Physical Chemistry III

Unit – V

Statistical Thermodynamics

MACROSCOPIC AND MICROSCOPIC VIEWPOINT OF THERMODYNAMICS

The behaviour of a matter can be studied at two levels: a) Macroscopic. b) Microscopic.

Macroscopic (or classical thermodynamics):

- In this approach, a certain quantity of matter is considered, without taking into account the events occurring at the molecular level.
- This macroscopic approach to the study of thermodynamics **that does not require** knowledge of the behaviour of individual particles.
- Macroscopic thermodynamics is only concerned with the effects of the action of many molecules, and **these effects can be perceived by human senses.**
- The macroscopic observations are completely **independent** of the assumptions regarding the nature of matter.
- **Example:** A moving car, a falling stone from a cliff, etc.

Microscopic (or statistical thermodynamics):

- From the microscopic viewpoint, matter is composed of a large number of small molecules and atoms.
- This microscopic approach to the study of thermodynamics **that require** knowledge of the behaviour of individual particles.
- Microscopic thermodynamics is concerned with the effects of the action of many molecules, and **these effects cannot be perceived by human senses.**
- The microscopic observations are completely **dependent** on the assumptions regarding the nature of matter.
- **Example:** Individual molecules present in air, etc.

across them. Heat transfer then always occurs across a boundary not crossed by mass.

3 Microstates and Thermodynamic States

The state of a system is an important concept in thermodynamics and is defined as the complete set of all its properties which can change during various specified processes. The properties which comprise this set depend on the kinds of interactions which can take place both within the system and between the system and its surroundings. Any two systems, subject to the same group of processes, which have the same values of all properties in this set are then indistinguishable and we describe them as being in identical states.

A process in thermodynamics is defined as a method of operation in which specific quantities of heat and various types of work are transferred to or from the system to alter its state. As we pointed out, one of the objectives of thermodynamics is to relate these state changes in a system to the quantity of energy in the form of heat and work transferred across its boundaries.

In discussing non-thermodynamic processes, a system may be chosen as a single ultimate particle within a larger quantity of matter. In the absence of chemical reactions the only processes in which it can participate are transfers of kinetic or potential energy to or from the particle. In this case we would like to relate these energy transfers to changes in the microstate of the system. A microstate for this one-particle system is a set of coordinates in a multi-dimensional space indicating its position and its momenta in various vector directions. For example, a simple rigid spherical monatomic molecule would require a total of six such coordinates, three for its position and three for its momentum in order to completely define its microstate.

Now consider a system containing a large number of these ultimate particles. A microstate of this system is a set of all position and momentum values for all the particles. For example, if there were N rigid spherical molecules we would then need 6N coordinates to give a complete set of all the microstate properties and define a microstate for this system. In a multiparticle system a particular microstate exists only for an instant and is then replaced by another so that there is no experimental way to measure the set of positions and motions which comprise one microstate among the vast number of them which occur sequentially.

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With this common origin all the thermodynamic properties are therefore related to each other and we need to develop this relationship. The set of all the thermodynamic properties of a multiparticle system its temperature, pressure, volume, internal energy, etc., is defined as the thermodynamic state of this system.

An important aspect of this relationship between thermodynamic properties is the question of how many different thermodynamic properties of a given equilibrium system are independently variable. The number of these represents the smallest number of properties which must be specified in order to completely determine the entire thermodynamic state of the system. All other thermodynamic properties of this system are then fixed and can be calculated from these specified values. The number of these values which must be specified is called the variance or the degrees of freedom of the system.

5 *Microstate Driving Forces*

In order to explain the nature of driving forces, suppose we consider first a system defined as a single ultimate particle of a simple fluid, either a gas or a liquid. The system in this case is a rigid spherical mass with no possibilities for any internal changes and obeying Newtonian mechanics. In its surroundings are similar ultimate particles of this fluid. From a Newtonian point of view the mass of this system resists any change in its condition of motion and a specific change occurs only with the application of an external force to overcome the inertial resistance inherent in the mass. In the presence of mutual attraction and repulsion between this system and neighboring particles it may be considered to resist any displacement from a position in which this attraction and repulsion are balanced. In this situation a force vector directed toward the center of mass must be applied for a fixed time period to produce a change. This force is produced by the environment around the particle chosen as the system. The mechanism for its generation is by the action of neighboring particles in exerting attraction or repulsion or in colliding with the system. The scalar product of the vector force generated in this manner with other vectors which represent the resulting displacements in position and velocity of the system determine the energy added to the system when its velocity is increased, when its position is moved away from attracting neighbors, or when moved toward neighbors which repel it.

Since these displacements represent changes in microstate properties, we define the force vector producing them as a "microstate driving force." According to Newtonian mechanics this applied force is always opposed by an equal and opposite force representing the resistance of the system to change. Although mechanically we could position these two forces anywhere along their line of action, in terms of the system it is convenient to think of *them as opposing one another at the boundary of the system to describe energy in transition across it and then as opposing one another within the system when we describe this quantity of energy as the energy change of the system. An important characteristic of microstate driving forces is that they are true force vectors in the Newtonian sense and there is never a condition of unbalanced driving forces. This is not at all the case for what we will define as "thermodynamic driving forces" which are the agents of change for thermodynamic properties in multiparticle systems.*

18 Microstates in Isolated Systems

To explain why molecules always behave as though instructions of this type are completely ignored, imagine that we have a fantastic camera capable of making a multidimensional picture which could show at any instant where all the ultimate particles in the system are located and reveal every type of motion taking place, indicating its location, speed, and direction. Every type of distinguishably different action at any moment, the vibration, twisting, or stretching within molecules as well as their translational and rotational movements, would be identified in this manner for every molecule in the system. This picture would thus be a photograph of what we have defined as an instantaneous microstate of the system.

Now, instead of the instructions on the signs in Figure I, suppose we ask the molecules to do everything they can do by themselves in a rigid walled and isolated container where no external arranging or directing operations are possible. We will say, "Molecules, please begin now and arrange yourselves in a sequence of poses for pictures which will show every possible microstate which can exist in your system under the restrictions imposed by your own nature and the conditions of isolation in the container". If we expressed these restrictions as a list of rules to be followed in assigning molecules to *molecules which have the same mass, size, shape, and the same interaction potential with their neighbors can be individually rotated among the same sets of positions and motions with no change at all in the total energy, volume, or total number of molecules. However, other thermodynamic properties may be affected by this procedure depending on whether or not any of these molecules are in some way distinguishable among themselves. For example, suppose that in one of the containers half the molecules were isotopes of the other half, or were painted a different color, or had some other feature which distinguished them, but otherwise did not alter their identical individual properties and interactions. In this case, one of the thermodynamic properties, the change in the Helmholtz free energy measures the minimum work needed to make an isothermal separation of the molecules of each kind from an initially homogeneous mixture into two subregions of the container. If the molecules are distinguishable, this work exists and a change in Helmholtz free energy occurs. However, if they are not, then every arrangement of them is, according to all possible detection methods, at all times both separated to any degree and also simultaneously mixed to any degree. Consequently there is no work involved in obtaining any degree of separation or mixing and therefore no change in Helmholtz free energy as the molecules are interchanged with each other.*

We also note that, since no two molecules can have exactly the same position and motion, the number of permutations of an allowable assignment of N molecules to the same set of positions and motions in a particular molecular state is N! and this number is the same for all other microstates. Consequently no one microstateis given a greater number of ways of being produced than any other merely by permutation of the individual molecules among their assignments. For indistinguishable molecules then, in collecting all possible microstate pictures we shall omit all the duplicates caused by these permutations and consider them as one single state.

various positions and motions, the list would appear as follows:

1. *In distributing yourselves among the various positions and motions for each microstate picture, do not violate any energy conservation laws. Consequently, because you are in an isolated system the sum of all your individual translational, vibrational, and rotational kinetic energies plus all your intermolecular potential energies must always be the same and equal to the fixed total internal energy of the system.*
2. *Likewise, do not violate any mass conservation laws. There are to be no chemical reactions among you so that the total number of individual molecules assigned must always remain the same.*
3. *All of you must, of course, remain at all times within the container so the total volume in which you distribute yourselves must be constant.*
4. *Do not violate any laws of physics applicable to your particular molecular species. You must remember that no two of you can have all of your microstate position and motion characteristics exactly the same otherwise you would have to occupy the same space at the same time. Furthermore, do not be concerned that there might not be enough different microstates available for each of you to have a different one. Although you are numerous, the number of different possible position and motion values is even more numerous, so that there will never be enough of you to fill all of them and many possible values will be left unoccupied by a molecule in each picture for which you pose.*

19 Distinguishable and Indistinguishable Microstates

With these rules explained, the molecules then arrange themselves for their first microstate picture. Immediately, however, a question arises. The molecules could express this best by saying: "You asked us to show you every different way we could assign ourselves to all possible positions and motions, but there are billions and billions of us which are exactly alike and there is no way that you or your camera can distinguish one individual from another. Also, we are such a disorderly group that you won't be able to identify anyone by observing where he came from. As a result, we could make the very same pose for you again and again by rotating different individuals of the same species among the same particular set of positions and motions of a given overall microstate. If you photographed all of these you would have an enormous number of pictures all exactly alike. Do you want all of these?"

This requires some careful consideration. The reason we want the microstate pictures is to be able to explain the thermodynamic properties and behavior of the group. Any

Now that it is clearly understood that as a nonlocalized system only one assignment of individual molecules to each set of positions and motions is needed, the molecules then continue to pose for pictures of every distinguishable microstate possible in a rigid walled isolated system. We might at first worry that there could be an infinitely large number of these so that we would never see them all, but as a consequence of an important principle in physics, this number is finite although enormously large.

Because of the uncertainty principle there is a lower limit to the variations which can be detected between any two microstates, even when our camera is capable of the maximum possible resolution. This minimum arises because the product of the smallest difference in a position coordinate of a molecule and the smallest difference in a coordinate representing one of its momentum components forms a tiny area which represents the smallest detectable different detail which can distinguish a microstate from the one it most nearly resembles. This small area lies in a two-dimensional slice of the multi-dimensional picture of all the position and momentum coordinates for all the molecules in the system. According to our camera with the highest possible resolution, two such microstate pictures show no detectable difference unless one coordinate of a molecule's position and one coordinate of its momentum are altered enough to shift its microstate just outside this small area. Because this area is not zero but a small number, equal to Planck's constant, the difference between any two microstates cannot be made as small as we please. This means that there are then a finite number of different microstates for a system with a fixed total energy, volume, and number of molecules.[4] *Thus cheered by the fact that there is indeed an end to the process, we continue until we have photographed all possible different microstates which accompany the assigned total internal energy, volume, and number of molecules in the system.*[5] *We then count the number of these states and represent it by the symbol* $\boldsymbol{\Omega}$.

7.a. The Statistical Method

In thermodynamics the equilibrium properties of macroscopic systems are defined in terms of observable parameters like pressure, volume, etc. These properties can be experimentally determined by suitable measurements on macroscopic systems. However, the observable properties of a macroscopic system (the properties of the total bulk or bulk properties) are the result of the contributions of its microscopic constituents, atoms, molecules or ions.

It should be possible to calculate macroscopic properties of a system from a suitable summation of the properties of microscopic constituents. This is precisely the aim of statistical mechanics. Statistical thermodynamics is concerned with the calculation of quantities such as heat capacity, entropy, etc. in terms of atomic and molecular parameters.

Atoms and molecules being so small, it is generally not possible to keep track of the very large number of atoms and molecules constituting a macroscopic system. One can obtain information about individual atoms or molecules by solving quantum mechanical equations and obtaining wave functions or by using spectroscopic techniques of various kinds. Any theory that attempts to interpret the behaviour of such systems in terms of their constituents must therefore rely on statistical methods. The statistical method is applicable to both, systems in equilibrium and time-dependent systems or rate processes. The former aspect will be discussed here.

Even in the absence of any information about specific individual particles in a large assembly of particles, the properties can be predicted by using the laws of probability. The precision of these predictions increases with the number of particles. For example, it is not possible to predict whether an isolated atom of radium will disintegrate within a stipulated period. However, if one milligram of radium (approximately 2.73×10^{18} atoms) is considered, it can be shown that nearly 7×10^{10} atoms will decay in a period of 30 minutes. The word probability is commonly used to indicate the likelihood of an event taking place. Suppose a coin is flipped or tossed. Only two results are possible, *i.e.* either the head or the tail will show up. The probability of the head showing up is 1/2. This does not mean that if a person tosses a coin 10 times or tosses 10 coins, the chance of getting 'heads' is 5. In practice it will be different from 5. However, as the number of trials or number of coins increases, the chances of getting 'heads' is closer to 50% of the trials. The probability of any event occurring is given by

$$\text{Probability} = \frac{\text{number of cases } \textit{favouring} \text{ a given occurrence}}{\text{total number of equally possible cases}} = \frac{c}{r} \qquad (7.1)$$

For example, one card can be drawn from a deck of cards in 52 different ways *i.e.* r = 52. Of the 52, there are 26 red cards and 26 black cards. The probability of drawing a black or red card = 26/52 = $\frac{1}{2}$. There are 13 in each of the following, diamond, club, heart and spade. A spade can be drawn from the deck in 13 different ways, *i.e.* c = 13 and so the probability of drawing a spade is 13/52 or 1/4. Since there are four aces, c = 4, the probability of drawing an ace is 4/52 or 1/13. However, there is only one ace of spades (c = 1) and so the probability of drawing the ace of spades is the same as the probability of drawing any specific card from a deck of 52 *i.e.* 1/52.

The probability of a certain distribution of molecules among the energy levels can be defined as the ratio of the number of ways of realizing the given distribution and the total number of possible arrangements. For a given system, the probability of a distribution is proportional to the number of ways of achieving the distribution. This can also be arrived at in another way.

7.b. The Language of Statistical Thermodynamics

In the case of a large number, N of particles, there is an energy distribution. If we have n_0 molecules having energy ε_0, n_1 molecules each having energy ε_1, n_2 molecules having energy ε_2 etc. the total energy E is given by

$$E = n_0\varepsilon_0 + n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots\cdots + n_i\varepsilon_i = \sum_0^i n_i\varepsilon_i \qquad (7.2)$$

$$N = n_0 + n_1 + n_2 + n_3 + \cdots\cdots n_i = \sum_0^i n_i \qquad (7.3)$$

In order to calculate the value of E, it is necessary to know the distribution numbers n_0, n_1, n_2 etc. and also the values of ε_0, ε_1, ε_2 etc. In principle the energy corresponding to the various energy levels can be obtained by solving the appropriate Schrodinger equation.

According to the classical theory, the energy levels are continuous and there is no restriction regarding the energy that can be assumed. But according to quantum theory, the energy levels are discrete and discontinuous and the molecules, if they behave like harmonic oscillators, can assume energies only in integral multiples of a quantum of energy, *i.e.* ε, which is given by the Planck's eqn. $\varepsilon = h\nu$, where h is the Planck's constant and ν the frequency of radiation.

The central problem in statistical mechanics is to determine the possible distributions of particles among energy levels and energy states (fig. 7.1). A specification of the number of particles n_i in each energy level is said to define a *macrostate* of the assembly. The macrostate of the assembly (configuration) in fig. 7.1 is $n_1 = 3$, $n_2 = 4$, $n_3 = 3$ and $n_4 = 2$. If the particles are indistinguishable, a specification of the total number of particles in each state (in fig. 7.1) is said to define a *microstate* of the assembly. The number of *energy states* in an energy level is the *degeneracy* of the level. In fig. 7.1, the first level is non-degenerate ($g_1 = 1$) whereas the degeneracies of levels 2, 3 and 4 are 3, 4 and 6, respectively. The particles may be distributed among the

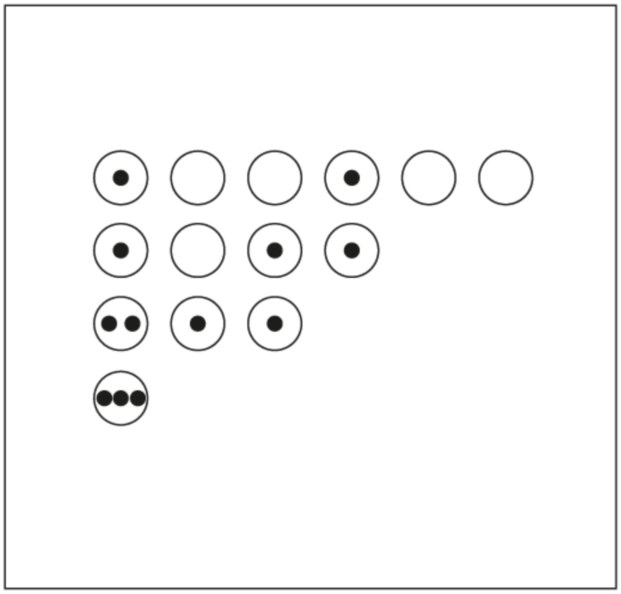

Fig. 7.1. Schematic representation of a set of energy levels. ε_i (i = 1, 2, 3, 4, etc.), their degeneracies g_i (i = 1, 2, 3, etc.) and their occupation numbers n_i (i = 1, 2, 3, etc.)

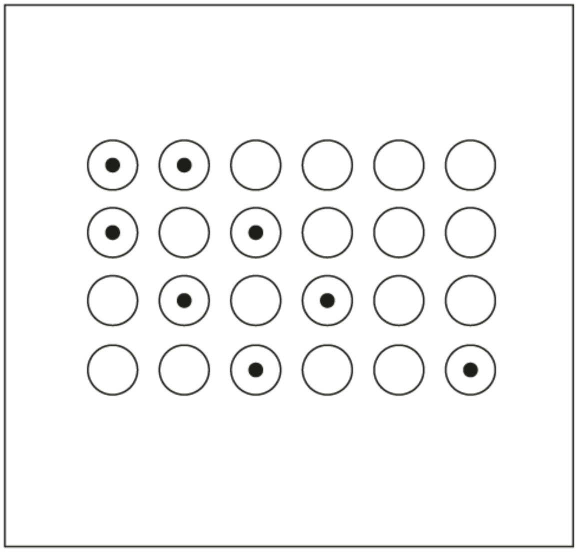

Fig. 7.2 Distribution of particles among various energy states in an energy level.

various energy states. For energy level 4, a few of the possible distributions are shown in (fig. 7.2).

These are the various microstates but they correspond to the same macrostate of the assembly. However, if the particles are distinguishable, one must specify not only how many particles are in each state, but which particles they are. For example, in the energy states of level 4, if the particles are labelled a and b, some of the microstates can be represented as follows.

Energy States →	1	2	3	4	5	6
Distribution of Particles	a	b	—	—	—	—
	a	—	b	—	—	—
	a	—	—	b	—	—
	—	a	—	—	b	—
	—	—	a	—	—	b

etc.

It is seen that the number of microstates for a given occupation number is greater if the particles are distinguishable. However, in the same energy state, if there are two particles a and b, the arrangement ‘a b’ is the same as ‘b a’ and no new microstate is possible.

There are many ways in which the particles can distribute themselves among the various energy levels, but whatever be the distribution, it should be consistent with equations 7.2 and 7.3. One has to find out the most probable distribution of particles among the energy levels for a particular fixed value of

Table 7.1. Number of ways (W) of distributing four distinguishable particles between two energy levels

ε_1	ε_2	W	Total = ΣW
0	(a. b, c, d)	1	16
(a, b, c, d)	0	1	
a	bcd	4	
b	acd		
c	abd		
d	abc		
bcd	a	4	
acd	b		
abd	c		
abc	d		
ab	cd	6	
ac	bd		
ad	bc		
cd	ab		
bc	ad		
bd	ac		

the total energy and a fixed number of energy levels. For this, it is necessary to know the number of ways (W) in which n particles can be distributed among the energy levels. Let us consider a simple case where n = 4 and that there are two energy levels *i.e.* ε_1 and ε_2. Let the molecules be labelled a, b, c and d. If there are no restrictions on the number of particles in any energy level, the various ways of distributing the particles are given in table 7.1.

The different orders in which the groups of letters are arranged are called ***permutations***. Each of the arrangements that can be made by changing the order of arrangement of some or all of a number of objects is called a permutation. If there are two objects a and b, they can be arranged in two ways, ab and ba. So the number of arrangements is 2 or 2 × 1. If there are three objects a, b, c, the third object can occupy three different places in each of the first two arrangements giving abc, cab, acb and cba, bac, bca. The total number of permutations is 6 or 3 × 2 × 1 equal to 3!. The permutations of 3 objects taking all the three at a time is denoted by ${}_3P_3$ equal to 6 or 3!. Generally ${}_nP_n$ is equal to n!.

If of the n objects only r are taken at a time the total permutations possible is represented by ${}_nP_r$. Of the r objects needed to form the arrangements, the first can be taken in n ways. For each of the ways in which the first object was taken there are (n – 1) ways of adding the second object. The total number of ways of arranging these two objects is therefore n (n – 1). For each of these arrangements there are (n – 2) ways of adding the third object. So the total arrangements there are (n – 1) (n – 2). So when each of the arrangements for completion involves r objects, the total number of arrangements is

$$_nP_r = n\,(n-1)\,(n-2)\ \ldots\ldots\ldots\ldots(n-r+1)$$

This can be written as

$$\frac{n(n-1)(n-2)\cdots(n-r+1)\cdots1}{(n-r)(n-r+1)\cdots1} = \frac{n!}{(n-r)!}$$

$$_nP_r = \frac{n\,!}{(n-r)\,!}$$

The number of permutations of n objects, all being taken at a time is n!. The ways in which the four objects a, b, c, and d can be arranged taking all of them at a time is 4! equal to 24. They are represented below:

1 a b c d
2 a c b d
3 a d b c
4 a d c b
5 a c d b
6 a b d c
7 b a c d
8 b a d c
9 b c a d
10 b c d a
11 b d a c
12 b d c a
13 c a b d
14 c a d b
15 c b a d
16 c b d a
17 c d a b
18 c d b a
19 d a b c
20 d a c b
21 d b a c
22 d b c a
23 d c a b
24 d c b a

Let us consider the filling of two levels, each one of the levels containing two objects. Considering the distribution $n_1 = 2$ and $n_2 = 2$, the 24 ways of arranging the 4 letters such that each level contains only two are given below.

	ε_1	ε_2
(*i*)	1 a b	c d
	7 b a	c d
	6 a b	d c
	8 b a	d c
	4 a d	c b
	20 d a	c b

	ε_1	ε_2
(*ii*)	2 a c	b d
	13 c a	b d
	5 a c	d b
	14 c a	d b
	9 b c	a d
	15 c b	a d

(*iii*)	3 a d	b c
	19 d a	b c
	11 b d	a c
	21 d b	a c

(*iv*)	10 b c	d a
	16 c b	d a
	17 c d	a b
	23 d c	a b

(*v*)	12 b d	c a
	22 d b	c a

(*vi*)	18 c d	b a
	24 d c	b a

These 24 arrangements are represented in sets of 4. Within an energy level the arrangement ab is indistinguishable from ba. So each set consisting of four arrangements actually represents only one combination. Hence there are only 6 *combinations. Each of a set of arrangements that can be made by taking a few or all of a number of objects without considering the internal arrangement within any group is called a* ***combination***. In permutations the order of arrangement of the various objects is important. In combinations attention is paid only to the presence or absence of the object. The number of combinations of n objects taking r objects at a time is represented by ${}_nC_r$.

If there are two objects a and b and one wants the number of combinations possible taking two objects at a time, there is only one combination since one does not distinguish between the arrangements ab and ba unlike in the case of permutations. If there are four objects a, b, c and d and one wants to find out the combinations takings two objects at a time one will find six combinations: ab, ac, ad, bc, bd, cd. For each one of these combinations there are two permutations. So the total number of permutations will be given by

$${}_4P_2 = \frac{4\,!}{2\,!} = \frac{24}{2} = 12$$

If there are n objects and one needs to know the number of combinations taking r at a time one can proceed as follows. The total number of permutations of n objects taking r at a time can be determined. Because in each of these arrangements there are r objects, the same r objects are giving rise to a group of permutations each permutation having the same objects. The number of such permutations forming the group is given by

$${}_rP_r = r\,!$$

While trying to arrive at the number of combinations one is not concerned with the order of arrangement of objects, but only the identity. Therefore it will be noted that each combination has got multiplied by r! in arriving at the total number of permutations. So the total number of permutations of n objects taking the objects r at a time is to be divided by r! to obtain the number of combinations of n objects taking r of them at a time.

$${}_nP_r = {}_nC_r \times r\,! = \frac{n!}{(n-r)!}$$

$${}_nC_r = \frac{n!}{(n-r)\,!r\,!}$$

Ensembles

The energy of a molecule keeps changing with time due to intermolecular collisions, energy transfers and motion through available space. It is necessary to take the energy of a molecule as the average over a certain time. To do the impossible task of time averaging for a system containing of the order of an Avogadro number L of molecules, Willard Gibbs introduced the idea of ensembles. Consider a system and the surroundings with which it is in contact as constituting a distinct unit. An *ensemble* is formed by reproducing this distinct unit many times. The ensemble is a set of imaginary replications and is a mental construction. Each member of the ensemble is subject to similar thermodynamic constraints as the original system. The number of replicas can be as large as is desired and when appropriate can become infinite. There are three types of ensembles. When the units are separated by impermeable adiabatic walls, the energy of every system is the same and the ensemble is said to be *microcanonical*. For example, the number of molecules N, the volume V and the energy of the units E will be the same in all the units (see diagram). On the other hand, if the units are separated by a diathermic wall letting the energy fluctuate about some average value *E*, while the temperature T remains the same, the ensemble is called a *canonical* ensemble (see diagram). The third type of ensemble is based on open systems where the number of molecules in a unit is not kept constant while V and T and the chemical potential μ are the same in all the units. These ensembles are called *grand-canonical* ensembles.

N V T	N V T	N V T	N V T	N V T
N V T	N V T	N V T	N V T	N V T
N V T	N V T	N V T	N V T	N V T
N V T	N V T	N V T	N V T	N V T
N V T	N V T	N V T	N V T	N V T
N V T	N V T	N V T	N V T	N V T
N V T	N V T	N V T	N V T	N V T

Canonical ensemble of 35 systems

N V E	N V E	N V E	N V E	N V E
N V E	N V E	N V E	N V E	N V E
N V E	N V E	N V E	N V E	N V E
N V E	N V E	N V E	N V E	N V E
N V E	N V E	N V E	N V E	N V E
N V E	N V E	N V E	N V E	N V E
N V E	N V E	N V E	N V E	N V E

Microcanonical ensemble of 35 systems

μ V T	μ V T	μ V T	μ V T	μ V T
μ V T	μ V T	μ V T	μ V T	μ V T
μ V T	μ V T	μ V T	μ V T	μ V T
μ V T	μ V T	μ V T	μ V T	N V T
μ V T	μ V T	μ V T	μ V T	μ V T
μ V T	μ V T	μ V T	μ V T	μ V T
μ V T	μ V T	μ V T	μ V T	μ V T

Grandcanonical ensemble of 35 systems

7.c. Statistical Thermodynamic Formulation of the Boltzmann Equation

In general let us consider N molecules being grouped into i levels such that the first level contains n_1 molecules, the second level n_2 molecules and so on. Maxwell–Boltzmann distribution law which gives the canonical distribution is applicable to ***distinguishable*** particles as in crystals. The number of arrangements or permutations of N things taken all at a time is N!. This includes equivalent arrangements such as ab and ba in the same level. Hence N! must be divided by the number of equivalent ways in which each combination is arrived at. The number of ways in which n_1 molecules can be arranged in an energy level is $n_1!$. The number of non-equivalent arrangements or combinations or *complexions* (W) is given by eqn. 7.4.

$$W = \frac{N!}{n_1!\, n_2!\, n_3! \ldots\ldots n_i!} \text{ or } N!/\prod_{1}^{i} n_i! \qquad (7.4)$$

Since nature has no preference for any particular type of distribution, the probability, *P*, of any particular distribution can be considered to be directly proportional to the number of ways (complexions W) in which the distribution can be arrived at. The symbol W, comes from the German word, Wahrscheinlichkeit, for probability. The total number of different ways (W) in which a given system, in a given thermodynamic state, may be realized is related to the thermodynamic probability. *The fundamental postulate of statistical thermodynamics is that all possible microstates (complexions) of an isolated assembly are equally probable*. By taking the logarithm of both sides of eqn. 7.4, the product term in the denominator is reduced to a summation.

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

$$= \ln N! - \sum_1^i \ln n_i!$$

When the number N is large, *Stirling's approximation* (eqn. 7.5) can be used to evaluate the factorials.

$$\ln N! = N \ln N - N \tag{7.5}$$

$$\sum_1^i \ln n_i! = \sum_1^i n_i \ln n_i - \sum_1^i n_i \tag{7.6}$$

$$= \sum_1^i n_i \ln n_i - N \quad (\because \sum_1^i n_i = N)$$

$$\ln W = N \ln N - N - \sum_1^i n_i \ln n_i + N$$

$$\ln W = N \ln N - \sum_1^i n_i \ln n_i \tag{7.7}$$

In an isolated system the energy E and the total number of particles, N are both constant. Though the total energy of the system is constant, due to collision among particles themselves and with the walls of the container, the distribution numbers change. However, every possible microstate taken together must satisfy the conditions of constant E and N. For each microstate of a system of particles there is a particular most favoured distribution. When this is reached the system attains statistical equilibrium. This state of equilibrium is one with a maximum probability and results from the most probable distribution (sec. 4.i)

The values of n_1, n_2 etc. which make W or P a maximum have to be determined, subject to the conditions that the total number of particles should remain constant and the total energy of the system remains constant. In the absence of such constraints W can increase indefinitely. Since N and E are constants any small variation in these must be zero *i.e.* $\delta N = 0$ and $\delta E = 0$. Since neither N nor total energy of the system changes

$$\sum_{1}^{i} \delta n_i = 0 \ \text{ and } \ \sum_{1}^{i} n_1 \ \delta \varepsilon_1 = 0 \tag{7.8}$$

$$\delta \sum_{1}^{i} n_i \ \varepsilon_1 = \sum_{1}^{i} n_i \ \delta \varepsilon_1 + \sum_{1}^{i} \varepsilon_i \ \delta n_i = 0 \ \text{ and so } \ \sum_{1}^{i} \varepsilon_i \ \delta n_i = 0 \tag{7.9}$$

When P is maximum the variation of P and hence of $\ln P$ is zero.

$P \propto$ W or $\qquad P = C'W$, where C' is a constant.

$$\ln P = \ln C' + \ln W$$

Substituting for ln W from eqn. 7.7 in the above expression for $\ln P$ equation 7.10 is obtained

$$\ln P = \ln C' + N \ln N - \sum_{1}^{i} n_i \ \ln n_i \tag{7.10}$$

Since N and C' are constants and the condition for a maximum is

$$\delta (\ln P) = 0$$

$$\delta(-\ln P) = \delta\left(\sum_{1}^{i} n_i \ln n_i \right) = 0 \tag{7.11}$$

$$\sum_{1}^{i} (\delta n_i) \ln n_i + \sum_{1}^{i} n_i \ \delta(\ln n_i) = 0$$

$$\sum_{1}^{i} (\delta n_i) \ln n_i + \sum_{1}^{i} n_i \ \frac{1}{n_i} \delta n_i = 0$$

$$\sum_{1}^{i} (\delta n_i) \ln n_i + \sum_{1}^{i} \delta n_i = 0 \tag{7.12}$$

$$\sum_{1}^{i} n_i = N = \text{constant, } \textit{i.e.}, \sum_{1}^{i} \delta n_i = 0$$

and so eqn. 7.12. becomes $\sum_{1}^{i} \ln n_i = 0$ (7.13)

We require all the three conditions eqns. 7.8, 7.9 and 7.13 to hold good simultaneously and the required mathematical technique that is useful to deal with this condition is *Lagrange's method of undetermined multipliers.* This is useful in the treatment of problems involving constrained or conditioned maxima. In this technique, equations 7.8 and 7.9 are multiplied by two arbitrary constants, α' and β respectively and combined with eqn. 7.13 to give eqn. 7.14.

$$\sum_{1}^{i}[\ln n_i + \alpha' + \beta\varepsilon_i]\,\delta n_i = 0 \tag{7.14}$$

or
$$(\alpha' + \beta\varepsilon_1 + \ln n_1)\,\delta n_1 + (\alpha' + \beta\varepsilon_2 + \ln n_2)\,\delta n_2 +$$
$$(\alpha' + \beta\varepsilon_3 + \ln n_3)\,\delta n_3 + \ldots\ldots = 0$$

Eqn. 7.14 is an identity based on three independent equations. α' and β may have any values and so are independent.

Let α' and β be given such values that $\ln n_1 + \alpha' + \beta\varepsilon_1 = 0$ and $\ln n_2 + \alpha' + \beta\varepsilon_2 = 0$. Eqn. 7.14 reduces to the requirement that the sum of all the terms involving δn_3, δn_4, etc., must also be zero. Since the variations, δn_3, δn_4 etc. are arbitrary, this will be true only if each term is separately equal to zero.

(*i.e.*)
$$\alpha' + \beta\varepsilon_1 + \ln n_1 = 0 \tag{7.15}$$

or
$$n_i = e^{-\alpha'}\ e^{-\beta\varepsilon_i} = \ln n_i = -(\alpha' + \beta\varepsilon_i) \tag{7.16}$$

Eqn. 7.16 is the *Maxwell–Boltzmann distribution law*.

$$\sum_{1}^{i} n_i = N = e^{\alpha'}\sum_{1}^{i} e^{-\beta\varepsilon_i}$$

Hence
$$e^{-\alpha'} = N \Big/ \sum_{1}^{i} e^{-\beta\varepsilon_i} \tag{7.17}$$

Substituting this value of $e^{-\alpha'}$ in eqn. (7.16),

$$n_i = \frac{Ne^{-\beta\varepsilon_i}}{\sum_{1}^{i} e^{-\beta\varepsilon_i}} \text{ or } \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_{1}^{i} e^{-\beta\varepsilon_i}} \tag{7.18}$$

Eqn. 7.18 gives the populations of the most probable configuration of the ensemble. This is called the canonical distribution.

Eqn. 7.18 is another form of the Maxwell–Boltzmann distribution law. At constant temperature T, n_i/N is the fraction of the total number of molecules which possess the energy ε_i. The constant, β, can be shown to be equal to 1/kT (eqn. 7.28) where k is the Boltzmann constant. Eqn. 7.18 then becomes,

$$\frac{n_i}{N} = \frac{e^{-\varepsilon_i/kT}}{\sum_{1}^{i} e^{-\varepsilon_i/kT}} \tag{7.19}$$

So far it has been assumed that for each energy value there is only one level (non-degenerate). However, if two or more quantum states have the same energy, they may be grouped together and the energy level which was previously considered to be single is now composite. Such energy levels are *degenerate*. Consider three energy states a, b and c associated with an energy level 2. Let all of these have the same energy ε_2. From eqn. 7.18 we can write.

$$n_a = \frac{Ne^{-\beta\varepsilon_2}}{\sum_1^i e^{-\beta\varepsilon_i}}, n_b = \frac{Ne^{-\beta\varepsilon_2}}{\sum_1^i e^{-\beta\varepsilon_i}} \text{ and } n_c = \frac{Ne^{-\beta\varepsilon_2}}{\sum_1^i e^{-\beta\varepsilon_i}}$$

The total number of molecules in this energy level is

$$n_2 = n_a + n_b + n_c. \text{ It is seen that } n_2 = 3Ne^{-\beta\varepsilon_2} / \sum_1^i e^{-\beta\varepsilon_i}$$

If g_i is the number of energy states with the same energy ε_i, this quantum level is g_i fold degenerate. The number of molecules in that energy level increases g_i-fold. g_i is referred to as degeneracy number. Each level must be assigned a statistical weight of g_i. Then eqn. 7.19 becomes,

$$\frac{n_i}{N} = \frac{g_i e^{-\varepsilon_i/kT}}{\sum_1^i g_i e^{-\varepsilon_i/kT}} \tag{7.20}$$

The denominator of eqn. 7.20 is a dimensionless quantity called the *partition function*, or atomic or molecular partition function, *f*. Eqn. 7.20 can be written as

$$n_i = \frac{N\,g_i\,e^{-\varepsilon_i/kT}}{f} \quad \text{where}$$

$$f = \sum_1^i g_1\,e^{-\varepsilon_i/kT} = g_1\,e^{-\varepsilon_i/kT} + g_2\,e^{-\varepsilon_2/kT} + \cdots\cdots g_i\,e^{-\varepsilon_i/kT} \tag{7.21}$$

The constants α' and β

From eqn. 7.20, if $\varepsilon_i = 0$, n_i becomes equal to n_0 the number of particles in the lowest energy level (ground state) and for non-degenerate levels g_0 being 1, eqn. 7.20 becomes,

$$\frac{n_0}{N} = \frac{1}{f} \tag{7.22}$$

From eqn. 7.16, for this lowest energy level

$$n_0 = e^{-\alpha'} \tag{7.23}$$

Even if this level is degenerate, $e^{-\alpha'}$ will be a number proportional to n_0. The constant β can be evaluated as follows. Entropy (S) and W are related as

$$S = k \ln W \tag{4.65}$$

Using the value of ln W from eqn. 7.7,

$$S = k\,N \ln N - k\sum_{1}^{i} n_i \ln n_i \tag{7.24}$$

Substituting for, $-\ln n_i$ from eqn. 7.15,

$$S = k[N \ln N + \sum_{1}^{i} n_i\,(\alpha' + \beta\varepsilon_i)] \tag{7.25}$$

$$\sum_{1}^{i} n_i = N \text{ and } \sum_{1}^{i} n_i\varepsilon_i = E$$

$$\therefore \qquad S = k(N \ln N + \alpha' N + \beta E) \tag{7.26}$$

If E is identified with internal energy U and a constant volume system is considered (N = constant).

$$dU + PdV = TdS \tag{4.22}$$

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \tag{5.36}$$

Differentiating eqn. 7.26 with respect to U keeping V constant, α' being a number and N being a constant.

$$S = k(N \ln N + \alpha' N + \beta E) \tag{7.26}$$

$$\left(\frac{\partial S}{\partial U}\right)_V = k\beta = \frac{1}{T} \tag{7.27}$$

Hence

$$\beta = \frac{1}{kT} \tag{7.28}$$

From the Maxwell's law of distribution of velocities the translational kinetic energy of a molecule, ε can be shown to be 3/2 kT (sec. 7.g.2). Since a molecule can have three degrees of freedom for translational motion, for each degree of freedom, contribution towards the kinetic energy, ε_x is kT/2 [equipartition of energy (sec. 7.i.2)].

$$\varepsilon_x = kT/2$$

Substituting for kT from eqn. 7.28

$$\varepsilon_x = 1/2\ \beta$$

If n_0 is the number of molecules in the ground state ($\varepsilon_0 = 0$) it is possible to find the ratio of the number of molecules in any energy level ε_i relative to that in the ground state.

$$\frac{n_i}{n_0} = \frac{n_i}{N} \cdot \frac{N}{n_0} = \frac{g_i\ e^{-\varepsilon_i/kT}}{f} \cdot \frac{f}{g_0\ e^{-\varepsilon_0/kT}}$$

$$\frac{n_i}{n_0} = \frac{g_i\ e^{-\varepsilon_i/kT}}{g_0\ e^{-\varepsilon_0/kT}} = \frac{g_i}{g_0} e^{-(\varepsilon_i - \varepsilon_0)/kT}$$

or

$$n_i = n_0 \frac{g_i}{g_0} e^{-(\varepsilon_i - \varepsilon_0)/kT} \tag{7.29}$$

$$N = \sum_1^i n_i = \frac{n_0}{g_0} \cdot g_0 + \frac{n_0}{g_0} \cdot g_1\ e^{-\varepsilon_1/kT} + \frac{n_0}{g_0} g_2\ e^{-\varepsilon_2/kT} + \cdots$$

$$= \frac{n_0}{g_0} [g_0 + g_1\ e^{-\varepsilon_1/kT} + g_2\ e^{-\varepsilon_2/kT} + \cdots]$$

$$N = \frac{n_0}{g_0} \sum_0^i g_i e^{-\varepsilon_i/kT} = \frac{n_0}{g_0} f \tag{7.30}$$

If the degeneracy of the ground state $g_0 = 1$, from eqn. 7.30,

$$\frac{n_0}{N} = \frac{1}{f} \quad \text{or} \quad f = 1/(n_0 / N) = \frac{N}{n_0} \tag{7.31}$$

Thus the partition function may be defined as the reciprocal of the mol 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.* Thus, it indicates how the particles are distributed among the various energy states. The relative population of any two quantum states or levels 1 and 2 is given by

$$\frac{n_1}{n_2} = \frac{N\ g_1 e^{(-\varepsilon_1/kT)}/f}{N\ g_2 e^{(-\varepsilon_2/kT)}/f}$$

$$= \frac{g_1}{g_2} e^{-(\varepsilon_1 - \varepsilon_2)}/kT \tag{7.32}$$

If $\varepsilon_1 = \varepsilon_2$ and $g_1 = g_2$, $n_1 = n_2$ (*i.e.*) they are equally populated. At very low temperatures $(\varepsilon_1 - \varepsilon_0) << kT$, the number of molecules in any excited state n_i from eqn. 7.20 is

$$n_i \propto e^{-\varepsilon_i/kT} \simeq 0$$

Hence all the particles are in the lower most energy level. From eqn. 7.32 if $\varepsilon_2 > \varepsilon_1$, $n_1 > n_2$ and vice versa. As long as $(\varepsilon_1 - \varepsilon_2)$ is less than or is of the same order of magnitude as kT, n_1 and n_2 will be of the same order of magnitude. Thus, if there are many low lying levels of energy less than kT, they will be well populated in relation to the ground state. Such distributions correspond to large values of *f*. Widely spaced distribution of levels result in uneven distributions of molecules among states and *f* assumes smaller values.

7.k.2. Fermi–Dirac Statistics

Here the particles are *indistinguishable* and the total wave function is *antisymmetric* with respect to interchange of particles. Fermions are particles with half integral spins (e, p, n), and nuclei of atoms, ions and molecules with an odd number of e, p and n and *obey Pauli's exclusion principle.* If the sum of the numbers of protons, neutrons and electrons is **p**, **p** = 4 for H_2, **p** = 5 for ^3He, **p** = 6 for ^4He. There is a restriction on the number of fermions which can occupy an energy level, as given by the Pauli's principle. This can be stated as 'in any system of indistinguishable molecules (or other particles) for which **p** (*sum of the numbers of protons, neutrons and electrons*) *has an odd value, each molecular quantum state can be occupied by no more than one molecule at a time*.' This restriction leads to a distribution quite different from the Boltzmann distribution. Let g_i be the degeneracy of an energy level i (g_i = number of levels with the same energy). Since there can be only one particle in each energy level, n_i the number of particles can be a maximum equal to g_i. Let n_1 be the number of particles for an energy level ε_1. The first particle can be placed in any one of the available g_i states. The second particle can be arranged in $(g_i - 1)$ different ways, and so on. The total number of different ways of arranging n_i particles among the available g_i states all having energy ε_1 is given by

$$W' = g_i\,(g_i - 1)\,(g_i - 2)\,\ldots\ldots\,[g_i - (n_i - 1)]$$

$$= \frac{g_i(g_i-1)(g_i-2)\ldots..[g_i-(n_i-1)](g_i-n_i)[g_i-(n_i+1)]\ldots..1}{(g_i-n_i)\,[g_i-(n_i+1)]\ldots..1]}$$

or $\quad W' = g_i\,!/(g_i - n_i)!$ (7.139)

The particles are indistinguishable and n_i particles can be arranged in $n_i!$ ways. Eqn. 7.139 therefore must be divided by $n_i!$ to give the number of different or non-equivalent ways of arranging n_i particles.

$$W' = \frac{g_i\,!}{n_i\,!(g_i-n_i)\,!} \tag{7.140}$$

If g_i levels are available these can be occupied in $g_i!$ ways. If n_i is the number of particles, these can be arranged in $n_i!$ ways and for each of the arrangements the remaining $(g_i - n_i)$ levels that are free could have been occupied in $(g_i - n_i)!$ ways. The number of different ways of arranging these particles is thus given by eqn. 7.140. The total number of different and distinguishable ways of arranging n_1, n_2, n_3........ etc. particles among the energy levels ε_1, ε_2, ε_3, etc. is given by eqn. 7.141.

$$W' = \frac{g_1\,!}{n_1\,!(g_1-n_1)\,!}\,\frac{g_2\,!}{n_2\,!(g_2-n_2)\,!} \qquad \ldots.. \text{ or}$$

$$W' = \prod_1^i \frac{g_i\,!}{n_i\,!(g_i-n_i)\,!} \tag{7.141}$$

The most probable distribution is obtained by using the condition $d\ln W' = 0$ (sec. 7.c) and the Fermi–Dirac distribution law is obtained as eqn. 7.142.

$$n_i = g_i/(e^{\alpha'}\,e^{\beta\varepsilon i} + 1) \tag{7.142}$$

This can be derived as follows. Taking natural logarithms of both sides of eqn. 7.141

$$\ln W' = \sum_1^i \ln g_i\,! - \ln n_i\,! - \ln\,(g_i - n_i)! \tag{7.143}$$

Applying Stirling's formula to evaluate the factorial

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

$$\begin{aligned}
\ln W' &= \sum_{1}^{i} g_i \ln g_i - g_i - (n_i \ln n_i - n_i) - [(g_i - n_i) \ln (g_i - n_i) - (g_i - n_i)] \\
&= \sum_{1}^{i} g_i \ln g_i - g_i - n_i \ln n_i + n_i - (g_i - n_i) \ln (g_i - n_i) + g_i - n_i \\
&= \sum_{1}^{i} g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i) \qquad (7.144)
\end{aligned}$$

Differentiating eqn. 7.144 with respect to n_i

$$\begin{aligned}
d \ln W' &= \sum_{1}^{i} - \left[n_i \frac{1}{n_i} + \ln n_i - \left((g_i - n_i) \frac{1}{(g_i - n_i)} - \ln (g_i - n_i) \right) \right] dn_i \\
&= \sum_{1}^{i} [(\ln n_i - \ln (g_i - n_i)] \, dn_i \qquad (7.145)
\end{aligned}$$

The maximum value of W′ is obtained by equating dlnW′ to zero

$$\sum_{1}^{i} [\ln n_i - \ln (g_i - n_i)] \, dn_i = 0 \qquad (7.146)$$

But $\sum_{1}^{i} dn_i = 0$; (eqn. 7.8) and $\sum_{1}^{i} \varepsilon_i \, dn_i = 0$; (eqn.7.9)

Multiplying eqn. 7.8 by α', eqn. 7.9 by β (ref. sec. 7.c) and adding to eqn. 7.146

$$\sum_{1}^{i} [\ln n_i - \ln (g_i - n_i) + \alpha' + \beta \, \varepsilon_i] \, dn_i = 0 \qquad (7.147)$$

Each term of the summation is equal to zero (sec. 7.c)

$$\ln \frac{n_i}{(g_i - n_i)} = -\alpha' - \beta \, \varepsilon_i \quad \text{or}$$

$$\frac{n_i}{(g_i - n_i)} = e^{(-\alpha' - \beta\varepsilon_i)}$$

$$\frac{g_i - n_i}{n_1} = e^{(\alpha' + \beta\varepsilon_i)}$$

$$\frac{g_i}{n_i} = e^{(\alpha' + \beta\varepsilon_i)} + 1$$

or

$$n_i = \frac{g_i}{e^{(\alpha' + \beta\varepsilon_i)} + 1} \qquad (7.143)$$

7.k.3. Bose–Einstein Statistics

This is applicable to systems consisting of identical and *indistinguishable* particles, *there being no limit to the number of particles in any level*. The spin of the particles to be arranged in a three fold degenerate energy level. The degeneracy can be indicated by partitioning an energy level. For a three fold degenerate energy level there are two partitions. In general for g_i degenerate levels, there are $(g_i - 1)$ partitions. The different arrangements are seen to be six for a three-fold degenerate level (Fig. 7.7.). These can be considered to be derived from (*i*) finding the total number of permutations of partitions and particles, and (*ii*) making allowance for the fact that the particles are identical and the partitions are equivalent. The total number of partitions and particles = 4, *i.e.* (2 + 2) can be permutated in 4! ways or $(n_i + g_i - 1)!$ ways. The two particles can be arranged in 2! ways and the partitions can be arranged in 2! or $(g_i - 1)!$ ways. The number of ways in which the n_i particles can be placed in the i*th* level is shown in Fig. 7.7.

$$W = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \qquad (7.148)$$

In the present case

$$W = \frac{4!}{2!2!} = 6$$

The total number of different and distinguishable ways of arranging N particles among all energy levels is

$$W = \prod_{1}^{i} \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \qquad (7.149)$$

The most probable distribution is given by the eqn. dln W = 0 (sec. 7.c.). The Bose–Einstein distribution law given by eqn. 7.150 can be derived as follows.

$$n_i = g_i/[e^{\alpha'} e^{\beta\varepsilon_i} - 1] \qquad (7.150)$$

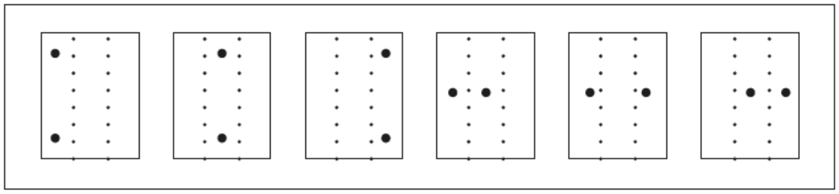

Fig. 7.7. Different ways of arranging two indistinguishable particles among three fold degenerate energy levels.

Taking natural logarithms of eqn. 7.149

$$\ln W = \sum_{1}^{i} [\ln (n_i + g_i - 1)! - \ln n_i! - \ln (g_i - 1)!] \qquad (7.151)$$

Applying Stirling's approximation

$$\ln W = \sum_{1}^{i} (n_i + g_i - 1) \ln (n_i + g_i - 1) - (n_i + g_i - 1)$$

$$-n_i \ln n_i + n_i - (g_i - 1) \ln (g_i - 1) + (g_i - 1) \qquad (7.152)$$

$$= \sum_{1}^{i} (n_i + g_i - 1) \ln (n_i + g_i + 1) - (n_i + g_i - 1)$$

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

$$\ln W = \sum_{1}^{i} [(n_i + g_i - 1) \ln (n_i + g_i - 1) - n_i \ln n_i - (g_i - 1) \ln (g_i - 1)] \qquad (7.153)$$

Differentiating eq. 7.153

$$d \ln W = \sum_{1}^{i} [\ln (n_i + g_i - 1)\, dn_i - \ln n_i\, d\, n_i] = 0$$

$$- d \ln W = \sum_{1}^{i} [- \ln (n_i + g_i - 1)\, dn_i + \ln n_i\, d\, n_i] = 0$$

or $$\sum_{1}^{i} \left\{- [\ln (n_i + g_i - 1) + \ln n_i]\, dn\right\}_i = 0 \qquad (7.154)$$

$$\sum_{1}^{i} dn_i = 0; \text{ (eqn. 7.8) and } \sum_{1}^{i} \varepsilon_i\, dn_i = 0; \text{ (eqn. 7.9)}$$

Multiplying eqn. 7.8 by α' and eqn. 7.9 by β and adding to eqn. 7.154

$$\sum_{1}^{i} [- \ln (n_i + g_i - 1) + \ln n_i + \alpha' + \beta\varepsilon_i]\, dn_i = 0$$

Each term of the summation is equal to zero (sec. 7.c).

$$- \ln (n_i + g_i - 1) + \ln n_i + \alpha' + \beta\varepsilon_i = 0 \qquad (7.155)$$

$$(n_i + g_i) > 1 \text{ and } (n_i + g_i - 1) \approx n_i + g_i)$$

$$\ln \frac{n_i}{(n_i + g_i)} = -\alpha' - \beta\varepsilon_i$$

or
$$\frac{n_i}{(n_i + g_i)} = e^{(-\alpha' - \beta\varepsilon_i)}$$

or
$$\frac{n_i + g_i}{n_i} = e^{(\alpha' + \beta\varepsilon_i)}$$

$$\frac{g_i}{n_i} = e^{(\alpha' + \beta\varepsilon_i)} - 1$$

or
$$n_i = \frac{g_i}{e^{(\alpha' + \beta\varepsilon_i)} - 1} \tag{7.150}$$

From eqns. 7.142 and 7.150 it is seen that if $e^{\alpha'}\, e^{\beta\varepsilon_i} > 1,\ n_i = g_i/(e^{\alpha'}\, e^{\beta\varepsilon_i})$ *i.e.* the Maxwell–Boltzmann distribution law (eqn. 7.16) appears to be the classical limit of the Fermi–Dirac and Bose–Einstein distributions. Except in the case of electrons in metals, or temperatures very near absolute zero, Boltzmann distribution law is applicable to all systems. A comparative account of the three distribution laws is given in Table 7.5.

D.2.a. Ideal Fermi–Dirac (FD) Gas-electrons in Metals

An assembly of fermions is known as an FD gas. Consider an ideal FD gas at low temperatures or high densities. A well-known system of this kind is electrons in metals. According to the *free-electron model of metals*, the valence electrons of the atoms of a metal can be considered to be similar to molecules of an ideal gas and hence referred to as "*electron gas*". Coulomb repulsion by other electrons is roughly balanced by coulombic attraction of the nuclei. The potential energy of the electrons is assumed to be constant and independent of temperature. Hence the contribution to the total energy of the electrons can be considered to be translational kinetic energy. Like the atoms of a monoatomic ideal gas, these electrons would have allowed energy levels with degeneracies for their translational motion. It is therefore possible to calculate the translational kinetic energy distribution in different energy states.

Consider an ideal FD gas of N fermions in a volume V. Let these particles be distributed among various energy states such that there are $n_1, n_2, \ldots, n_i$ number of particles in quantum states with average energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i$, respectively. If g_i is the degeneracy or the statistical weight of the i-th quantum state, the most probable number of fermions with energy ε_i is given by the FD distribution (eqn. 7.143).

$$n_i = \frac{g_i}{[\exp(\alpha' + \beta\varepsilon_i) + 1]} \tag{7.143}$$

The parameter α' is determined as a function of N and T, by the condition:

$$N = \sum_{i=0}^{\infty} n_i = \sum_i \frac{g_i}{[\exp(\alpha' + \beta\varepsilon_i) + 1]} \tag{D.42}$$

Because of the factor + 1 in the denominator of eqn. (D.42), α' need not be restricted to $\alpha' \geq 0$ as in the BE case. For the FD gas α' can be positive or negative. As indicated earlier, the translational levels are so closely spaced that the summation in eqn. (D.42) can be replaced by integration. Though any number of identical bosons can occupy a given quantum state, no more than one fermion can occupy a given state. The restriction in the case of FD particles arises since fermions obey the Pauli exclusion principle according to which no two fermions can be in the same quantum state. Since a sizeable fraction of the particles will *not* be in the ground state we can approximate the sum in eqn. (D.42) by an integral (cf.BE case, page 3). If FD distribution function is written as:

$$f(\varepsilon) = \frac{1}{[\exp(\alpha' + \beta\varepsilon_i) + 1]} \tag{D.43}$$

eqn. (D.42) can be written as:

$$N = \int_0^{\infty} f(\varepsilon)\, g(\varepsilon)\, d\varepsilon \tag{D.44}$$

In the case of *electrons*, g(ε) dε as given by eqn. (D.43) can be written as eqn. (D.45)

$$g(\varepsilon)\, d\varepsilon = g_s \left(\frac{2\pi V}{h^3}\right)(2\mathbf{m})^{3/2}\ \varepsilon^{1/2}\ d\varepsilon \tag{D.45}$$

Here $g_s = 2s + 1$. This is the spin degeneracy and comes from (2s + 1) different spin orientations possible for the same energy ε.

An electron has two spin states (± 1/2) associated with each translational state. For electrons, s = 1/2 and so $g_s = 2$. Hence, from eqns. (D.44) and (D.45), one can write:

$$N = 2\left(\frac{2\pi V}{h^3}\right)(2\mathbf{m})^{3/2} \int_0^{\infty} \frac{\varepsilon^{1/2} d\varepsilon}{[\exp(\alpha' + \beta\varepsilon_i) + 1]} \tag{D.46}$$

As discussed on page 5, if $x = \varepsilon/\mathrm{kT}$ and $\mathrm{d}x = \mathrm{d}\varepsilon/\mathrm{kT}$, eqn. (D.46) can be written as eqn. (D.47):

$$\mathrm{N} = \frac{2\mathrm{V}}{\mathrm{h}^3}(2\pi\mathbf{m}\mathrm{kT})^{3/2}\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}\mathrm{d}x}{[\exp(\alpha' + x) + 1]}$$
$$= \frac{2\mathrm{V}}{\mathrm{h}^3}(2\pi\mathbf{m}\mathrm{kT})^{3/2}\mathrm{F}(\alpha') \tag{D.47}$$

As discussed earlier (pp6) eqn. (D.47) can be written as eqn. (D.48) where $\exp(-\alpha')$ is written as A.

$$\mathrm{F}(\alpha') = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\mathrm{A}x^{1/2}\exp(-x)\mathrm{d}x}{[1 + \mathrm{A}\exp(-x)]} \tag{D.48}$$

The integral in eqns. (D.47) and (D.48) must be evaluated for both positive and negative values of α'. For this purpose, it is convenient to express α' as $-\mu/\mathrm{kT}$, where μ is the chemical potential. It is more convenient to work with chemical potential μ in this case since μ approaches a finite value, μ_0 at $\mathrm{T} = 0$, whereas α' becomes negatively infinite [ref. eqn. (D.51)].

Eqns. (D.46) and (D.47) can be written as:

$$\mathrm{N} = \left(\frac{2\mathrm{V}}{\mathrm{h}^3}\right)(2\pi\mathbf{m}\mathrm{kT})^{3/2}\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\varepsilon^{1/2}\mathrm{d}\varepsilon}{[\exp(\varepsilon - \mu)/\mathrm{kT}] + 1} \tag{D.49}$$

Sommerfeld solved it by expressing the result as an infinite series and obtained eqn. (D.51):

$$\mu = \varepsilon_\mathrm{F}[1 - \frac{\pi^2}{12}(\mathrm{kT}/\varepsilon_\mathrm{F})^2 + \frac{\pi^4}{80}(\mathrm{kT}/\varepsilon_\mathrm{F})^4 + \cdots] \tag{D.50}$$

The quantity ε_F is constant for a given metal and is called the *Fermi energy*. When $\mathrm{T} = 0$, $\mu = \mu_0 = \varepsilon_\mathrm{F}$.

The FD distribution function can be written as eqn. (D.51)

$$\mathrm{f}(\varepsilon) = \frac{1}{[\exp([\varepsilon - \mu]/\mathrm{kT}) + 1]} \tag{D.51}$$

The significance of the Fermi energy (ε_F) can be seen as follows. If $\varepsilon < \mu$, $(\varepsilon - \mu) < 0$ at $\mathrm{T} = 0$, the term $(\varepsilon - \mu)/\mathrm{kT} = -\infty$. Therefore, the exponential term in eqn. (D5-1) becomes zero and so $\mathrm{f}(\varepsilon) = 1$. This means that all levels with energies less than $\mu = \mu_0 = \varepsilon_F$ (at T = 0) are fully occupied with one electron in each state. If $\varepsilon > \mu$, the term $(\varepsilon - \mu)$ is positive. Hence at T = 0, the exponential term equals $+\infty$ and so, $f(\varepsilon)$ is equal to zero. Thus there are no electrons in energy levels having energies greater than ε_F. In other words, at absolute zero of temperature, all the states with energy less than ε_F are occupied and those with energy greater than ε_F unoccupied. Thus ε_F has the property of being the cutoff energy. *Fermi energy is defined as the maximum energy of an electron at absolute zero and the corresponding level is called Fermi level*. This information about ε_F can be used to derive a function to calculate ε_F. Eqn. (D.46) can be written as eqn. (D.52)

$$N = \frac{4\pi V}{h^3}(2\mathbf{m})^{3/2}\int_0^{\varepsilon_F} \varepsilon^{1/2} d\varepsilon \tag{D.52}$$

Or

$$N = \frac{8\pi}{3}\left(\frac{2\mathbf{m}}{h^2}\right)^{3/2} V\varepsilon_F^{3/2}$$

$$\therefore \varepsilon_F = \mu_0 = \frac{h^2}{\mathbf{2m}}\left(\frac{3}{8\pi}\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}$$

$$= \frac{h^2}{\mathbf{8m}}\left(\frac{3N}{\pi V}\right)^{2/3} \tag{D.53}$$

The FD distribution function [eqn. (D.51)] can be expressed in the form of Fig. D.4, where $f(\varepsilon)$ is plotted vs. ε schematically. It will be seen from Fig. (D.4) that at T = 0, $f(\varepsilon) = 1$ for $\varepsilon < \mu$ and zero for $\varepsilon > \mu$. For a particular level at which $\varepsilon = \mu$, $(\varepsilon - \mu) = 0$ and at any temperature T above T = 0, $f(\varepsilon) = 0.5$. If the temperature is not too great, $\mu \cong \varepsilon_F$ and so one can say that any temperature above T = 0, the Fermi level is 50% occupied.

It is seen from eqn. (D.53) that ε_F is a function of electron density (number of electrons per unit volume) but is independent of T.

7.g.4. Diatomic Molecules—Rotational Partition Function

If a diatomic molecule is considered as a rigid or rotating dumb bell, the energy of rotation is $\varepsilon_r = \frac{1}{2} I\omega^2$, where I is the moment of inertia (Ref. Prob. 7.10) and $\boldsymbol{\omega}$ is the angular velocity of rotation. According to the quantum theory the angular momentum, $I\omega$ is quantized and is given by the equation,

$$I\omega = [J(J+1)]^{1/2}\, h/2\pi$$

where J is the rotational quantum number that can have only integral values, 0, 1, 2, 3 etc. For linear molecules, the permitted rotational energies are given by eqn. 7.75.

$$\varepsilon_r = \frac{(I\omega)^2}{2I} = \frac{J(J+1)h^2}{8\pi^2 I} \tag{7.75}$$

If $h^2/8\pi^2 I$ is denoted by B, eqn. 7.75 can be written as

$$\varepsilon_r = BJ\,(J+1) \tag{7.76}$$

Every J level has $(2J + 1)$ states corresponding to $(2J + 1)$ different orientations of the rotating molecule. These states are distinguished by quantum numbers $-J$ to $+J$. Every J level is $(2J + 1)$ fold degenerate. The rotational partition function becomes

$$f_r = \Sigma\, g_i\, e^{-\varepsilon_r/kT}$$

$$f_r = \sum_{J=0}^{J=\infty} (2J+1)\, e^{[-J(J+1)h^2/(8\pi^2/IkT)]} \tag{7.77}$$

For non-linear polyatomic molecule like methane the rotational partition function is given by eqn. 7.96 (*vide infra*).

If I is sufficiently large, the rotational energy levels become so closely spaced as to be practically continuous. This is the case for all diatomic molecules except those like, H_2, D_2 etc. I being of the order of about 10^{-47} kg m^2, the exponential term becomes very small. Hence the summation can be replaced by an integration

$$f_r = \int_0^\infty (2J+1)\, e^{[-J(J+1)h^2/(8\pi^2 IkT)]}\, .dJ$$

If $\dfrac{h^2}{8\pi^2 IkT}$ is represented as β', the above eqn. becomes

$$f_r = \int_0^\infty (2J+1)\, e^{[-J(J+1)\beta']}\, .dJ \tag{7.78}$$

Let $\alpha' = J(J+1)$

$$d\alpha' = (2J+1)\, dJ$$

Eqn. 7.78 then becomes

$$f_r = \int_0^\infty e^{-\alpha'\beta'}\, d\alpha' \tag{7.79}$$

or

$$f_r = \frac{1}{\beta'} = \frac{8\pi^2 IkT}{h^2} \tag{7.80}$$

One has to take into account the fact that every molecule cannot take all values of *J*. In the case of a homonuclear diatomic molecule like $^{14}N^{14}N$, $^{35}Cl^{35}Cl$, $^{16}O^{16}O$ etc. rotation by 180° interchanges two equivalent nuclei, and the new orientation is indistinguishable from the original. In counting all the *J* values we are counting such identical orientations also. So we must divide the degeneracy by two or the integral giving the total partition function for rotation by two. This enables one to avoid counting indistinguishable orientations as though they were distinguishable. The factor two is the *symmetry number* (σ) for the homonuclear diatomic molecule. Eqn. 7.80 is applicable to heteronuclear diatomic molecules. For a molecule like ammonia, though heteronuclear, the symmetry number is three and for methane it is twelve.

The symmetry number can be calculated simply by counting the number of indistinguishable orientations of the molecule that can be reached by rotational symmetry elements.

The symmetry number is obtained by considering the three dimensional model of the molecule and determining the number of indistinguishable positions when the molecule is rotated through 360°. For complicated molecules this is a tedious procedure. However, if one finds out the point group to which the molecule belongs, the symmetry is immediately revealed because each point group has associated with it a particular symmetry number. More than one point group has the same symmetry number. Table 7.2 gives the symmetry numbers and moments of inertia of some common molecules.

Eqn. 7.80 thus becomes $f_r = \dfrac{8\pi^2 IkT}{\sigma h^2}$ (7.81)

For linear polyatomic molecules like CO_2 having a plane of symmetry, eqn. 7.81 with $\sigma = 2$ can be used. For other linear triatomic molecules like $N = N = O$ also, eqn. 7.81 can be used but with $\sigma = 1$. The rotational energy per mol of a diatomic gas molecule, U_r is given by eqn. 7.82.

$$U_r = LkT^2 \frac{d(\ln f_r)}{dT} = LkT^2 \frac{d}{dT} \ln [8\pi^2 IkT/\sigma h^2]$$

$$= LkT \tag{7.82}$$

7.g.5. Partition Function and Vibrational Energy

A harmonic oscillator can be taken as the simplest model of a vibrating molecule. *In harmonic vibration, the restoring force is directly proportional to* *the displacement and the potential energy curve is parabolic. If the restoring force is not proportional to the displacement, an anharmonic vibration results.*

The vibrational energy levels are given by the equation

$$\varepsilon_v = \left(v + \frac{1}{2}\right)h\nu \tag{7.83}$$

where v the vibrational quantum number can be zero, 1, 2 etc., ν is the frequency of vibration and h is the Planck's constant. The energy levels are equally spaced in the case of a simple harmonic oscillator but for an anharmonic oscillator the levels get closer together as **v** increases. Many molecules can be considered to be harmonic oscillators at low values of **v** and this is a reasonable approximation for molecules at ordinary temperatures, since most of the molecules will be in lower energy levels.

For the lowest energy level **v** = 0, the vibrational energy *i.e.* the zero point energy is equal to hν/2. The vibrational energy of any level referred to the zero point energy is given by

$$\varepsilon_v = \left(v + \frac{1}{2}\right)h\nu - h\nu/2 = \mathbf{v}h\nu \tag{7.84}$$

For each mode of vibration eqn. 7.84 holds good. A linear polyatomic molecule can have (3n–5) vibrational modes while a non-linear polyatomic molecule can have (3n–6) vibrational modes (secs. 7.i.2 and 7.i.3). Some of the vibrational modes may have identical frequencies and are degenerate.

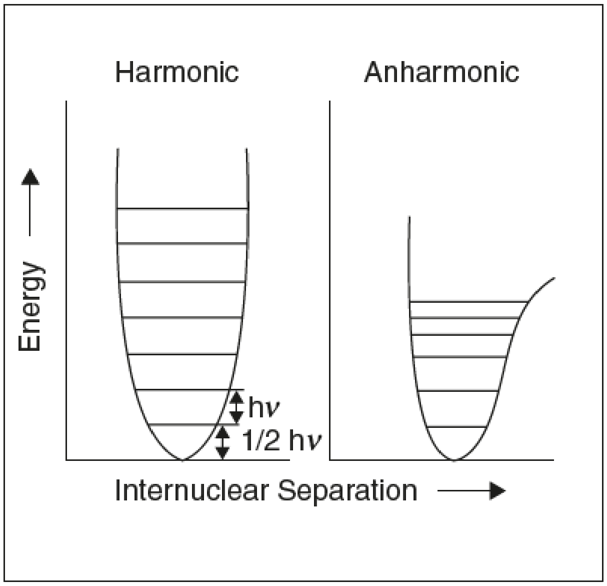

Fig. 7.3. A schematic representation of energy levels in harmonic and anharmonic oscillators.

The vibrational energy relative to the lowest vibrational level is given by eqn. 7.84 and can be written as

$$\varepsilon_v = \varepsilon'_v - \varepsilon'_{v(o)}$$

where ε'_v is the vibrational energy of a given level and $\varepsilon'_{V(o)}$ is that of the lowest vibrational level (ground state). $\varepsilon'_{v(o)}$ is given by $h\nu/2$ and $\varepsilon'_v = \left(v + \frac{1}{2}\right)h\nu$.

By using ε'_v the vibrational partition function can be written as

$$f'_v = \sum_{v=0}^{v=\infty} e^{-\left(v+\frac{1}{2}\right)h\nu/kT} = e^{-h\nu/2kT}\sum_{v=0}^{v=\infty} e^{-v\,h\nu/kT}$$

$$= e^{-h\nu/2kT}(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + ...)$$

If $e^{-h\nu/kT} = y$, the sum (S)

$$1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \ldots = 1 + y + y^2 + \ldots$$

$$S = 1 + y + y^2 + \ldots$$

Multiplying both sides by y, one obtains

$$yS = y + y^2 + y^3 + \ldots = S - 1$$

$$yS = S - 1 \text{ (i.e.) } S - yS = 1$$

$$S(1 - y) = 1$$

$$S = \frac{1}{1-y}$$

Thus, $1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \ldots = \dfrac{1}{1-e^{-h\nu/kT}}$

$$f'_v = e^{-h\nu/2kT}/(1 - e^{-h\nu/kT})$$

However if the vibrational energies are measured with reference to the lowest vibrational level, the partition function (f_v) is given by eqn. 7.85. The 'scaled-partition function' f_v and f'_v the actual partition function are related as

$$f'_v = f_v e^{-h\nu/2kT}$$

$$f_v = \sum_{v=0}^{v=\infty}(e^{-\varepsilon_v/kT}) = \sum_{v=0}^{v=\infty} e^{-vh\nu/kT} \tag{7.85}$$

In many molecules the vibrational frequencies are high and so $h\nu/kT >> 1$. Consequently the value of f'_v becomes equal to f_v and approaches unity (eqn. 7.86).

If hν/kT is written, as x, equation 7.85 becomes,

$$f_v = \sum_{v=0}^{v=\infty} e^{-vx}; (v = 0, 1, 2, ...)$$

$$= 1 + e^{-x} + e^{-2x} + e^{-3x} + ...$$

$$= 1/(1 - e^{-x})$$

$$f_v = 1/(1 - e^{-x}) = (1 - e^{-x})^{-1}; (\textit{vide supra}) \qquad (7.86)$$

Because e^{-x} is negligible compared to 1, $f_v = 1$. *hν/k* has the dimension of temperature [(Js × s^{-1}/J k^{-1}) = k] and is called the *characteristic temperature for vibration, θ_v*.

Thus eqn. 7.86 can be written as

$$f_v = (1 - e^{-\theta_v/T})^{-1}$$

If there are several vibrational modes and if these are independent, one has to take the products of the *f* terms, one for each vibrational mode *i.e.* $f_v = \prod_1^i f_{i(v)}$ At moderate temperatures hν/kT is large and so $e^{-h\nu/kT}$ is rather small. The vibrational partition function f_v is then close to unity (prob. 7.7) *i.e.* all the molecules are likely to be in the lowest vibrational level. As the temperature is raised hν/kT decreases and f_v increases. At high temperature the molecules occupy higher vibrational levels also (v = 1, 2 etc). The contribution from the vibrational partition function to the energy becomes appreciable at high temperatures.

Eqn. 7.86 can be used to calculate the vibrational partition function for a diatomic molecule at all temperatures, on the basis of the assumption that the diatomic molecule is considered as a simple harmonic oscillator. Since the vibration frequency, *ν*, is known from spectroscopic data, it is possible to calculate f_v.

Problem 7.7. Calculate the vibrational partition function for nitrogen gas at 300 K, if the vibration frequency is 2360 × 10^2 m^{-1}.

$$f_v = [1 - e^{-h\nu/kT}]^{-1}$$

The vibration frequency is given in wave number units *i.e.* in m^{-1}. If $\bar{\nu}$ is the wave number corresponding to the vibration frequency *ν*, $\bar{\nu}\, c = \nu$. Hence

$$f_v = [1 - e^{-hc\bar{\nu}/kT}]^{-1}$$

$$hc\bar{\nu}/kT = \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 2360 \times 10^2}{1.38 \times 10^{-23} \times 300}$$

$$= 11.33$$

$$f_v[1 - e^{-hc\bar{\nu}/kT}]^{-1} = [1 - e^{-11.33}]^{-1} = 1.000$$

The vibrational contribution to the total energy of the molecule, in excess of the zero point energy can be calculated by using eqn. 7.85.

$$U_v = RT^2 \frac{d}{dT}[\ln . f_v] = \frac{RT^2}{f_v} . \frac{d}{dT}(f_v)$$

If eqn. 7.86 is written as $f_v = (1 - e^{-u})^{-1}$ where $u = \theta_v/T$, then

$$U_v = \frac{RT^2}{f_v}\frac{d}{dU}(f_v)\times\frac{dU}{dT} = \frac{RT^2}{(1-e^{-u})^{-1}}\frac{d}{dU}[(1-e^{-u})^{-1}]\frac{dU}{dT}$$

$$= \frac{RT^2}{(1-e^{-u})^{-1}}\frac{e^{-u}}{(1-e^{-u})^2}\frac{\theta_v}{T^2} = RT^2\frac{e^{-u}}{(1-e^{-u})}.\frac{\theta_v}{T^2}$$

$$U_v = R\,\theta_v \frac{1}{(e^u - 1)} \tag{7.87}$$

Eq. 7.86 expressed as $f_v = (1 - e^{-x})^{-1}$ on similar treatment gives,

$$U_v = RT^2\frac{d}{dT}[\ln(1-e^{-h\nu/kT})]^{-1}$$

$$= -RT^2\frac{d}{dT}\ln(1-e^{-h\nu/kT})$$

$$= \frac{-RT^2}{(1-e^{-h\nu/kT})}e^{-h\nu/kT}\left(\frac{-h\nu}{kT^2}\right)$$

Writing $h\nu/kT$ as x

$$= \frac{RT^2}{(1-e^{-x})}e^{-x}\left(\frac{x}{T}\right) = \frac{RTxe^{-x}}{(1-e^{-x})} \tag{7.88}$$

Eqn. 7.88 can also be derived by using f_v'. The vibrational energy, $U_v = kT^2\frac{d}{dT}[\ln f_v']^L$

$$U_v = LkT^2\frac{d}{dT}\ln[e^{-h\nu/2kT}/(1-e^{-h\nu/kT})]$$

$$= LkT^2\left[\frac{h\nu}{2kT^2} + \frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})}\times\frac{h\nu}{kT^2}\right]$$

$$= \frac{Lh\nu}{2} + Lh\nu\frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})}$$

$Lh\nu/2$ is the zero point energy per mol *i.e.* U_0.

$$U_v - U_0 = Lh\nu \frac{e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})}$$

$$(U_v - U_0)/T = \frac{Lh\nu}{T}\left(\frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}\right)$$

If $h\nu/kT$ is written as x

$$(U_v - U_0)/T = \frac{Rx.e^{-x}}{(1 - e^{-x})}$$

The values of $(U_v - U_0)/T$ corresponding to various values of x have been tabulated by Aston [H.S. Taylor and S. Glasstone, Treatise on Physical Chemistry, III Edn. Vol. 1, p. 655]. If ν is known one can calculate the vibrational contribution to the internal energy at any temperature. It will be seen that this equation reduces to eqn. 7.88 if $U_0 = 0$ *i.e.* if the scaled partition function is used.

Dividing both the numerator and denominator by e^{-x}, eqn. 7.88 becomes

$$U_v = \frac{RT.x}{(e^x - 1)} \qquad (7.89)$$

The vibrational contribution to the heat capacity is

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[RT\frac{h\nu/kT}{(e^{h\nu/kT} - 1)}\right]$$

$$= R\left(\frac{h\nu}{k}\right)\frac{-1}{(e^{h\nu/kT} - 1)^2}e^{h\nu/kT}\left(-\frac{h\nu}{kT^2}\right)$$

$$= R\left(\frac{h\nu}{kT}\right)^2 e^{h\nu/kT}(e^{h\nu/kT} - 1)^{-2}$$

$$C_v = \frac{Rx^2e^x}{(e^x - 1)^2}; (x = h\nu/kT) \qquad (7.90)$$

The vibrational contributions to other thermodynamic functions are given below.

$$G_v = A_v = RT \ln (1 - e^{-x}) \qquad (7.91)$$

($\because f_v$ does not depend on V and $dP = 0$)

$$H_v = U_v = RTx\,(e^x - 1)^{-1} \qquad (7.92)$$

$$S_v = R[x(e^x - 1)^{-1} - \ln (1 - e^{-x})] \qquad (7.93)$$

Problem 7.8. The vibrational frequencies in m^{-1} for CO^2 are $\bar{v}_1 = 1350 \times 10^2$, $\bar{v}_2 = 672.2 \times 10^2$ and $\bar{v}_3 = 2396 \times 10^2$. The second mode of vibration has a degeneracy of 2. Calculate the following for CO_2(g) at 298 K.

(*i*) Vibrational partition function (f_v),

(*ii*) Vibrational contribution to C_v,

(*iii*) Vibrational contribution to entropy and

(*iv*) Characteristic temperature for vibration for each vibrational frequency.

(*i*) The partition function has to be calculated for each mode of vibration. Let these be f_1, f_2 and f_3.

$f_v = f_1, f_2^2, f_3$ ($\because$ second vibrational mode is doubly degenerate, so f_2^2 is used)

$$f_v = [1 - \exp(-hc\bar{v}/kT)]^{-1}$$

$$hc/kT = (6.625 \times 10^{-34} \times 3 \times 10^8)/(1.38 \times 10^{-23})(298) = 4.83 \times 10^{-5}$$

Hence for each $\bar{v}$ value the values required can be tabulated as follows.

$10^{-2}\bar{v}$ / m^{-1}	$x = \frac{hc\bar{v}}{kT}$ or $\frac{\theta_v}{T}$	θ_v/K	e^{-x}	f_v
1351	6.52	1942	0.00147	1.001
672.2	3.24	965.5	0.0389	1.040
672.2	3.24	965.5	0.0389	1.040
2396	11.56	3445	9.44×10^{-6}	1.000

$\therefore$ $f_v = 1.001\ (1.04)^2\ 1 = 1.083$

(*ii*) $C_v\ (\text{vib}) = Rx^2 e^x/(e^x - 1)^2$. (7.90)

The contribution from each mode of vibration has been calculated using the values of x and added.

x	$x^2e^x/(e^x - 1)^2$
6.52	0.063
3.24	0.445
3.24	0.445
11.56	0.0013
	0.9543

$$\therefore \quad C_v\ (\text{vib}) = 8.314 \times 0.9543$$
$$= 7.93\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(*iii*) Here also the contribution from each mode of vibration has to be calculated. Using Eqn. 7.93, S_V can be calculated.

$$S_V = R[x\ (e^x - 1)^{-1} \ln\ (1 - e^{-x})]$$

x	$x/(e^x - 1)$	$-\ln(1 - e^{-x})$	$\left[\frac{x}{(e^x - 1)} - \ln(1 - e^{-x})\right]$
6.52	0.0096	0.0015	0.0111
3.24	0.130	0.04	0.170
3.24	0.130	0.04	0.170
11.56	0.001	9.54×10^{-6}	0.00011
			0.35121

$$\therefore \quad S_V = 8.314\ (0.35121)$$
$$= 2.92\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(*iv*) The values of $\theta_v = h\nu/k$ are in the first table.

7.g.6. Electronic Partition Function

The electronic partition function, f_e' is given by the expression

$$\begin{aligned} f_e' &= (g_0)_e e^{-\beta(\varepsilon_e)_0} + (g_1)_e e^{-\beta(\varepsilon_e)_1} + (g_2)_e c^{-\beta(\varepsilon_e)_2} + \cdots \\ &= e^{-\beta(\varepsilon_e)_0}[(g_0)_e + (g_1)_e c^{-\beta(\Delta\varepsilon_e)_1} + (g_2)_e e^{-\beta(\Delta\varepsilon_e)_2} + \qquad (7.94) \end{aligned}$$

Here $\beta = 1/kT$, $(g_i)_e$ is the degeneracy of the i^{th} level and $(\Delta\varepsilon_e)_i = [(\varepsilon_e)_i - (\varepsilon_e)_0]$ is the difference in energy between the i^{th} electronic energy level and zeroth electronic energy level. The values of ε_e can be obtained directly from the electronic spectra of atoms and molecules.

Eqn. 7.94 can be written as

$$f_e' = f_e e^{-(\varepsilon_e)_0/kT}$$

where f_e is the scaled partition function, since the energies of all the electronic energy levels are measured with respect to the lowest electronic energy level (ground state). Except in a few cases, the values of $(\Delta\varepsilon_e)_i$ are quite large compared to kT (4.14×10^{-14} erg or 4.14×10^{-21} J at 300 K) so that an atom or molecule is more likely to be in its electronic ground state. In general, the lowest electronic levels of atoms and molecules are non-degenerate *i.e.* $(g_0)_e = 1$, except in the case of a few species like Tl $[(g_e)_0 = 2]$, $O_2[(g_e)_0 = 3]$, and NO $[(g_e)_0 = 2]$. Thus

$$f_e = (g_0)_e \text{ or } f_e' = (g_0)_e e^{-(\varepsilon_e)_0/kT}$$

In the evaluation of many of the thermodynamic quantities like U, G, S etc. (sec. 7.e.2) the term, $d \ln f_e'/dT$ occurs.

$$\ln f_e' = \ln(g_0)_e - [(\varepsilon_e)_0/kT]$$

$$\frac{d \ln f_e'}{dT} = (\varepsilon_e)_0/kT^2$$

If $(U_T)_e$ is the electronic contribution to internal energy at a temperature T and $(U_0)_e$ is that at 0 K.

$$(U_T)_e = kT^2\,(d\ln Z/dT) = L\,kT^2\,\left(d\ln f_e'/dT\right)$$

$$(U_T)_e = L\,kT^2\,(\varepsilon_e)_0/kT^2 = L(\varepsilon_e)_0$$

It will be noted that at low and lower temperatures the electronic contribution to the internal energy is independent of temperature.

$(U_T)_e - (U_0)_e$ is thus zero. Similarly

$$(S_T)_e = Lk\ln f_e' + L\,kT\left(d\ln f_e'/dT\right)$$

$$= Lk\ln (g_0)_e - \frac{Lk(\varepsilon_e)_0}{kT} + LkT\frac{(\varepsilon_e)_0}{kT^2}$$

$$(S_T)_e = Lk\ln (g_0)_e$$

The electronic contributions to entropy and energy of an assembly are thus the same at all ordinary temperatures. It will be seen that the same conclusion is arrived at by using f_e instead of f_e' since

$$f_e' = f_e e^{-(\varepsilon_e)_0/kT}$$

and $(\varepsilon_e)_0$ is small compared to kT. Electronic energy separations $(\Delta\varepsilon)_e$ are usually very large and so the exponential terms in eqn. 7.94 are all very small. For the ground state $(\varepsilon_e)_0$ is zero. Hence from eqn. 7.94, f_e' or f_e is unity.

An important exception to this result is encountered in the case of atoms and molecules having a degenerate ground state. In such a case from eqn. 7.94 it is seen that f_e' or $f_e = (g_0)_e$. In the case of alkali metals, for example, the ground state is doubly degenerate and the electronic partition function is 2. In the case of nitric oxide the first excited electronic energy level is doubly degenerate and lies 121×10^2 m^{-1} above the ground level which is also doubly degenerate. From eqn. 7.94,

$$f_e = 2 + 2e^{-(\Delta\varepsilon_e)_1/kT}$$

$$(\Delta\varepsilon_e)_1/kT = hc\bar{v}/kT$$

$$= \frac{6.625\times 10^{34}\times 3\times 10^8\times 121\times 10^2}{1.38\times 10^{-23}\,T}$$

$$= 174.2/T$$

$$f_e = 2 + 2\,e^{-174.2/T}$$

At room temperature (300 K), $f_e = 2 + 2\,(0.56) = 3.12$. Only at very high temperature will f_e approach 4.

7.g.7. Total or Combined Partition Function

This is given by the product of the separate partition functions (sec. 7.g.1). For a monoatomic species the translational partition function f_t alone is to be considered.

$$f_{\text{monoatomic}} = \frac{(2\pi \text{mkT})^{3/2}\text{V}}{\text{h}^3} \qquad (7.66)$$

For a diatomic molecule, it is assumed that the molecule is a rigid rotor even though the atoms are vibrating and the vibration is assumed to be harmonic in nature. Further these rotations and vibrations are considered to be independent. The total or combined partition function is represented as f^0

$$f_{\text{diatomic}} = f_t \cdot f_r \cdot f_v$$

$$f^0 = \frac{(2\pi \mathbf{m}\text{kT})^{3/2}\text{V}}{\text{h}^3} \cdot \frac{8\pi^2\ \text{IkT}}{\sigma \text{h}^2}(1-\exp[-\text{h}\,\nu/\text{kT}])^{-1} \qquad (7.95)$$

For polyatomic molecules it is generally supposed that the ground state of the molecule is non-degenerate *i.e.* consists of a single electronic level. The excited states do not contribute to the total partition function. A linear molecule containing more than 2 atoms is considered like a diatomic molecule. It has only two rotational modes. For a nonlinear polyatomic molecule the rotational partition function is given by eqn. 7.96.

$$f_r = \frac{8\pi^2(8\pi^3\ \text{I}_\text{A}\text{I}_\text{B}\text{I}_\text{C})^{1/2}(\text{kT})^{3/2}}{\sigma \text{h}^3} \qquad (7.96)$$

because of the three degrees of rotational freedom. Here I_A, I_B and I_C are the moments of inertia of the molecule with respect to three mutually perpendicular axes. While a linear molecule has (3n – 5) modes of vibration, a nonlinear molecule containing n atoms has (3n – 6) modes of vibration (sec. 7.i.3). Each of these vibrational modes will contribute one factor analogous to eqn. 7.86

to the total partition function. Hence in eqn. 7.95 one should include (3n – 6) or (3n – 5) factors, each of the form $[1 - \exp(-\text{h}\nu/\text{kT})]^{-1}$.

$$\text{i} = (3\text{n} - 5) \text{ or } (3\text{n} - 6) = \text{x}$$

or

$$f_v = \prod_{\text{i}=1}^{\text{i}=\text{x}} \left[1 - e^{-\text{h}\nu_\text{i}/\text{kT}}\right]^{-1} \qquad (7.97)$$

Depending upon the temperature, i will assume different values ranging from i = 1 to i = (3n – 5) or (3n – 6). Only at very high temperatures its value will become (3n – 5) or (3n – 6).

Table 7.5. Comparison of the three distribution laws

Sl. No.	Maxwell–Boltzmann	Fermi–Dirac	Bose–Einstein
1.	Particles are distinguishable ($a \neq b$)	Particles are indistinguishable	Particles are indistinguishable
2.	There is no restriction on the number of particles that can occupy the same energy state Possible distributions of two particles a, b between three energy states 1, 2 and 3 = 9 1 2 3 a b — a — b — a b b a — b — a — b a ab — — — ab — — — ab	There can be not more than one particle in each energy state Possible distribution of two particles a, a between three energy states = 3 1 2 3 a a — a — a — a a	There is no restriction on the number of particles that can occupy an energy state Possible distribution of two particles a, a between three energy states = 6 1 2 3 a a — a — a — a a aa — — — aa — — — aa
3.	Applicable to ideal gases and ideal crystals	Applicable to fermions *i.e.* electrons, protons, neutrons as well as atoms, ions or molecules with an odd number of elementary particles such as electrons, protons and neutrons (e.g.,) H^+, ^3He, etc.	Applicable to bosons *i.e.* photons, and atoms, ions and molecule with an even number of elementary particles such as electrons, protons and neutrons (e.g.) D^+, ^4He
4.	Number of complexions of non-equivalent arrangements $\dfrac{N!}{\pi_1^i n_i!}$ (where $N = \sum_1^i n_i$)	$\pi_1^i \dfrac{g_i!}{(g_i - n_i)!\, n_i!}$	$\pi_1^i \dfrac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}$
5.	$n_i = g / (e^{\alpha'} e^{\beta\varepsilon_i})$ (n_i = number of particles in the ith energy level having energy ε_i and degeneracy g_i	$n_i = \dfrac{g_i}{(e^{\alpha'} e^{\beta\varepsilon_i} + 1)}$	$n_i = \dfrac{g_i}{(e^{\alpha'} e^{\beta\varepsilon_i} - 1)}$