \cdot \frac{(g_1)^{n_1}}{n_1!} \dots \frac{(g_i)^{n_i}}{n_i!} \tag{4.69}$$

Taking log on both sides and using Stirling's formula we get

$$\ln W = \sum n_i \ln g_i - \sum n_i \ln n_i + N \tag{4.71}$$

According to most probable distribution

$$n_i = \frac{N g_i e^{-\epsilon_i/kT}}{Q}$$

For translation motion, the above equation takes the form

$$n_i = \frac{N g_i e^{-\epsilon_i/kT}}{Q_i} \tag{4.80}$$

Substituting the value of n_i into (4.71), we get

$$\ln W = \sum n_i \ln g_i - \sum n_i \ln \left[\left(\frac{N}{Q_i} \right) g_i e^{-\epsilon_i/kT} \right] + N$$

$$\ln W = \sum n_i \ln g_i - \sum n_i \ln \left(\frac{N}{Q_i} \right) - \sum n_i \ln g_i + \frac{\sum n_i \epsilon_i}{kT} + N$$

$$\ln W = - \sum n_i \ln \left(\frac{N}{Q_i} \right) + \frac{1}{kT} \sum n_i \epsilon_i + N \tag{4.90}$$

But $\sum n_i \epsilon_i = E_1 - E_{00} = RT^2 \left(\frac{\partial \ln Q_i}{\partial T} \right)_V$

Putting this value in equation (4.90) we get

$$\ln W = - \sum n_i \ln \left(\frac{N}{Q_i} \right) + \frac{RT}{k} \left(\frac{\partial \ln Q_t}{\partial T} \right)_V + N$$

$$\ln W = N \ln \left(\frac{Q_t}{N} \right) + \frac{RT}{k} \left(\frac{\partial \ln Q_t}{\partial T} \right)_V + N \quad \dots (4.91)$$

Multiplying equation (4.91) both sides by Boltzmann constant k , we get

$$k \ln W = Nk \ln \left(\frac{Q_t}{N} \right) + RT \left(\frac{\partial \ln Q_t}{\partial T} \right)_V + kN$$

For one mole of an ideal gas

$$k \ln W = N_A k \ln \left(\frac{Q_t}{N} \right) + RT \left(\frac{\partial \ln Q_t}{\partial T} \right)_V + N_A k$$

$$k \ln W = R \ln \left(\frac{Q_t}{N} \right) + RT \left(\frac{\partial \ln Q_t}{\partial T} \right)_V + R \quad \dots (4.92)$$

$$k \ln W = S_t \quad (4.93)$$

$$\therefore S_t = R \ln \left(\frac{Q_t}{N} \right) + RT \left(\frac{\partial \ln Q_t}{\partial T} \right)_V + R \quad \dots (4.93)$$

Therefore,

$$K_1 = k \text{ This equation (4.93) becomes}$$

$$S = k \ln W \quad (4.94)$$

Equation (4.94) represents the general relationship between entropy and probability.

4.13 STATISTICAL EXPRESSION FOR EQUILIBRIUM CONSTANT

The free energy of a mole of an ideal gas can be related to the partition function. Since the methods of deriving partition functions for various types of molecules are available, at least in principle, it should be possible to calculate the free energies of the substances taking part in a chemical reaction. The free energy ΔF° , for reactants and products in the standard state, is related to the equilibrium constant K of the reaction by the equation

$$- \Delta F^\circ = RT \ln K \quad \dots (4.95)$$

Hence, there should be a close connection between partition function of the substances involved in the reaction and equilibrium constant of the system.

For translation

$$F_t^0 = H_t^0 - S_t^0$$

$$F_t^0 = E_t^0 + RT - TS_t^0 \quad \dots (4.96)$$

$$\Delta E_t = RT^2 \left(\frac{\partial \ln Q_t^0}{\partial T} \right)_V$$

$$\text{and } S_t = RT \left(\frac{\partial \ln Q_t^0}{\partial T} \right)_V + R \ln \left(\frac{Q_t^0}{N} \right) + R$$

Substituting the value of E_t and S_t into equation (4.96) we get

$$F_t^0 = RT^2 \left(\frac{\partial \ln Q_t^0}{\partial T} \right)_V + RT - T \left[RT \left(\frac{\partial \ln Q_t^0}{\partial T} \right)_V + R \ln \left(\frac{Q_t^0}{N} \right) + R \right]$$

$$F_t^0 = RT^2 \left(\frac{\partial \ln Q_t^0}{\partial T} \right)_V + RT - RT^2 \left(\frac{\partial \ln Q_t^0}{\partial T} \right)_V - RT \ln \left(\frac{Q_t^0}{N} \right) - RT$$

$$F_t^0 = -RT \ln \left(\frac{Q_t^0}{N} \right)$$

..... (4.97)

where Q_t^0 is the partition function for the standard state, i.e., $P = 1$ atm. Using the equation (4.97) for translation and equation $F_i^0 - E_{o(i)}^0 = -RT \ln Q_i^0$ for standard force energies of rotation, vibration and electronic excitation, we obtain for the total F^0 of an ideal gas

$$F^0 = F_t^0 + F_r^0 + F_v^0 + F_e^0$$

$$F^0 = -RT \ln \left(\frac{Q_t^0}{N} \right) + E_{t(r)}^0 - RT \ln Q_r^0 + E_{o(v)}^0 - RT \ln Q_v^0 + E_{o(e)}^0 - RT \ln Q_e^0$$

$$F^0 = E_{o(r)}^0 + E_{o(v)}^0 + E_{o(e)}^0 - RT \ln \left(\frac{Q_t^0}{N} \right) - RT \ln Q_r^0 - RT \ln Q_v^0 - RT \ln Q_e^0$$

$$F^0 = E_o^0 - RT \ln \left(\frac{Q_t^0 Q_r^0 Q_v^0 Q_e^0}{N} \right)$$

$$F^0 = E_o^0 - RT \ln \left(\frac{Q^0}{N} \right) \quad \text{..... (4.98)}$$

where E_o^0 is the total standard state energy of the gas and Q^0 the total partition function.

Equation (4.98) can be used to derive the relation between the equilibrium constant of a reaction and Q^0 's of the substances involved. Consider a general reaction involving ideal gases such as



In terms of equation (4.98) for F^0 per mole, the equation for ΔF^0 of the reaction will be

$$\Delta F^0 = [(cE_{OC}^0 + dE_{OD}^0) - (aE_{OA}^0 + bE_{OB}^0)] - RT \ln \frac{(Q_C^0/N)^c (Q_D^0/N)^d}{(Q_A^0/N)^a (Q_B^0/N)^b}$$

$$\Delta F^0 = \Delta E_o^0 - RT \ln \frac{(Q_C^0/N)^c (Q_D^0/N)^d}{(Q_A^0/N)^a (Q_B^0/N)^b} \quad \dots (4.99)$$

where ΔE_o^0 is the standard energy change of the reaction at $T = 0$.

But $\Delta F^0 = -RT \ln K_p$, therefore,

$$-RT \ln K_p = \Delta E_o^0 - RT \ln \frac{(Q_C^0/N)^c (Q_D^0/N)^d}{(Q_A^0/N)^a (Q_B^0/N)^b}$$

$$\text{or } \ln K_p = \frac{-\Delta E_o^0}{RT} + \ln \frac{(Q_C^0/N)^c (Q_D^0/N)^d}{(Q_A^0/N)^a (Q_B^0/N)^b}$$

$$\text{or } K_p = e^{-\Delta E_o^0/RT} + \frac{(Q_C^0/N)^c (Q_D^0/N)^d}{(Q_A^0/N)^a (Q_B^0/N)^b} \quad \dots (4.100)$$

Equation (4.100) shows that K_p of a reaction can be calculated from the total partition functions of the reactants and products where ΔE_o^0 is available. The latter can be obtained for some reactions from spectroscopic data, while for others, spectroscopic data are required to obtain ΔE_o^0 .

4.14 THE SACKURE-TETRODE EQUATION

In case of monatomic gases, rotational and vibrational motions and hence energies are absent. The internal energy in case of monatomic molecules will be only due to its translational energy, i.e.,

$$E_t = RT^2 \left(\frac{\partial \ln Q_t}{\partial T} \right)_V \quad \dots (4.64)$$

where Q_t (for a monatomic molecule) is the translational partition function and its value is given by

$$Q_t = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V \quad \dots (4.40)$$

On taking logarithm of equation (4.40) as both sides

$$\ln Q_t = \ln \left(\frac{2\pi m k}{h^2} \right)^{3/2} V + \frac{3}{2} \ln T$$

Differentiate this equation w.r.t. temperature under constant volume

$$\left(\frac{\partial \ln Q_t}{\partial T} \right)_V = \frac{3}{2T}$$

Substituting this value in equation (4.64), we get

$$E_t = RT^2 \times \frac{3}{2T} = \frac{3}{2} RT \quad \dots (4.101)$$

Further, we know that molar entropy of an ideal monatomic gas is given by

$$S_t = R \ln \left(\frac{Q_t}{N} \right) + RT \left(\frac{\partial \ln Q_t}{\partial T} \right)_V + R \quad \dots (4.78)$$

$$S_t = R \ln \left(\frac{Q_t}{N} \right) + RT \times \frac{3}{2T} + R$$

$$S_t = R \ln \left(\frac{Q_t}{N} \right) + \frac{3}{2} R + R$$

$$S_t = R \ln \left(\frac{Q_t}{N} \right) + \frac{5}{2} R$$

Substituting the value of Q_t in above equation and taking R as common

$$S_t = R \left[\ln \frac{(2\pi m k T)^{3/2}}{N h^3} V + \frac{5}{2} \right] \quad \dots (4.102)$$

For ideal gases $PV = nRT$

For one mole of an ideal gas

$$PV = RT$$

or
$$V = \frac{RT}{P}$$

$$S_t = R \left[\ln \frac{(2\pi m k T)^{3/2}}{N h^3 P} \cdot RT + \frac{5}{2} \right] \quad \dots (4.103)$$

Equation (4.102) and (4.103) are the alternative forms of Sackur-Tetrode equation.

4.15 THE BOSE-EINSTEIN STATISTICS

Boltzmann statistics predicts the behaviour and proportion of the substances. It satisfactorily explains the behaviour of gases and crystalline solids at low density. But the results obtained in many cases show deviations, number of complications and shortcomings. These are

- (i) At low densities of gases, Boltzmann distribution law shows little agreement with the experimental facts.
- (ii) Energy of a photon is proportional to its frequency. From classical statistics we have the energy distribution which gives us the distribution of frequency. As the frequency increases, there should be a continuous increase in the number of photons per unit range of frequency. But we know that there is a maximum in the actual distribution.
- (iii) Boltzmann statistics again fails to explain the behaviour of electron gas in metallic conductors.

All these anomalies called for a modification of classical statistics. This led to the formation of a new chemical statistics called Quantum statistics, in two different ways namely (1) Bose-Einstein and (2) Fermi-Dirac statistics.

The limitations of the Boltzmann distribution law have been removed by S.N. Bose and A. Einstein (1924-25). In Bose-Einstein statistics, we deal with the distribution of indistinguishable particles among the energy levels or states with no limit on the number of particles in any of the energy state.

Let the particles be lettered a, b, c , etc. (Although the particles are distinguishable, we assign letters to them temporarily as an aid in explaining how the thermodynamic probability is computed). In some one arrangement of the particles in an arbitrary level i , we might have particles a and b in state (1) of that level, particle c in state (2), no particle in state (3), particles d, e, f in state (4), and so on. The distribution of the particles among states can be represented by the following mixed sequence of numbers and letters.

$$[1(a, b)] [(2) c] [(3)] [(4) def]$$

where in each bracketed group three letters following a number designate the particles in the state corresponding to the number.

If the number and letters are arranged in all possible sequences, each sequence will represent a possible distribution of particles among states, provided the sequence begins with a number. There are different g_i ways in which the sequences can begin, one for each of the g_i states, and in each of these sequences the remaining $(g_i + n_i - 1)$ numbers and letters can be arranged in any order.

The number of different sequences in which n distinguishable particles can be arranged is $n!$ (n factorial). As an example, the three letters a, b , and c can be arranged in the following sequences.

$$abc, acb, bea, bac, cba, cab$$

There are six possible sequences equal to $3!$ (3 factorial).

The number of different possible sequences or ways of the $(g_i + n_i - 1)$ numbers and letters is therefore,

$$(g_i + n_i - 1)! \quad \dots\dots (4.104)$$

and the total number of possible sequences of g_i numbers and n_i letter is

$$g_i [(g_i + n_i - 1)!] \quad \dots\dots (4.105)$$

Although each of these sequences represents a possible distribution of particles among energy states, many of them represent the same distribution. For example, one of the possible sequences will be the following.

$$[(3)] [(1) ab] [(4) def] [(2) c]$$

This is the same distribution as the previous one, since the same states contain the same particles and it differs only in the bracketed groups appear in a different sequence. There are g_i groups in the sequence, one for each state, so the number of different sequences of groups is $g_i!$ and we must divide (4.105) by $g_i!$ to avoid connecting the same distribution more than once.

Also since the particles are actually indistinguishable, a different sequence of letters such as

$$[(1) ca] [(2) c] [(3)] [(4) def]$$

also represents the same distribution as first one because any given state contains the same number of particles. The n_i letters can be arranged in $n_i!$ different ways, so (4.105) must also be divided by $n_i!$. Hence the actual number in which the n_i particles may be allocated in g_i states is given by

$$W = g_i \frac{[(g_i + n_i - 1)!]}{g_i! n_i!}$$

which may be more conveniently written as

$$W = \frac{(g_i + n_i - 1)!}{(g_i - 1)! n_i!} \quad g_i! = g_i(g - 1)!$$

The product over all the energy levels or states is the thermodynamic probability

$$W = \prod \frac{(g_i + n_i - 1)!}{(g_i - 1)! n_i!} \quad \dots\dots (4.106)$$

where the symbol Π means that one is to form the product of all terms following it, for all values of i . It corresponds to the symbol Σ for the sum of the series of the terms.

The system to which B.E. statistics is applicable is found to have the characteristics of $g_i \geq 1$. In such situation, the number 1 appearing in the numerator and denominator of thermodynamic probability (Eq. 4.106) can be neglected. The expression is reduced to

$$W = \Pi \frac{(g_i + n_i)!}{g_i! n_i!} \quad \dots\dots (4.107)$$

The expression for $\ln W$ becomes

$$\ln W = \Sigma [\ln(g_i + n_i)! - \ln g_i! - \ln n_i!] \quad \dots\dots (4.108)$$

For a system containing very large number of g_i and n_i , one can use Stirling's approximation to eliminate factorials. Here we get

$$\begin{aligned} \ln W &= \Sigma [(g_i + n_i) \ln(g_i + n_i) - (g_i + n_i) - g_i \ln g_i + g_i - n_i \ln n_i + n_i] \\ \ln W &= \Sigma (g_i + n_i) \ln (g_i + n_i) - g_i \ln g_i - n_i \ln n_i \quad \dots\dots (4.109) \end{aligned}$$

The condition of maximizing $\ln W$ is

$$\delta \ln W = \Sigma \left(\frac{\partial \ln W}{\partial n_i} \right) \delta n_i = 0 \quad \dots\dots (4.109)$$

Now

$$\begin{aligned} \frac{\partial \ln W}{\partial n_i} &= \ln (g_i + n_i) + 1 - \ln n_i - 1 \\ &= \ln (g_i + n_i) - \ln n_i \\ &= \ln \left(\frac{g_i + n_i}{n_i} \right) \end{aligned}$$

With this, equation (4.109) becomes

$$\delta \ln W = \Sigma \left[\ln \left(\frac{g_i + n_i}{n_i} \right) \delta n_i \right] = 0 \quad \dots\dots (4.110)$$

Since n_i and g_i for each quantum groups have been assumed to be large, the distribution of energy within a group may be regarded as virtually continuous, it is therefore, possible to write

$$\delta N = \Sigma \delta n_i = 0 \quad \text{and} \quad \delta E = \Sigma \epsilon_i \delta n_i = 0$$

Multiply these equations by two arbitrary constants, $-\alpha$ and $-\beta$ and adding these to equation (4.110), we get

$$\delta \ln W = \Sigma \left[\ln \left(\frac{g_i + n_i}{n_i} \right) - \alpha - \beta \epsilon_i \right] \delta n_i = 0$$

Since the variations δn_i are independent of one another.

$$\ln \left(\frac{g_i + n_i}{n_i} \right) - \alpha - \beta \epsilon_i = 0$$

or
$$\ln \frac{g_i + n_i}{n_i} = \alpha + \beta \epsilon_i$$

$$\ln \frac{g_i}{n_i} + 1 = \alpha + \beta \epsilon_i$$

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

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

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

$$n_i = \frac{g_i}{e^{\alpha} \cdot e^{\epsilon_i/kT} - 1} \quad \dots (4.101)$$

Equation (4.101) is the mathematical representation of Bose-Einstein statistics for the most probable distribution of the particles among various energy levels or states.

Derivation of Planck's equation for the distribution of energy in black body radiation is possible with the help of Bose-Einstein equation. It appears that radiation in thermal equilibrium in a box with walls, which do not absorb any of the radiation, may be treated as system of elements, viz. photons, obeying the Bose-Einstein statistics.

4.16 THE FERMI DIRAC STATISTICS

In the Boltzmann or in the Bose-Einstein statistics no restriction was made to the number of particles present in any energy state. But in applying Fermi-Dirac statistics to particles like electrons, the Pauli Exclusion principle is also taken into consideration, i.e., two electrons in an atom cannot possess the same energy state. In simple words, it implies that not more than one particle can be assigned to a particular energy state. Evidently, the number of particles n_i in any level cannot exceed the number of states g_i in that level. The latter condition requires that $n_i \leq g_i$.

To calculate the thermodynamic probability of a macrostate, we again temporarily assign numbers to the energy states of a level and letters to the particles, and we represent a possible arrangement of the particles in a level by a mixed sequence of numbers and letters. A possible arrangement might be the following

$$[(1) a] [(2) b] [(3)] [(4) c] [(5)] \dots$$

meaning that states (1), (2), (4), ... are occupying with their quota of one particle each while states (3), (5), ... are empty. For a given sequence of numbers, we first select some arbitrary sequence of letters. There are g_i possible locations for the first letter, following any one of g_i numbers. This leaves only $(g_i - 1)$ locations for the second particles, $(g_i - 2)$ locations for the third, down to $[g_i - (n_i - 1)]$ or $(g_i - n_i + 1)$ locations for the last letter. Since for any one location of any one letter we may have any one

the possible locations of each of others, the total number of ways in which a given sequence of n_i letters can be assigned to g_i states is

$$g_i(g_i - 1)(g_i - 2) \dots (g_i - n_i + 1) = \frac{g_i!}{(g_i - n_i)!} \quad \dots (4.102)$$

$$\text{Since } g_i! = g_i(g_i - 1)(g_i - 2) \dots (g_i - n_i + 1)(g_i - n_i)!$$

Because the particles are indistinguishable, a state is occupied regardless of the particular letter that follows the number representing the state. Since there are $n_i!$ different sequences in which n_i letters can be written, we must divide equation (4.102) by $n_i!$. Hence the number of ways of placing n_i indistinguishable particles in g_i distinguishable energy states with a limit of no more than one particle for energy state is

$$W = \frac{g_i!}{(g_i - n_i)! n_i!} \quad \dots (4.103)$$

The thermodynamic probability of a given distribution of particles over energy levels is the product of number of arrangements of all energy levels, i.e.,

$$W = \prod \frac{g_i!}{(g_i - n_i)! n_i!} \quad \dots (4.104)$$

Taking logarithm on both sides of above equation.

$$\ln W = \sum [\ln g_i! - \ln(g_i - n_i)! - \ln n_i!] \quad \dots (4.105)$$

For a system containing very large number of g_i and n_i , we can use Stirling's approximation to eliminate factorial.

$$\ln W = \sum [(g_i \ln g_i - g_i) - [(g_i - n_i) \ln(g_i - n_i) - (g_i - n_i)] - (n_i \ln n_i - n_i)]$$

$$\ln W = \sum [g_i \ln g_i - g_i - (g_i - n_i) \ln(g_i - n_i) + g_i - n_i - n_i \ln n_i + n_i]$$

$$\ln W = \sum [g_i \ln g_i - (g_i - n_i) \ln(g_i - n_i) - n_i \ln n_i]$$

The condition for maximizing $\ln W$ is

$$\delta \ln W = \sum \frac{\partial \ln W}{\partial n_i} \delta n_i = 0 \quad (4.106)$$

As g is constant

Now

$$\frac{\partial \ln W}{\partial n_i} = 0 - \{-\ln(g_i - n_i) - 1\} - \{\ln n_i + 1\}$$

$$= \ln(g_i - n_i) + 1 - \ln n_i - 1 = \ln(g_i - n_i) - \ln n_i$$

$$\frac{\partial \ln W}{\partial n_i} = \ln \frac{g_i - n_i}{n_i}$$

$$\delta \ln W = \sum \left[\ln \frac{g_i - n_i}{n_i} \delta n_i \right] = 0 \quad \dots (4.107)$$

Further we know that

$$\delta N = \sum \delta n_i = 0 \quad \text{and} \quad \delta E = \sum \epsilon_i \delta n_i = 0$$

Multiplying these equations by two arbitrary constants $-\alpha$ and $-\beta$ and these to equation (4.107) we get

$$\sum \left[\ln \left(\frac{g_i - n_i}{n_i} \right) - \alpha - \beta \epsilon_i \right] \delta n_i = 0$$

Now each term in the summation is independent and therefore, must be individually zero. Here

$$\ln \left(\frac{g_i - n_i}{n_i} \right) - \alpha - \beta \epsilon_i = 0$$

or
$$\ln \left(\frac{g_i - n_i}{n_i} \right) = \alpha + \beta \epsilon_i$$

$$\frac{g_i}{n_i} - \frac{n_i}{n_i} = e^\alpha \cdot e^{\beta \epsilon_i}$$

$$\frac{g_i}{n_i} - 1 = e^\alpha \cdot e^{\beta \epsilon_i}$$

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

$$n_i = \frac{g_i}{e^\alpha \cdot e^{\beta \epsilon_i} + 1} \quad \dots (4.108)$$

Equation (4.108) is the mathematical representation of the Fermi-Dirac statistics. Fermi-Dirac statistics can be used to explain gas degeneracy, electron gas in metals and thermionic emission of electrons from metals.

4.17 COMPARISON AMONGST BOLTZMANN, BOSE-EINSTEIN AND FERMI-DIRAC STATISTICS

For the purpose of comparison of the three forms of statistics, the essential equations obtained are as follows.

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

Maxwell-Boltzmann statistics

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

Bose-Einstein statistics

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

Fermi-Dirac statistics

It is important to note that if g_i/n_i is very large in comparison to unity ($n_i \gg 1$), one can neglect one in the denominators of Bose-Einstein and Fermi-Dirac statistic, because $g_i/n_i \approx g_i/n_i + 1 = \frac{g_i}{n_i} - 1$ and B.E. and F-D distribution take the form of Maxwell-Boltzmann distribution.

The various differences among the three statistics are as follows.

Maxwell-Boltzmann	Fermi-Dirac	Bose-Einstein
(i) Particles are distinguishable and only particles are taken into consideration	(i) Particles are indistinguishable and only quantum states are taken into consideration	(i) Particles are indistinguishable and only quantum states are taken into consideration
(ii) No restriction is put on the number of particles in a given state	(ii) Restriction is put in the number of particles in a given quantum state	(ii) No restriction is put on the number of particles in a given quantum state
(iii) Volume of state in six dimensional space is not known	(iii) Phase space is known	(iii) Phase space is known
(iv) Number of distinguishable ways may be given by $W = n! \left(\frac{\prod g_i^{n_i}}{n_i!} \right)$	(iv) Number of distinguishable ways may be given by $W = \prod \frac{g_i!}{(g_i - n_i)! n_i!}$	(iv) Number of distinguishable ways may be given by $W = \prod \frac{(n_i + g_i - 1) g_i!}{(g_i - 1)! n_i!}$
(v) Applicable to ideal gas molecules	(v) Applicable to electrons of high concentration	(v) Applicable to photons and α -particles
(vi) Particles obeying M.B. statistics are called Maxwellions or Boltzmannions	(vi) These are called Bosons.	(vi) These are called Fermions
	(vii) At higher temperature F.D. distribution approaches M.B. distribution	(vii) At higher temperature B.E. distribution approaches M.B. distribution.
(viii) $n_i = \frac{g_i}{e^{\alpha} e^{\beta \epsilon_i}}$	(viii) $n_i = \frac{g_i}{e^{\alpha} e^{\beta \epsilon_i} + 1}$	(viii) $n_i = \frac{g_i}{e^{\alpha} e^{\beta \epsilon_i} - 1}$