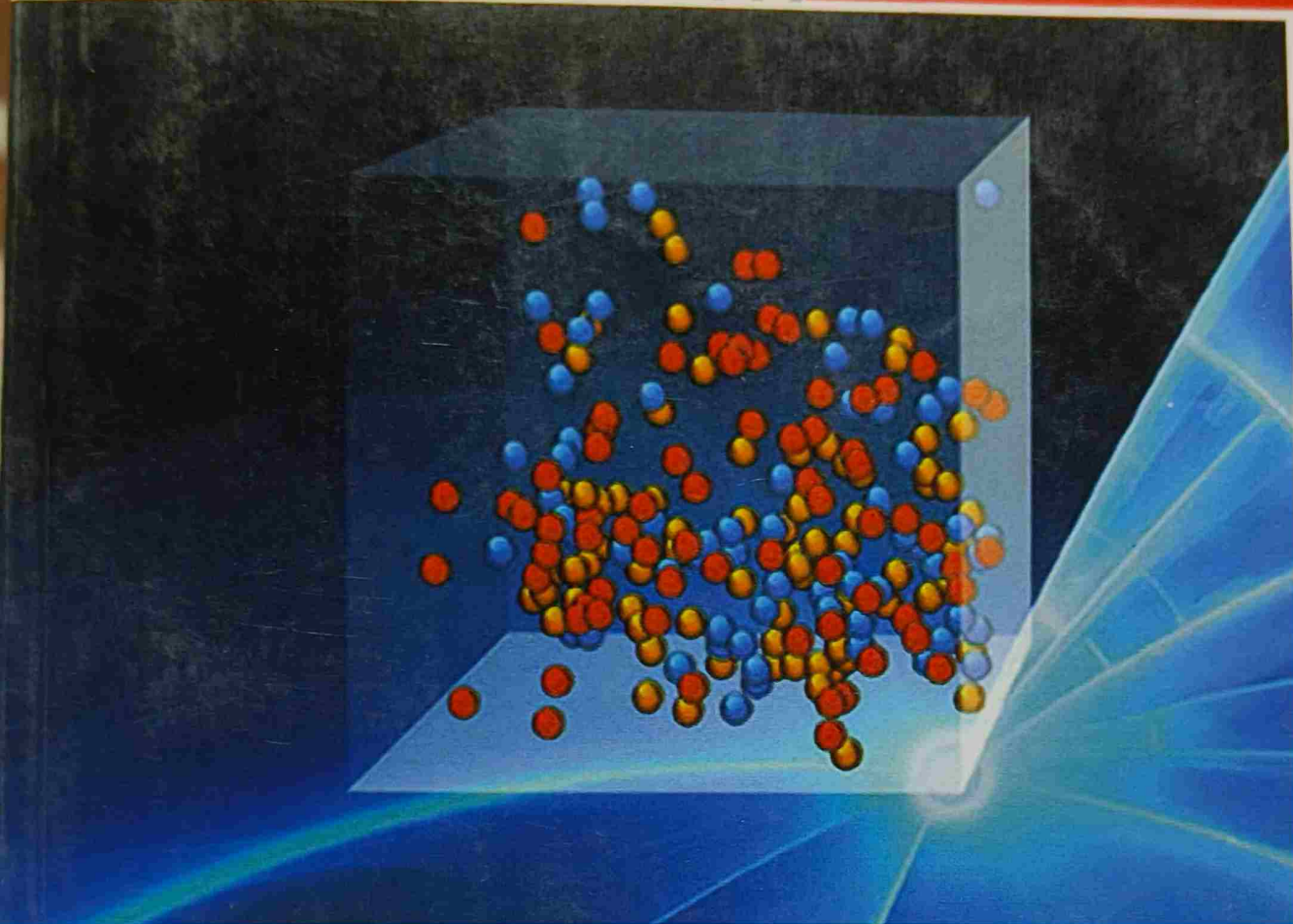




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MODERN'S

STATISTICAL MECHANICS

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B.Sc. PART-II, SEMESTER-IV
(GURU JAMBHESHWAR UNIVERSITY)

Syllabus

GURU JAMBHESHWAR UNIVERSITY

B.Sc. II Sem. IV

STATISTICAL MECHANICS

Marks for Major test (External) : 80

Marks for internal Exam : 20

Time : 3 Hours

Paper setter is required to set nine questions in all. Question No. 1 is Compulsory and is based on the entire syllabus consisting of eight short answer type questions each of 2 marks. The remaining eight questions is to be set uniformly having two questions from each unit. The student is required to attempt five questions in all selecting one question from each unit and Question No. 1 is Compulsory. The paper will include at least 20% of total marks as numerical problems.

UNIT-I

Statistical Basis of Thermodynamics. Statistical Basis, Probability and Frequency, Permutations and Combinations, Distribution of n distinguishable and indistinguishable particles in two boxes, Macrostate and Microstate, Thermodynamic Probability, Fluctuations and their Dependence on n : (narrowing of probability distribution with increasing n), Constraints on a System, Static and dynamics system, most probable state, Concept of cell in compartment, Concept of Ensembles and type of Ensembles (Qualitative Idea only).

Universal Law in Statistics. Fundamental Postulates of Statistical Mechanics, Density of Quantum states of energy of a particle, Entropy and thermodynamics Probability, Statistical Interpretation of 2nd law of thermodynamics, Partition function and Relation with Thermodynamics Quantities.

UNIT-II

Kinetic Theory of Gases. Maxwell-Boltzmann law of Distribution of Particle speed in an Ideal Gas and its Experimental Verification, Mean, RMS and Most Probable Speeds.

Molecular Collisions. Mean Free Path. Collision Probability. Estimates of Mean Free Path, Transport Phenomenon in Ideal Gases : (1) Viscosity, (2) Thermal Conductivity (3) Diffusion Brownian Motion and its Significance.

Equipartition Law. Degrees of Freedom, Law of Equipartition of Energy (No proof required) and its application to the specific heat of monoatomic and diatomic gases and its limitations.

UNIT-III

Classical Statistics. Phase space and Application to One Dimension Harmonic Oscillator and Free particle, Division of phase space into cells, Basic approach in three statistics, Maxwell-Boltzmann Distribution Law, Thermodynamic Functions of Finite Number of Energy Levels, Negative Temperature, Thermodynamic Functions of an Ideal Gas, Classical Entropy Expression, Gibbs Paradox.

UNIT-IV

Bose-Einstein Statistics. B.E. distribution law, Thermodynamic functions of a Completely Degenerate Bose Gas, Bose-Einstein condensation, properties of liquid He (qualitative description), Radiation as photon gas, Bose's derivation of Planck's law.

Fermi-Dirac Statistics. Fermi-Dirac Distribution Law, Thermodynamic functions of an ideal Completely Degenerate, Fermi Gas, Fermi Energy, Electron gas in a Metal, Specific Heat of Metals, Comparison of three statistics M-B, B-E and F-D.

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1

UNIT

STATISTICAL BASIS OF THERMODYNAMICS AND UNIVERSAL LAW IN STATISTICS

1.1. STATISTICAL PHYSICS

Statistical Physics is a branch of physics that deals with the study of physical behaviour of an assembly of large number of particles using the concepts of statistics. The particles may be molecules, atoms, neutrons, protons, electrons or photons. It has found extensive applications in thermodynamics, electrodynamics, optics, nuclear physics, radioactivity, solid state physics as well as in chemistry and biology. In this book, we will study the applications of statistical physics to thermodynamics.

Statistics is the science of collection, classification, presentation, analysis and interpretation of the numerical data. It aims at finding out the order in the data using the concepts of the theory of probability. For example, in a sample of gas, the individual molecules move about randomly, yet there is a certain law in which the velocity is distributed among the molecules. Thus, there exists some order in the apparent disorderly behaviour of the molecules. Statistical physics helps in the discovery of this order or the law of distribution of speeds.

To investigate and analyse a physical phenomenon, we generally separate (mentally or physically, if possible) a portion of the matter from rest of the universe. This separated portion of universe is called a *system* and the rest of universe around this system is called its environment. For studying a physical phenomenon, we focus our attention on the system and the environment in its immediate neighbourhood, which is also called the surrounding of the system. As explained earlier, the systems studied with the help of statistical physics consist of a large number of particles. Depending upon the nature of the particles constituting the systems we have two types of statistics, namely the classical statistics and the quantum statistics. Before embarking upon the study of thermodynamics of the physical systems, we are going to explain the nature and scope of these statistics. This will be the subject of chapter 2 and 3. In the rest of this chapter, we are going to introduce some of the basic concepts of probability and statistics.

1.2. DEFINITIONS OF BASIC TERMS USED IN THE STUDY OF PROBABILITY

1. System. Any object of interest is defined as a system. It is of two types :

(a) **Microscopic System.** A system containing of a few particles is called microscopic system. For example—electron, proton, atom, molecule etc. Generally, a system having about 10^3 particles is called microscopic system.

(b) **Macroscopic System.** A system containing a very large number of particles is known as macroscopic system. For example a drop of water (10^{20} molecules), 1 c.c. of hydrogen at N.T.P. (10^{19} molecules).

2. Experiment. The process of observing a phenomenon under deliberately arranged conditions to obtain the answers to certain questions connected with the phenomenon is called experiment. For example, tossing a single coin a number of times to find the percentage of the number of times we get **head up** is an experiment. Similarly tossing a number of coins simultaneously to find the percentage of the coins falling with heads up is also an experiment.

The experimental process is carried out according to certain set rules to ensure the completion of the process each time.

3. Trial. The performance of an experiment for the purpose of collecting data is called trial. The trial should have the following characteristics.

- It should be carried out in accordance with certain clearly defined rules.
- It can be repeated arbitrarily often.

4. Random trial. If the outcome of a trial depends on chance and so cannot be predicted uniquely, the trial is said to be random. The trials such as tossing a coin, rolling a die, drawing a card out of the well shuffled pack or drawing a ball out of the bag are the examples of random trials.

5. Event. The outcome of a trial is called event. For example, when we toss a coin, the coin may fall with its head upwards. It is an event. Similarly, when we roll a die, it may stop having the side with 4 dots upwards. It is also an event. Then with a coin two events are possible and with a die six events can take place.

6. Equally likely events. The events are said to be equally likely when there is no reason to expect any one of them in preference to the other. For example, when we toss a coin, both the 'head up' and 'tail up' events are equally likely to occur. Similarly, when we roll a die, any one of the six sides is equally likely to show up.

7. Exhaustive events. Total number of all possible outcomes of a trial are called exhaustive events. For example, when we toss a coin, the exhaustive events are 2. In throwing a die, the exhaustive events are 6. In drawing a card from a pack of 52 cards, the exhaustive events are 52.

8. Mutually exclusive events. Two or more events are said to be mutually exclusive if they cannot occur simultaneously as the outcome of a trial. For example, when we toss a coin there are two mutually exclusive events: 'head up' and 'tail up'. Only one of them can occur as a result of a trial. In rolling a die, there are six mutually exclusive events, and only one of them occurs as a result of the trial.

The mutually exclusive events are also called incompatible events.

9. Favourable events. The possible result of a trial which ensures the occurrence of a particular outcome is called favourable event. Suppose, we throw two dice. The number of cases in which the sum of the dots shown up on both the dice is 7 are as follows: (6, 1); (5, 2); (4, 3); (3, 4); (2, 5); (1, 6).

That is, in all there are six favourable events. In rolling one die, only one event is favourable to the showing up of face 6. Same is the case with other faces. In tossing a coin, one event favours head up and the other event favours the tail up.

10. Successive events. If two or more events take place one after the other, they are called successive events. Suppose we throw two coins one after the other, the events are called successive events.

11. Simultaneous events. If two or more events take place at the same time are called successive events. Suppose we throw two coins simultaneously, the events are called simultaneous events.

12. Independent events. Two events are said to be independent, if the occurrence of any one of them does not influence the chances of occurrence of other. Suppose, we have 5 red and 6 green balls in a bag. Let us draw a ball at random out of the bag. Suppose, the ball is red. Let us replace the red ball and then draw another ball. In this case, the result of the second draw will not depend upon the first one. That is, the events concerning the two draws are independent of each other.

13. Dependent events. Two events are said to be dependent, if the occurrence of any one of them influences the chance of occurrence of the other. In the above example (item 12), if the red ball taken out in the first draw is not replaced, before drawing the second ball, then the events concerning the two draws are said to be dependent. Because, the chances of occurrence of the second event will depend upon that of the first.

14. Sample space. The set of all possible outcomes of an experiment is called sample space. For example, when we toss a coin, the sample space consists of two events (H and T). If we throw a die the sample space consists of 6 events. When two coins are tossed, the sample space consists of $2 + 2 = 4$ events and throwing of two dice has a sample space of $6 \times 6 = 36$ events.

1.3. PROBABILITY

"Probably, it may rain today." What is implied in the above statement? It shows some amount of uncertainty about the rain. If we could quantify this uncertainty, we could talk of the probability of raining today. Laplace had defined the term probability as follows:

"Probability is the ratio of the number of favourable cases to the total number of equally likely cases." Suppose n is the number of favourable cases, and N is the total number of equally likely cases, then probability is given by:

$$P = \frac{n}{N} = \frac{\text{Number of cases in which the event of interest occurs}}{\text{Total number of equally likely possible cases}}$$

e.g. the probability of drawing a king of heart from a well shuffled pack of 52 cards is $\frac{1}{52}$ because here $n = 1$ and $N = 52$.

$$\therefore P = \frac{n}{N} = \frac{1}{52}$$

Note: Here in this definition, we have assumed that all events are equally likely to occur.

The Probability is of two types:

- 'a priori' probability and
- Statistical probability or empirical probability.

1.4. A PRIORI AND EMPIRICAL (OR STATISTICAL) PROBABILITY

(a) A Priori Probability.

It is the probability, which exists in our minds, before conducting the experiment.

The 'A priori' probability is a number between 0 and 1, indicating the chances of occurrence of the event, independent of the actual trial. It is something, that exists in our mind. In other words, it can be determined prior to the conduct of the actual experiment or a trial. It is specified on the basis of understanding or what is called the common sense about the occurrence of the event. However, there is a logic behind the manner in which it is determined. The logic concerns the equal probability of the occurrence of all events of the sample space. For example, when we toss a single coin, the sample space consists of 2 events H or T and each one of them is equally likely to occur. Similarly, when we toss two coins, the sample space consists of 4 events (HH, HT, TH, TT) and each one of them is equally likely to occur.

The a priori probability of an event is defined as the ratio of the cases favouring the event to the total number of the cases in the sample space.

$$P = \frac{\text{Cases favouring the event}}{\text{Total number of cases in the sample space}}$$

If 'N' be the total number of cases and out of them n are favourable to the event, then the probability of the event is:

$$P = \frac{n}{N}$$

For example, suppose, we wish to find the 'a priori' probability of showing up the face with one dot, when we throw a die. Then the sample space consists of:

$$S = \{1, 2, 3, 4, 5, 6\}$$

i.e. six events, out of which only one event favours the showing up of face 1. That is $N = 6$ and $n = 1$. Therefore, the a priori probability of showing the face 1 up is :

$$P(1) = \frac{1}{6}.$$

(b) Empirical (or Statistical) Probability.

The empirical probability is a number between 0 and 1, indicating the fraction of the cases in which the event actually occurs as a result of the experiment.

Thus, the empirical probability may be defined as the ratio of the cases in which the event actually occurs to the total number of trials in which we observed the occurrence of the event. That is :

$$P_{\text{empirical}} = \frac{\text{Actual number of cases in which the event occurs}}{\text{Total number of exhaustive cases in which the occurrence of the event is observed}}$$

If M be the total number of exhaustive cases and m be the number of cases in which the event E actually occurs, then

$$P_{\text{empirical}} = \frac{m}{M}.$$

Suppose we toss a coin 10 times and we find that the coin falls with head up 6 times, then the empirical probability of the head up event is :

$$P(H)_{\text{empirical}} = \frac{6}{10}.$$

Now, it may be recalled that, the a priori probability of the head up event is $\frac{5}{10} = \frac{1}{2}$. So, the two probabilities (a priori and empirical) may not be equal.

Relation between statistical and a priori probabilities.

The statistical probability tends to be equal to the 'a priori' probability when the number of trials is very very large. When we toss a coin only once, then it may fall with head up. So, the statistical probability of the 'head up' event is $\frac{1}{1} = 1$ and that of the 'tail up' event is $\frac{0}{1} = 0$. However, the a

priori probability even in this case, both for the head up or tail up events, was $\frac{1}{2} = 0.5$. Now, if we have 500 trials of tossing the coin, we may find head up 260 times and tail up 240 times. So, the statistical probability of head up event is $260/500 = 0.520$ and that of the tail up event is $240/500 = 0.480$. Both of them are very near the a priori probability 0.5.

Suppose the number of trials is 5000. In such a case, we may find head up 2520 times and tail up 2480 times. So the statistical probability of the head up event will be $2520/5000 = 0.504$ and that of the tail up event will be $2480/5000 = 0.496$. These values are still nearer to the a priori probability of 0.5. Therefore we can conclude that the statistical probability is equal to the a priori probability when the number of trials is very-very large (tends to infinity).

$$\lim_{M \rightarrow \infty} P_{\text{statistical}} = P_{\text{a priori}}$$

Remarks.

1. The 'a priori' probability is basically a theoretical concept. It cannot be applied when each of the events of the sample space is not equally likely to occur.
2. The empirical probability obtained from a single trial or from a trial involving small number of objects may be misleading.
3. The 'a priori' probability is also called mathematical probability or classical probability.
4. The empirical probability is also called statistical probability.

In the discussion that follows, the term probability will mostly refer to the 'a priori' probability, unless mentioned otherwise.

Example 1.1. Calculate the 'a priori' probability of drawing a queen out of a well shuffled pack of cards.

Solution. The pack of cards contains 52 cards, out of which four are queens. Each one of the queens is likely to be drawn out. Therefore :

Number of cases favourable to the event, $n = 4$.

Total number of possible cases $N = 52$.

A priori probability of the event, $P = \frac{n}{N}$

$$= \frac{4}{52} = \frac{1}{13}.$$

Example 1.2. Find the probability of getting two tails, when three coins are tossed in a single trial.

Solution. The possible events (sample space) are as follows :

TTT, TTH, THT, HTT, TTH, HTH, HHT, HHH.

Total number of (exhaustive) events, $N = 8$

No. of events in which we get two tails $n = 3$

$$\text{Probability of getting two tails, } P = \frac{n}{N} = \frac{3}{8}.$$

Example 1.3. Two dice are rolled simultaneously. Find the probability of getting the sum (of dots on the faces showing up) as 9.

Solution. Total number of equally likely events with two dice are $N = 36$.

Cases in which we will get a sum of 9 are as follows :

(6, 3); (5, 4); (4, 5); (3, 6).

So, the number of events favouring the sum of 9 are $n = 4$.

$$\text{Probability } P = \frac{n}{N} = \frac{4}{36}.$$

$$\text{or } P = \frac{1}{9}.$$

Example 1.4. In single throw of two dice, find the probability that the total number of dots showing up is a multiple of 3.

Solution. Total number of (exhaustive) events with two dice, $N = 36$.

The sum of dots showing up varies from 2 to 12. The sum of the dots which is multiple of 3 are : 3, 6, 9 and 12.

So the favourable cases are as follows :

For sum 3 : (2, 1), (1, 2)

For sum 6 : (5, 1), (4, 2), (3, 3), (2, 4), (1, 5)

For sum 9 : (6, 3), (5, 4), (4, 5), (3, 6)

For sum 12 : (6, 6)

Total number of favourable cases, $n = 12$

$$\text{Probability } P = \frac{n}{N} = \frac{12}{36} = \frac{1}{3}.$$

Example 1.5. What is the probability of drawing a king from a deck of 52 cards ?

Solution. Total number of cards = 52

Total number of exhaustive ways in which a card can be drawn out of the deck is $N = 52$.

Number of kings in the deck = 4

Total number of ways in which a king can be drawn out of the 4 kings is $N = 4$.

$$\text{Probability of drawing a king, } P = \frac{n}{N} = \frac{4}{52}$$

$$\text{or } P = \frac{1}{13}.$$

Example 1.6. What is the probability of drawing :

(i) a king (ii) king of diamond (iii) any card of diamond from a deck of 52 cards ?

Solution. (i) Total number of cards = 52

$$\text{Probability of getting a king in a draw} = \frac{4}{52} = \frac{1}{13}$$

(ii) There is only 1 king of diamond.

$$\therefore \text{Probability of getting king of diamond} = \frac{1}{52}$$

(iii) There are 13 cards of diamond.

$$\therefore \text{Probability of getting any one card of diamond} = \frac{13}{52} = \frac{1}{4}.$$

1.5. PROBABILITY OF OCCURRENCE AND NON-OCCURRENCE OF AN EVENT

Suppose p denotes the probability of occurrence of an event and q denotes the probability of non-occurrence of the same event. However, it is certain that if we make a trial the event will either occur or will not occur. So, the combined probability of occurrence and non-occurrence of the event is 1. Hence we can write

$$p + q = 1$$

or

$$q = 1 - p$$

That is, the probability of non-occurrence of an event is $1 -$ (the probability of its occurrence). For example, when we throw a dice, the probability of showing the face 1 up is $1/6$ and that of not showing the face 1 up is $1 - 1/6 = 5/6$.

1.6. MICROSTATES AND MACROSTATES OF A SYSTEM OF PARTICLES

The distinct arrangements of the particles of a system is called its microstate. For example, If three distinguishable particles are distributed in two compartments, then eight distinct arrangements are possible as shown below :

$[abc, \times], [ab, c], [ac, b], [bc, a],$

$[a, bc], [b, ac], [c, ab], [\times, abc].$

That is, there are eight microstates in which the system can exist. Thus, a microstate is the distribution of distinguishable particles among themselves. Each microstate to the system has the same a priori probability.

Macrostate.

The arrangement of the particle of a system without distinguishing then from one another is called macrostate of the system.

For example, if three particles are to be distributed in two compartments without distinguishing among the particles, then there are four possible arrangements as follows :

Arrangement 1, (3 0) = $[abc, \times]$

Arrangement 2, (2, 1) = $[ab, c]$ or $[ac, b]$ or $[bc, a]$

Arrangement 3, (1, 2) = $[a, bc]$ or $[b, ac]$ or $[c, ab]$

Arrangement 4, (0, 3) = $[\times, abc]$

Each one of them is called macrostate of the system. Thus, the number of particles in the two compartments defines the macrostate of the system. Accordingly, a macrostate in which there are 2 particles in one compartment and 1 particle in the other is denoted by (2, 1). Each macrostate may contain one or more microstates. For example, in distributing 3 particles in 2 compartments, there are three microstates in the macrostates (2, 1) and (1, 2). But there is only one microstate each in the macrostates (3, 0) and (0, 3). It is found that when n particles are to be distributed in two compartments, we have $(n + 1)$ macrostates and 2^n microstates.

1.7. DISTRIBUTION OF PARTICLES IN TWO EQUAL SIZED COMPARTMENTS

Distribution of osne particle in two compartments

Suppose an open box is divided into two equal sized compartments by means of a partition as shown in Fig. 1.7.1. Let a particle be thrown into the box from a certain distance. The particle is equally likely to fall into any one of the two compartments, because there is no reason why the particle should prefer any one of the compartment over the other. Thus, the a priori probability



Fig 1.7.1

of the particle entering the compartment 1 and $1/2$. Also, the a priori probability of the particle not entering the compartment 1 is $1/2$. Thus, entering of the particle into one of the two compartments is similar to the tossing of a coin. If we denote the particle by 'a', then the possible arrangement for distributing the particle into two compartments is as follows :

Comp. - 1	Comp. - 2
a	-
-	a

That is, there are two (2^1) possibilities, out of which one occurs, and the a priori probability of which is $1/2$.

Distribution of two particles in two equal sized compartments

If instead of one particle, we throw two particles into a box divided into two equal sized compartments, then the possible distribution of the particles is as shown in the table below. Let the particles be denoted by 'a' and 'b'.

Comp. - 1	Comp. - 2	Microstates	Macrostates
ab	-	$m_1 - (1)$	(2, 0)
a	b	m_2	(1, 1)
b	a	m_3	
-	ab	$m_4 - (1)$	(0, 2)

So, there are 2^2 microstates and $(2 + 1)$ macrostates.

Distribution of three particles in two equal sized compartments is shown in the table below :

Comp. - 1	Comp. - 2	Microstates	Macrostates
abc	-	$m_1 - (1)$	(3, 0)
ab	c	(3)	(2, 1)
ac	b		
bc	a		
a	bc	(3)	(1, 2)
b	ac		
c	ab		
-	abc	$m_8 - (1)$	(0, 3)

So, there are 2^3 microstates and $(3 + 1)$ macrostates.

Distribution of 4 distinguishable particles in 2 equal sized compartments is shown in the table below :

Comp. - 1	Comp. - 2	Microstates	Macrostates
abcd	×	$m_1 - (1)$	(4, 0)
abc	d	m_2	(3, 1)
bcd	a	m_3	
cda	b	m_4	
dab	c	m_5	
ab	cd	m_6	(2, 2)
ad	bc	m_7	
ac	bd	m_8	
bc	ad	m_9	
bd	ac	m_{10}	
cd	ab	m_{11}	
d	abc	m_{12}	(1, 3)
a	bcd	m_{13}	
b	cda	m_{14}	
c	dab	m_{15}	
×	abcd	$m_{16} - (1)$	(0, 4)

So there are 2^4 microstates and $(4 + 1)$ macrostates.

If the particles are indistinguishable, then

Compartment I	Compartment II	Microstates	Macrostates
(a, a, a, a)	-	1	(4, 0)
(a, a, a)	a	1	(3, 1)
(a, a)	(a, a)	1	(2, 2)
(a)	(a, a, a)	1	(1, 3)
-	(a, a, a, a)	1	(0, 4)

i.e. number of microstates depends upon whether the particles are distinguishable or indistinguishable.

e.g. the macrostates (3, 1) has four microstates if the particles are distinguishable and one microstate if the particles are indistinguishable.

Example 1.7. Write in tabular form the distribution of 3 particles in three compartments. Hence generalise the ways of distributing n particles in k compartments.

Solution.

Compartment		
1	2	3
abc	x	x
x	abc	x
x	x	abc
ab	c	x
bc	a	x
ca	b	x
x	ab	c
x	bc	a
x	ca	b
ab	x	c
bc	x	a
ca	x	b
a	bc	x
b	ca	x
c	ab	x
x	a	bc
x	b	ca
x	c	ab
a	x	bc
b	x	ca
c	x	ab
a	b	c
a	c	b
b	c	a
b	a	c
c	a	b
c	b	a

Thus, there are 27 ways in which the three particles can be distributed in three compartments. In other words, three particles can be distributed in three compartments in 3^3 ways.

Generalization.

From the above discussion, we can generalise that n particles can be distributed in k equal sized compartments in k^n ways.

If the particles are indistinguishable :

Compartment		
1	2	3
a, a, a	x	x
x	a, a, a	x
x	x	a, a, a
a, a	a	x
a	a, a	x
a, a	x	a
a	a, a	x
x	a	a, a
a	x	a, a
a	a	a

1.8. THERMODYNAMIC PROBABILITY OR FREQUENCY (W)

The number of microstates in a given macrostate is called thermodynamic probability of that macrostate. It may be denoted by W . For example, if three distinguishable particles are distributed in two compartments, then the macrostate (1, 2) has three microstates namely $[ac, b]$, $[ab, c]$, $[bc, a]$. Therefore, the thermodynamic probability of the macrostate (1, 2) is 3. We may denote it by :

$$W(1, 2) = 3$$

Similarly,

$$W(2, 1) = 3$$

$$W(3, 0) = 1$$

$$W(0, 3) = 1$$

W depends upon the distinguishable or indistinguishable nature of the particles.

The thermodynamic probability of a macrostate depends upon whether the particles are distinguishable or not. If the particles cannot be distinguished from one another, then each macrostate has only one microstate. So, the thermodynamic probability of each macrostate will be equal to 1.

Relation between thermodynamic probability and the probability of macro and microstates

If all the microstates of a given system have equal a priori probability, then the probability of a microstate is given by :

$$p = \frac{1}{\text{Total number of microstates of the system}} \quad \dots(1.8.1)$$

The probability of a macrostate is given by :

$$P = \frac{\text{Number of microstates in the given macrostate}}{\text{Total number of microstates of the system}}$$

But the number of microstates of the system is called thermodynamic probability W . Hence :

$$P = \frac{W}{\text{Total number of microstates of the system}} \quad \dots(1.8.2)$$

Comparing the equations (1.8.1) and (1.8.2), we find :

$$P = Wp$$

i.e. probability of a macrostate = Thermodynamic probability $\times$ probability of each microstate.

Significance of macrostates

It is found that the properties of a system depend upon the number of particles in the various compartments of the system. Therefore, knowledge of the macrostates (and not microstates) is essential for describing the behaviour of the system. It will be explained later that the compartments may be specified in terms of some property of the system such as energy, momentum etc. Suppose the two compartments differ with regards to the energy of the particles in them. Let each particle in compartment 1 have energy equal to $5\mu\text{J}$ and that in compartment 2 have energy equal to $10\mu\text{J}$. If the system consists of three particles, then the energies of the system in the different macrostates will be as follows :

Macrostate	Energy	Remarks
(3, 0)	$15\mu\text{J}$	$3 \times 5 + 0$
(2, 1)	$20\mu\text{J}$	$2 \times 5 + 1 \times 10$
(1, 2)	$25\mu\text{J}$	$1 \times 5 + 2 \times 10$
(0, 3)	$30\mu\text{J}$	$0 + 3 \times 10$

Since the thermodynamic probability of the macrostates (2, 1) and (1, 2) are higher than those of (3, 0) or (0, 3), therefore, the system has more chances of having energy $20\mu\text{J}$ or $25\mu\text{J}$ than $15\mu\text{J}$ or $30\mu\text{J}$.

Remarks. It may be mentioned here that the above example is a very crude one. It simply illustrates the significance of macrostates in describing the behaviour of the system.

1.9. PERMUTATIONS AND COMBINATIONS

The word permutation refers to *arrangement* and the word combination refers to the *formation of groups*.

Permutations

Suppose we have four objects marked a, b, c and d . If we take any two objects at a time, then they can be arranged as follows :

$ab, ba, ac, ca, ad, da, bc, cb, bd, db, cd, dc$.

That is, in all, 12 arrangements are possible. In arranging the objects, the order of their placing is also taken into consideration. Thus, ab and ba are two different permutations. Thus, *permutation* refers to the arrangement of n mutually distinguishable objects taking r at a time *such that the order of their placement is taken into account*. So, we say that 4 objects can be arranged in 12 ways by taking 2 objects at a time. That is, number of permutations of 4 objects by taking 2 at a time is 12. Mathematically, we denote it as :

$${}^4P_2 = 12.$$

It is found that the number of arrangements of n objects by taking r objects at a time is given by

$$P(n, r) = {}^nP_r = \frac{n!}{(n-r)!}$$

where

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

Similarly,

$$*(n-r)! = (n-r) \times (n-r-1) \times \dots \times 3 \times 2 \times 1$$

* $n!$ is read an n -factorial.

Thus :

$${}^4P_2 = \frac{4!}{(4-2)!} = \frac{4 \times 3 \times 2 \times 1}{2 \times 1} = 12.$$

Combination

In the combination, we form groups of the objects without paying attention to the order of their placements. Thus, four objects, marked a, b, c and d , can be combined by taking 2 at a time as follows :

ab, ac, ad, bc, bd, cd .

The order of placing the objects is immaterial in combination. Thus, ab and ba stand for the same combination, but different permutation.

Therefore, combination refers to the formation of groups of n mutually distinguishable objects by taking r objects at a time, such that the order of their placement is not taken into account.

So, we find that 4 objects can be combined together by taking 2 at a time in 6 ways. Symbolically, we write it as

$${}^4C_2 = 6$$

It is found that the number of combinations of n objects taking r at a time is given by :

$${}^nC_r = \frac{n!}{(n-r)!r!}$$

But

$$\frac{n!}{(n-r)!} = {}^nP_r$$

$\therefore$

$${}^nC_r = \frac{{}^nP_r}{r!}$$

or

$${}^nP_r = {}^nC_r \times r!$$

Also,

$${}^nP_n = \frac{n!}{(n-n)!} = \frac{n!}{0!}$$

But

$$0! = 1,$$

Therefore

$${}^nP_n = n!$$

And

$${}^nC_n = \frac{n!}{(n-n)!n!} = \frac{n!}{0!n!} = 1$$

1.10. MEANINGFUL AND MEANINGLESS ARRANGEMENTS

From the above discussion, we can conclude that the relation for permutations can be used when the order of placing the objects matters. However, when the same is immaterial, the relation for combinations should be used.

Suppose we wish to arrange n objects by taking r of them at a time. The total number of ways this can be done, when the order of their placing matters, is : nP_r . Now, the arrangement of r objects among themselves, can be done in $r!$ ways. If the order of placing the objects is not important, then nP_r arrangements in each combination are meaningless, because they are all alike. So, the meaningful arrangements will be the combinations of n objects taking r at a time, which will be nC_r .

$${}^n P_r = {}^n C_r \times r P_r$$

Therefore, we find :

Total number of arrangements = Number of meaningful arrangements $\times$ Number of meaningless arrangements

1.11. CONSTRAINTS AND EFFECTS OF CONSTRAINTS ON THE SYSTEM

The set of conditions that must be obeyed by a system are called constraints. For example, for distributing n particles in two compartments, we can put the constraints that no compartment should remain empty. The indistinguishable nature of the particles is also a constraint on the system.

The constraints may decrease the number of macro as well as microstates of the system. Suppose we wish to distribute three particles in two compartments. Then, the system will have the following macro and microstates provided the manner of relative placement of the objects is immaterial.

Macrostates	Microstates	
	Description	Number
(3, 0)	(abc, 0)	1
(2, 1)	(ab, c), (bc, a), (ca, b)	3
	(c, ab), (a, bc), (b, ca)	3
(0, 3)	(0, abc)	1

Now, if we put the constraint that no compartment should remain empty, then the macrostates (3, 0) and (0, 3) cannot exist. So, the system can have only two macrostates (2, 1) and (1, 2) with their corresponding microstates, which are six in all.

And, if we put the constraint on the system that the particles are indistinguishable, in such a case, we will have 4 macrostates (3, 0) ; (2, 1) ; (1, 2) and (0, 3). Each macrostate will have only one microstate and so the total number of microstates will also be reduced to 4.

Accessible and inaccessible states

A state that can exist in the light of given constraint is called accessible state. For example, in distributing 3 particles in 2 compartments under the constraint that no compartment should remain empty, only the macrostates (2, 1) and (1, 2) are accessible.

A state that cannot exist in the light of the given constraint is called inaccessible state. For example, in the case mentioned above, the macrostates (3, 0) and (0, 3) are inaccessible states.

1.12. DISTRIBUTION OF n PARTICLES IN TWO COMPARTMENTS

Suppose n particles are to be distributed in two compartments. Let there be no restriction on the number of particles that can occupy any one of the compartments.

Total number of micro and macrostates

We know that n particles can be distributed in k compartments in k^n ways, provided the particles are distinguishable and there is no restriction on the number of particles that can occupy any one of the compartments.

So, n particles can be distributed in 2 compartments in 2^n ways.

Therefore, the total number of microstates, in this case, is 2^n .

Possible macrostates are :

($n, 0$) ; ($n-1, 1$) ; ($n-2, 2$) ; ; ($n-r, r$) ; ; ($2, n-2$) ; ($1, n-1$) and ($0, n$).

That is, total number of macrostates = $n+1$.

Total number of arrangements

Let n particles are to be arranged among themselves. It means n particles are to occupy n positions. The first particle can occupy any one of the n positions. That is, there are n ways to arrange the first particle. The second particle can occupy any one of the ($n-1$) vacant positions. So, the first and the second particles can be arranged in $n(n-1)$ ways. Proceeding in the same way, we find that all the particles can be arranged in (n) ($n-1$) ($n-2$) ($n-3$) ($n-4$) (2) (1) ways.

Hence total number of ways to arrange n particles among themselves are :

$$n(n-1)(n-2)\dots\dots(3)(2)(1) = n! = {}^n P_n \quad (I)$$

Thermodynamic probability of the macrostate ($r, n-r$)

To arrange n particles in 2 compartments, let us consider the macrostate ($r, n-r$). In this state, r particles are in one compartment and ($n-r$) particles are in the other compartment. The arrangements of r particles among themselves in one compartment and that of ($n-r$) among themselves in the other compartment are meaningless. Now r particles can be arranged among themselves in $r!$ ways. Similarly ($n-r$) particles can be arranged among themselves in ($n-r$)! ways.

Therefore, total number of meaningless arrangements = $r!(n-r)!$ Also,

$$\left[\begin{array}{l} \text{Total number of} \\ \text{arrangements} \end{array} \right] = \left[\begin{array}{l} \text{No. of meaningful} \\ \text{arrangements} \end{array} \right] \times \left[\begin{array}{l} \text{No. of meaningless} \\ \text{arrangements} \end{array} \right]$$

$$\text{i.e.} \quad n! = \left[\begin{array}{l} \text{No. of meaningful} \\ \text{arrangements} \end{array} \right] [r!(n-r)!]$$

$$\therefore \text{Number of meaningful arrangements} = \frac{n!}{r!(n-r)!} \quad \dots(II)$$

Number of meaningful arrangements of a macrostate ($r, n-r$) is called thermodynamic probability of the state and is represented by the symbol $W(r, n-r)$.

$$\therefore W(r, n-r) = \frac{n!}{r!(n-r)!} = {}^n C_r = {}^n C_{n-r} \quad \dots(III)$$

Probability of a macrostate

The probability of a macrostate is defined as the ratio of number of microstates in that macrostate to the total number of microstates of the system. Suppose we wish to find the probability of the macrostate ($r, n-r$). Let us denote it by $P(r, n-r)$. Then,

$$P(r, n-r) = \frac{\text{Number of microstates in the macrostate } (r, n-r)}{\text{Total number of microstates of the system}}$$

$$= \frac{\text{Thermodynamic probability of the macrostates } (r, n-r)}{\text{Total number of microstates of the system}}$$

$$\text{or} \quad P(r, n-r) = \frac{W(r, n-r)}{2^n}$$

$$= \left[\frac{n!}{(n-r)!r!} \right] \times \frac{1}{2^n}$$

or

$$P(r, n-r) = \frac{n!}{(n-r)!r!} \times \frac{1}{2^n}$$

It is evident that

$$P(r, n-r) \propto W(r, n-r),$$

because 2^n is a constant for the given system.**Most probable macrostate**

The macrostate of a system having the highest probability is called the most probable macrostate. The probability of a macrostate is proportional to the thermodynamic probability of that macrostate. That is :

$$P(r, n-r) \propto W(r, n-r)$$

Therefore, probability of the macrostate is highest if its thermodynamic probability is the largest.

Suppose we wish to distribute n particles in 2 compartments, then the thermodynamic probability is the highest for a macrostate $(r, n-r)$, when $r = n/2$, provided n is even number. That is, highest

thermodynamic probability is for the macrostate $\left(\frac{n}{2}, n - \frac{n}{2}\right)$ or $\left(\frac{n}{2}, \frac{n}{2}\right)$. Hence, the thermodynamic probability of the most probable state of the system is :

$$W\left(\frac{n}{2}, \frac{n}{2}\right) = \frac{n!}{\frac{n}{2}! \frac{n}{2}!}$$

$\therefore$ Probability of most probable state,

$$P_m = \frac{n!}{\frac{n}{2}! \frac{n}{2}!} \cdot \frac{1}{2^n}$$

Minimum probability. The probability will be minimum when nC_r is minimum and value of nC_r is minimum when r is equal to either zero or n . The distribution $(0, n)$ or $(n, 0)$ has the minimum probability.

$$P(0, n) = \frac{n!}{0!n!} \cdot \frac{1}{2^n} = \frac{1}{2^n} = P(n, 0).$$

Example 1.8. 8 distinguishable particles are to be distributed in two compartments of 'equal a priori probability'. Calculate the total number of microstates of the system. What is the number of microstates in the most probable macrostate ?

Solution. The number of particles, $n = 8$

Number of microstates of the system $= 2^n = 2^8 = 256$

For the most probable macrostate $(r, n-r)$, we have $r = n/2$

Hence, the number of microstates in the macrostate $\left(\frac{n}{2}, \frac{n}{2}\right)$ is :

$$W\left(\frac{n}{2}, \frac{n}{2}\right) = \frac{n!}{\frac{n}{2}! \frac{n}{2}!}$$

$$= \frac{8!}{4!4!}$$

$$= \frac{8 \times 7 \times 6 \times 5 \times 4!}{4 \times 3 \times 2 \times 1 \times 4!} = 70$$

1.13. STIRLING FORMULA

When n is large, the $n!$ becomes very large and so the computation becomes quite a tedious process. Stirling had suggested a computational technique by taking the $\ln n!$ as follows :

Mathematically

For large value of n , $\ln n! = n \ln n - n$

Proof. We know that :

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

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

or

$$\ln n! = \sum_{x=1}^{x=n} \ln x \quad \dots(1.13.1)$$

Stirling showed that when n is large, the right hand side of the equation (1.13.1) can be written as :

$$\ln n! = \int_1^n \ln x \, dx = \int_1^n (\ln x) (1) \, dx$$

Integrating by parts, we get

$$\ln n! = \left[x \ln x \right]_1^n - \int_1^n \frac{1}{x} x \, dx$$

or

$$\ln n! = \left[x \ln x \right]_1^n - \int_1^n dx$$

or

$$\ln n! = \left[x \ln x \right]_1^n - \left[x \right]_1^n$$

or

$$\ln n! = n \ln n - 1 \ln 1 - (n-1)$$

But

$$\ln 1 = 0.$$

Therefore,

$$\ln n! = n \ln n - (n-1)$$

Since n is very very large, so we can write $(n-1) \cong n$.

Hence

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

This is called Stirling formula.

Example 1.9. Calculate the percentage error in using Stirling's formula

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

when $N = 5$

Solution.

Given

$$N = 5$$

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

$$\ln N! = \log 120 = 2.3026 \times \log_{10} 120$$

$$= 2.3026 \times 2.0792$$

$$= 4.7876$$

$$N \ln N - N = 5 \ln 5 - 5$$

$$= 5 \times 2.3026 \log_{10} 5 - 5$$

$$= 5 \times 2.3026 \times 0.6990 - 5$$

$$= 8.0476 - 5$$

$$\text{or } \ln N! = 3.0476$$

Error in using Stirling's formula,

$$\ln N! = 4.7876 - 3.0476$$

$$= 1.74$$

$$\% \text{ error} = \frac{1.74}{4.7876} \times 100$$

$$= 36.34\% \text{ Ans.}$$

1.14. STATIC AND DYNAMIC SYSTEMS

Static Systems

If the constituent particles of a system remain at rest in a particular microstate, it is called static system. Thus, the particles of the static system neither change their relative positions in the compartment nor do they move from one compartment to another. The static systems do not change on their own or due to internal causes (forces). They may be changed by external causes or forces.

If a static system is disturbed by some external agency, the system may transform from one macrostate to another. As soon as the cause of disturbance disappears, the system stays in its new macrostate. The probability of finding the system in a particular macrostate $(r, n-r)$ is proportional to its thermodynamic probability $W(r, n-r)$.

A system of coins or dice is an example of static systems. When the coins are tossed, they fall in a particular manner and stay as such. Same is the case with the dice.

Dynamic systems

If the constituent particles of a system can move so that the system goes from one microstate to another, it is called dynamic system. The particles of the dynamic system change their relative positions within the compartment and also go from one compartment to another, so that both the micro as well as macrostates of the system change with time. Thus, dynamic systems change on their own due to the internal causes (forces). They can also change due to the external causes or forces.

Most of the systems we wish to deal with are dynamic in nature. For example, a gas sample is an example of dynamic system. Its molecules are always in random motion, continuously colliding with

one another. They change their positions, momenta and energy. If a dynamic system is disturbed by some external cause and is then left to itself it tends to stay near a macrostate with maximum thermodynamic probability. That is, it tends to stay near the most probable macrostate.

1.15. EQUILIBRIUM STATE OF A DYNAMIC SYSTEM

The macrostate having maximum probability is termed as *most probable state*. For a dynamic system consisting of a large number of particles, the probability of deviation from the most probable state decreases very rapidly. As a result, we conclude that for a dynamic system the deviation from the most probable state is highly improbable. That is, appreciable deviation rarely occurs. So, for majority of time, the system stays in the most probable state. If the system is disturbed, it again tends to go towards the most probable state, because the probability of staying in the disturbed state is very small. Thus, the most probable state behaves as the equilibrium state to which the system returns again and again. It means that the behaviour of the system in general represents its properties in the most probable state.

The fraction of the time spent by a dynamic system in a particular macrostate is proportional to the thermodynamic probability of the macrostate. If the system consists of a small number of particles, then states other than the most probable state also have comparable thermodynamic probabilities. And in such a case, the system possesses good chances of remaining in states other than the most probable state or the equilibrium state. So, for a system consisting of a small number of particles, the most probable state may not be the equilibrium state. Such system cannot be dealt with by using the concepts of statistical physics. In other words, strictly speaking, statistical physics is useful in studying the behaviour of the systems which consist of a large number of particles.

1.16. DISTRIBUTION OF n DISTINGUISHABLE PARTICLES IN K COMPARTMENTS OF UNEQUAL SIZES

Suppose a system consists of n distinguishable particles contained in a box. The box itself may be divided into k compartments of unequal sizes (Fig. 1.16.1). Let us consider that in a particular macrostate denoted by $(n_1, n_2, n_3, \dots, n_k)$, n_1 particles are contained in 1st compartment, n_2 particles are contained in 2nd compartment, n_k particles are contained in the k th compartment. Therefore, the total number of particles in the system are :

$$n = n_1 + n_2 + n_3 + \dots + n_k$$

Suppose, the thermodynamic probability of this particular macrostate is denoted by $W(n_1, n_2, n_3, \dots, n_k)$. The expression for it can be obtained as follows.

The total number of microstates of the system of n particles (as explained in section 5.9) is given by $n! = n \cdot (n-1) \cdot (n-2) \cdot \dots \cdot 1$.

The arrangement of n_1 particles among themselves in the first compartment can be done in $n_1!$ ways. These arrangements of n_1 particles among themselves are meaningless. Similarly, $n_2!$ permutations of n_2 particles in the second compartment are meaningless. The total number of meaningless permutations in the first and second compartments are $(n_1!) \times (n_2!)$. In the same way, the total number of meaningless permutations of the particles among themselves in the various compartments (k in all) will be given by :

$$N_{ml} = (n_1!) \times (n_2!) \times (n_3!) \times \dots \times (n_k!)$$

$$\text{or } N_{mf} = \prod_{i=1}^{i=k} n_i! \quad \dots(i)$$

where $\prod$ stands for the product $(n_1!) \times (n_2!) \times \dots \times (n_k!)$

Also, we know that :

$$\left[\text{Total number of arrangements} \right] = \left[\text{Meaningful arrangements} \right] \times \left[\text{Meaningless arrangements} \right]$$

$$\text{or } n! = \left[\text{Meaningful arrangements} \right] \times \left[\prod_{i=1}^{i=k} n_i! \right] \quad \dots(ii)$$

The meaningful arrangements = thermodynamic probability of the macrostate $W(n_1, n_2, n_3, \dots, n_k)$

Therefore, the above relation can be written as :

$$n! = W(n_1, n_2, n_3, \dots, n_k) \prod_{i=1}^{i=k} n_i! \quad \dots(1.16.1)$$

$$\text{or } W(n_1, n_2, n_3, \dots, n_k) = \frac{n!}{\prod_{i=1}^k n_i!} \quad \dots(1.16.1)$$

Division of space into cells

The relation (1.16.1) has been obtained when the space or the box is divided into unequal sized compartments. The probability of a particle going into anyone of the k compartments is not the same. The distribution of the particles in the space or the box can be further analysed by dividing the box into small cells, each of the same size, so that the a priori probability of a particle going into anyone of the cells is the same. Since the compartments are of different sizes, therefore the number of cells in the cells is the same. Suppose, $g_1, g_2, g_3, \dots, g_k$ are the number of cells in the first, second, third, ..., k th compartment respectively. If G be the total number of cells into which the space is divided, we have :

$$g_1 + g_2 + g_3 + \dots + g_k = G$$

The division of space into cells further changes the thermodynamic probability of the state $(n_1, n_2, n_3, \dots, n_k)$, because now the distribution of n_i particles in the i th compartment becomes meaningful, which was not the case when the compartment was not divided into cells. If N_{mf} denotes the number of meaningful arrangements in the presence of the cells, then the values of N_{mf} can be obtained as given ahead.

Suppose there is no restriction to the number of particles that can go to any cell. Let us consider the distribution of n_i particles in g_i cells. The first particle can go into g_i cells in g_i ways. The second particle can also go into g_i cells in g_i ways. If we throw both the particles, then they go into g_i cells in $g_i \times g_i = g_i^2$ ways. In this way, it can be shown that n_i particles can go into g_i cells in $(g_i)^{n_i}$ ways. So, considering all the compartments, we find that the number of meaningful arrangements of the particles

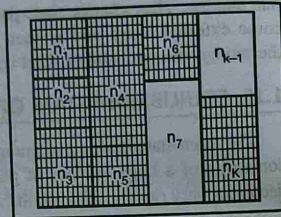


Fig. 1.16.1

in all the cells of the space is given by :

$$N_{mf} = (g_1)^{n_1} (g_2)^{n_2} (g_3)^{n_3} \dots (g_k)^{n_k}$$

$$\text{or } N_{mf} = \prod_{i=1}^{i=k} (g_i)^{n_i}$$

Now when we consider the cells into which each compartment has been divided, the arrangement of particles within the compartment into its various cells becomes meaningful. The relation

$$W(n_1, n_2, n_3, \dots, n_k) = \frac{n!}{n_1! n_2! n_3! \dots n_k!}$$

must be multiplied by the total number of ways (N_{mf}) in which the particles in various compartments can be arranged in cells within those very compartments.

Hence the total number of equally likely ways in which the particles can be arranged in $g_1, g_2, g_3, \dots, g_k$ cells belonging to compartments 1, 2, ..., k respectively in such a way that $n_1, n_2, n_3, \dots, n_k$ particles go into respective compartments.

Thus the total number of microstates in the macrostate $(n_1, n_2, \dots, n_k)$ is given by

$$W(n_1, n_2, \dots, n_k) = \frac{n!}{n_1! n_2! \dots n_k!} \times (g_1)^{n_1} \times (g_2)^{n_2} \dots (g_k)^{n_k}$$

$$\text{or } W = n! \left[\prod_{i=1}^k \frac{(g_i)^{n_i}}{n_i!} \right] \quad \dots(i)$$

$W(n_1, n_2, \dots, n_k)$ is the thermodynamic probability for the macrostate $(n_1, n_2, \dots, n_k)$.

Since each of W microstate has the same probability say p , the total probability for the macrostate is

$$P(n_1, n_2, \dots, n_k) = p \cdot W(n_1, n_2, \dots, n_k)$$

Therefore, the probability of a macrostate is proportional to the thermodynamic probability W .

In the above discussion we have considered cells of equal size. In two dimensional case equal size means **equal area** and in three dimensional case equal size means **equal volume**.

Example 1.10. 10 distinguishable particles are distributed in 4 compartments of equal sizes. Find the number of microstates in a macrostate (5, 3, 1, 1).

Solution. Thermodynamic probability of the macrostate $(n_1, n_2, \dots, n_k)$ is given by

$$W(n_1, n_2, \dots, n_k) = \frac{n!}{n_1! n_2! \dots n_k!}$$

Here $n = 10$ and $k = 4$

$$\begin{aligned} W(5, 3, 1, 1) &= \frac{10!}{5! \times 3! \times 1! \times 1!} \\ &= \frac{10 \times 9 \times 8 \times 7 \times 6 \times 5!}{5! \times 3 \times 2 \times 1} = 5040 \end{aligned}$$

1.17. DEVIATION FROM THE STATE OF MAXIMUM PROBABILITY

(Statistical fluctuations and their dependence on n)

When n particles are distributed in two compartments, the number of macrostates comes out to be $(n+1)$. The macrostate $(r, n-r)$ is of maximum probability if $r = n/2$. That is the macrostate with maximum probability is $\left(\frac{n}{2}, \frac{n}{2}\right)$. The probability of the macrostate $(r, n-r)$ is given by

$$P(r, n-r) = \frac{n!}{r!(n-r)!} \times \frac{1}{2^n} \quad \dots (1.17.1)$$

Let the probability of the most probable macrostate $\left(\frac{n}{2}, \frac{n}{2}\right)$ i.e. $P\left(\frac{n}{2}, \frac{n}{2}\right)$ be written as P_m and that for a macrostate $\left[\left(\frac{n}{2}+x\right), \left(\frac{n}{2}-x\right)\right]$ slightly different than the most probable state be written as P_x .

Here x is the deviation from the most probable state.

Then from equation (1.17.1) we can write :

$$P_m = \frac{n!}{\left(\frac{n}{2}\right)!\left(\frac{n}{2}\right)!} \times \frac{1}{2^n} \quad \dots (1.17.2)$$

Let us consider a macrostate which is slightly different from most probable state by x s.t. $x \ll n$.

This macrostate can be written as $\left(\frac{n}{2}+x, \frac{n}{2}-x\right)$.

The probability of this new macrostate P_x is given by

$$P_x = \frac{n!}{\left(\frac{n}{2}+x\right)!\left(\frac{n}{2}-x\right)!} \times \frac{1}{2^n} \quad \dots (1.17.3)$$

Multiplying and dividing R.H.S. of above equation by $\left(\frac{n}{2}\right)!^2$, we get

$$P_x = \frac{n!}{\left(\frac{n}{2}\right)!^2} \frac{\left(\frac{n}{2}\right)!^2}{\left(\frac{n}{2}+x\right)!\left(\frac{n}{2}-x\right)!} \cdot \frac{1}{2^n}$$

$$P_x = P_m \frac{\left(\frac{n}{2}\right)!^2}{\left(\frac{n}{2}+x\right)!\left(\frac{n}{2}-x\right)!} \quad \dots (1.17.4)$$

Taking natural logarithms, we find

$$\ln P_x = \ln P_m + \ln \frac{n!}{\left(\frac{n}{2}+x\right)!\left(\frac{n}{2}-x\right)!} - \ln \left(\frac{1}{2^n}\right) \quad \dots (1.17.5)$$

Applying Stirling's formula to relation (1.17.5), we get :

$$\ln P_x = \ln P_m + 2 \left[\frac{n}{2} \ln \frac{n}{2} - \frac{n}{2} \right] - \left[\left(\frac{n}{2}+x\right) \ln \left(\frac{n}{2}+x\right) - \left(\frac{n}{2}+x\right) \right] - \left[\left(\frac{n}{2}-x\right) \ln \left(\frac{n}{2}-x\right) - \left(\frac{n}{2}-x\right) \right]$$

$$\ln P_x = \ln P_m + n \ln \frac{n}{2} - n - \left(\frac{n}{2}+x\right) \ln \left(\frac{n}{2}+x\right)$$

$$- \left(\frac{n}{2}-x\right) \ln \left(\frac{n}{2}-x\right) + \left[\left(\frac{n}{2}+x\right) + \left(\frac{n}{2}-x\right)\right]$$

$$= \ln P_m + n \ln \frac{n}{2} - n - \left(\frac{n}{2}+x\right) \ln \left(\frac{n}{2}+x\right) - \left(\frac{n}{2}-x\right) \ln \left(\frac{n}{2}-x\right) + n$$

$$\text{i.e.} \quad \ln P_x = \ln P_m + n \ln \frac{n}{2} - \left(\frac{n}{2}+x\right) \ln \left(\frac{n}{2}+x\right) - \left(\frac{n}{2}-x\right) \ln \left(\frac{n}{2}-x\right) \quad \dots (1.17.6)$$

$$\text{Now} \quad \ln \left(\frac{n}{2}+x\right) = \ln \left[\frac{n}{2} \left(1 + \frac{2x}{n}\right)\right] = \ln \frac{n}{2} + \ln \left(1 + \frac{2x}{n}\right)$$

$$\ln \left(\frac{n}{2}-x\right) = \ln \frac{n}{2} \left(1 - \frac{2x}{n}\right) = \ln \frac{n}{2} + \ln \left(1 - \frac{2x}{n}\right)$$

Using Taylor's theorem to the second term, we find :

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \dots$$

$$\text{and} \quad \ln(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \dots$$

$$\therefore \quad \ln \left(\frac{n}{2}+x\right) = \ln \frac{n}{2} + \frac{2x}{n} - \left(\frac{2x}{n}\right)^2 \cdot \frac{1}{2} + \dots$$

Here higher terms are negligible, because n is very very large.

$$\text{Similarly :} \quad \ln \left(\frac{n}{2}-x\right) = \ln \frac{n}{2} - \frac{2x}{n} - \left(\frac{2x}{n}\right)^2 \cdot \frac{1}{2} - \dots$$

Substituting in equation (1.17.6), we get :

$$\ln P_x = \ln P_m + n \ln \frac{n}{2} - \left(\frac{n}{2} + x\right) \left[\ln \frac{n}{2} + \frac{2x}{n} - \left(\frac{2x}{n}\right)^2 \cdot \frac{1}{2} \right]$$

$$- \left[\frac{n}{2} + x\right] \left[\ln \frac{n}{2} + \frac{2x}{n} - \frac{2x^2}{n^2} \cdot \frac{1}{2} \right]$$

$$= \ln P_m + n \ln \frac{n}{2} - \left[\frac{n}{2} + x\right] \left[\ln \frac{n}{2} + \frac{2x}{n} - \frac{2x^2}{n^2} \right]$$

$$- \left[\frac{n}{2} - x\right] \left[\ln \frac{n}{2} + \frac{2x}{n} - \frac{2x^2}{n^2} \right]$$

$$\ln P_x = \ln P_m + n \ln \frac{n}{2} - \frac{n}{2} \left[\ln \frac{n}{2} + \frac{2x}{n} - \frac{2x^2}{n^2} + \ln \frac{n}{2} - \frac{2x}{n} - \frac{2x^2}{n^2} \right]$$

$$- x \left[\ln \frac{n}{2} + \frac{2x}{n} - \frac{2x^2}{n^2} - \ln \frac{n}{2} + \frac{2x}{n} + \frac{2x^2}{n^2} \right]$$

or $\ln P_x = \ln P_m + \frac{2x^2}{n} - \frac{4x^2}{n} = \ln P_m - \frac{2x^2}{n}$

or $\ln \frac{P_x}{P_m} = -2 \frac{x^2}{n}$

or $\frac{P_x}{P_m} = e^{-\frac{2x^2}{n}} = e^{-\frac{n}{2} \left(\frac{2x}{n}\right)^2}$

Putting

$$\frac{2x}{n} = f, \text{ we get}$$

$$\frac{P_x}{P_m} = e^{-\frac{nf^2}{2}} \quad \dots (1.17.7)$$

Here f is called fractional deviation from the most probable state.

Discussion.

Now, we analyse the relation between P_x and P_m for various values of the fractional deviation and the number of particles n .

Let $f = 0.1\%$. That is $f = 0.001 = 10^{-3}$

Then

$$\frac{P_x}{P_m} = e^{-n} \times 10^{-6} = \frac{1}{e^n \times 10^{-6}}$$

The ratios $\frac{P_x}{P_m}$ for different values of n are given in the table below :

n	$\frac{P_x}{P_m}$
10^3	$\frac{1}{e^{0.0005}}$
10^6	$\frac{1}{e^{0.5}}$
10^9	$\frac{1}{e^{500}}$
10^{12}	$\frac{1}{e^{500000}}$

It is apparent that as n increases the probability for 0.1% deviation from the most probable state goes on decreasing very rapidly.

The graph between f and $\frac{P_x}{P_m}$ is shown in the

Fig. 1.17.1.

The graph is called probability distribution curve. As n increases, the graph gets narrower, indicating that the possibility of deviation from the most probable state goes on decreasing.

It is evident that as n increases the rate of fall of P_x/P_m becomes more rapid.

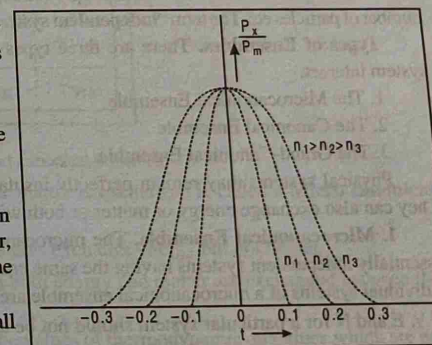


Fig. 1.17.1

Note that $e^{-\frac{1}{1,000,000}} \approx 10^{-434}$ and $e^{-\frac{1}{1,000,000}} \approx 10^{-434025}$. That is with 10^9 particles or with 10^{12} particles even 0.1% deviation from the most probable state is highly improbable. The system stays very near to the most probable state. In general, we may say that it stays in the most probable state. Therefore, the properties of the system will be same as those of the most probable microstate of the system.

Example 1.11. Calculate the percentage error in using Stirling's formula

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

when $N = 5$.

Solution.

Given that $N = 5$

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

$$\log N! = \log 120 = 2.3026 \times \log_{10} 120$$

$$= 2.3026 \times 2.0792$$

$$= 4.7876$$

$$N \log N - N = 5 \log 5 - 5$$

$$= 5 \times 2.3026 \log_{10} 5 - 5$$

$$\begin{aligned}
 &= 5 \times 2.3026 \times 0.6990 - 5 \\
 &= 8.0476 - 5 \\
 &= 3.0476 \\
 \text{Error in using Stirling's formula} \\
 &= 4.7876 - 3.0476 \\
 &= 1.74 \\
 \% \text{ error} &= \frac{1.74}{4.7876} \times 100 \\
 &= 36.34\% \text{ Ans.}
 \end{aligned}$$

1.18. STATISTICAL ENSEMBLES

The concept of ensembles was given by Gibbs. There can be infinite number of states of the gas for a given macroscopic condition of the gas, because there are infinite number of ways to distribute the molecules in space.

Thus, an ensemble may be defined as a collection of large number macroscopically identical but independent systems. Here the term "macroscopic identical" means that each of the system constituting an ensemble must satisfy the same macroscopic conditions such as volume, pressure, energy, temperature total number of particles etc. The term "independent systems" means that the systems are mutually non-interacting.

Types of Ensembles. There are three types of ensembles depending on manner in which their system interact.

1. The Microcanonical Ensemble
2. The Canonical Ensemble
3. The Grand-Canonical Ensemble.

Physical systems may remain perfectly insulated from each other or can interact in many ways. They can also exchange energy or matter or both with each other.

1. Microcanonical Ensemble. The microcanonical ensemble may be defined as a collection of essentially independent systems having the same energy E , volume V and number of particles N . All the individual systems of a microcanonical ensemble are separated by well insulated rigid walls. The values of V , E and N for a particular system should not be affected at all by the presence of other systems (see fig. 1.18.1). Hence, **energy and number of particles of systems are constant.**

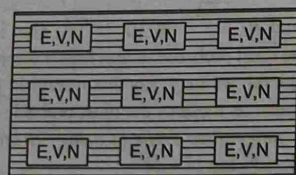


Fig. 1.18.1. Microcanonical ensemble

2. Canonical Ensemble. The canonical ensemble may be defined as a collection of essentially independent systems having the same volume V , temperature T and number of particles N . All the systems are in thermal contact with each other. A canonical ensemble is symbolically represented in fig. 1.18.2. We see that all the individual systems of the canonical ensemble are separated by rigid, impermeable, diathermic walls (conducting wall). Heat can be exchanged between the systems through these conducting walls, till they reach at common temperature T . Hence, In this canonical ensemble, the **systems can exchange only energy but matter (particles) does not exchange.**

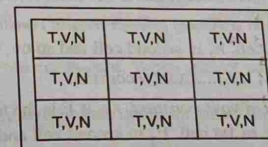


Fig. 1.18.2. Canonical ensemble.

3. Grand-Canonical Ensemble. The Grand-canonical ensemble may be defined as a collection of large number of essentially independent system having the same **volume V , temperature T and chemical potential μ** . Fig. 1.18.3 represents the Grand-canonical ensemble. All the **individual systems** of a grand-canonical ensemble are separated by permeable, rigid and conducting walls. Hence, the **exchange of heat energy and particles can take place between the systems** till all the systems arrive at common temperature T and the chemical potential μ .

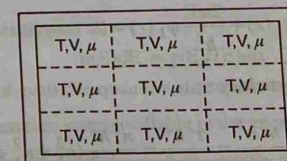


Fig. 1.18.3. Grand-canonical ensemble

Thus, an ensemble in which neither energy nor matter is exchanged is called a **Micro canonical ensemble.**

A **Canonical ensemble** is that in which the systems exchange energy but not matter.

A **Grand canonical ensemble** is that in which both energy and matter are exchanged between the systems.

Note. The concept ensemble is useful to find the values of thermodynamic quantities which are not very sensitive to the method of measurement.

1.19. POSTULATES OF STATISTICAL PHYSICS

Statistical mechanics is based on following postulates :

- (i) Any gas is considered to be made up of molecules which are in continuous random motion and these molecules behave like elastic spheres of extremely small size.
- (ii) In phase space, all the cells are of equal size.
- (iii) In a macrostate, all accessible microstates are equally probable. This is called the postulate of equal a priori probability. From this postulate, it follows that the probability of occurrence of a given macrostate is proportional to the number of microstates that corresponds to that given macrostate. The probability that the system will possess energy E is proportional to $W(E)$

$$\text{i.e.} \quad P(E) \propto W(E)$$

$$\text{or} \quad P(E) = c W(E),$$

where c is constant of proportionality.

- (iv) The equilibrium state of a gas corresponds to the macrostate of maximum probability.
- (v) Total number of molecules in a system always remain constants. i.e. if there are n molecules and n_1 molecules in the 1st cell, n_2 in second cell and so on, then
- $$n = n_1 + n_2 + \dots = \text{constant}$$
- (vi) Total energy of the system is always constant. i.e. if E is the total energy of the system and E_1 is the energy of each particle in 1st cell, E_2 in second cell and so on, then
- $$E = E_1 + E_2 + \dots = \text{constant}$$

1.20. DENSITY OF QUANTUM STATES OF ENERGY OF A PARTICLE

The density of states gives the number of allowed electron (or hole) states per unit volume at a given energy. It can be derived from basic quantum mechanics.

Let us consider a free particle of mass m in 3-dimensional cube of side L . The solution of time independent Schrodinger equation

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_k(r) + \frac{2mE}{\hbar^2} \psi_k(r) = 0$$

The allowed energy levels of particle is

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2 n^2}{2mL^2} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad \dots(1)$$

where,

$$n_x = 1, 2, 3, \dots$$

$$n_y = 1, 2, 3, \dots$$

$$n_z = 1, 2, 3, \dots$$

The lowest energy level (ground state) occurs for $n_x = n_y = n_z = 1$.

Which is non-degenerate, (i) If energy levels are degenerate then there will be a very large number of quantum states contained in (dE) small energy level. Which is represented in term of density of quantum states, denoted by $g(E)$ (ii) If the particle having same energy in first excited state can be in any of the three quantum states. Such energy level with three wave functions ψ_1 , ψ_2 and ψ_3 will be called three fold degenerate.

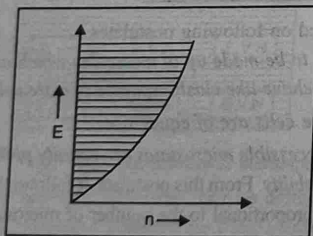


Fig. 1.20.1.

Statement. The density of quantum states $g(E)$ may be defined as the number of quantum states per unit energy range at the given energy E .

The number of quantum states in the energy range between E and $E + dE$ is given as

$$g(E) = \frac{2\pi}{h^3} (2m)^{3/2} E^{1/2} \quad \dots(2)$$

Here the spin of particle is not considered. When spin of particle is taken into consideration, like spin $\pm \frac{1}{2}$ for electrons, then there will be two quantum states for two possible spin orientations of the particle. Now, the number of quantum states is given as

$$g(E)dE = 2 \times \frac{2\pi}{h^3} (2m)^{3/2} E^{1/2} dE$$

$$g(E)dE = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE \quad \dots(3)$$

We can find the number of particles actually occupying quantum states in the energy range between E and $E + dE$.

The number of particles is expressed as

$$n(E)dE = g(E)f(E)dE \quad \dots(4)$$

Where $g(E)$ is the density of available quantum states at energy E .

$g(E)dE$ is the number of quantum states available in the energy range E and $E + dE$.

$f(E)$ is the distribution function of the system, which depend upon what kind of statistics (M.B., B.E, F.D.) we use.

The distribution function $f(E)$ can be defined as the average number of particles of the system occupying a single quantum state of energy E .

1.21. ENTROPY AND THERMODYNAMIC PROBABILITY

When an isolated system undergoes an irreversible process, there is a net increase of entropy of the system. Spontaneous expansion of gas into an evacuated space, diffusion of one gas into another etc. are all irreversible processes. There is an increase of randomness so entropy increases. All spontaneous processes represent changes from a less probable state to a more probable state and in such processes the entropy increases. There may be relation between the entropy of system in a given state and the probability of that state. In 1896, Boltzmann, derived an important relationship between entropy and probability (a statistical quantity). He conclude that the **probability** of the system in equilibrium state is **maximum**. The equilibrium state of a system is the state of its maximum entropy. If the given system is not in equilibrium then the change take place in the system until the equilibrium state is reached and the system attains a maximum entropy. Hence, both entropy and thermodynamic probability have their maximum value in the equilibrium state. The relation between them is called as Boltzmann's entropy relation ($S = k \log W$).

1.22. STATISTICAL INTERPRETATION OF 2ND LAW OF THERMODYNAMICS

Second law of thermodynamics cannot be derived from first law. It requires another thermodynamical parameter for description and mathematical formulation. This parameter is entropy. Entropy characterises the direction in which a thermodynamic process can take place. Second law of thermodynamics also

stands for the same. The second law of thermodynamics is a generalization of many observations and experiences. The important fact about this law is that it is concerned with the direction in which energy transfer takes place. In actual practice, there is no engine possible which can convert heat from the single source into useful work, without rejecting some amount of heat to a sink at a lower temperature. This is the base of the second law of thermodynamics.

In statistical mechanics, the basis of the second law is experiences and observations that the natural phenomenon must proceed from states of less probability to larger probability. The general rule states that more ordered states have smaller probability. Hence we can state that natural processes proceed from more ordered states to less ordered states.

1.23. PARTITION FUNCTION AND ITS RELATION WITH THERMODYNAMIC QUANTITIES

(a) **Partition Function (z)**: A partition function (z) gives information that how the gas molecules in a system are distributed or partitioned among the various energy levels.

Consider a system of ideal gas molecules obeying Maxwell Boltzmann distribution law. Suppose n_i molecules occupy i^{th} state with energy between E_i and $E_i + dE_i$ and g_i is the degeneracy.

$$\begin{aligned} n_i &= g_i e^{-\alpha} e^{-\frac{E_i}{kT}} \\ &= g_i A e^{-\beta E_i} \end{aligned} \quad \dots(1)$$

Where

$$\beta = \frac{1}{kT} \quad \text{and} \quad A = e^{-\alpha}$$

Total number of molecules in the system

$$N = \sum_i n_i$$

Using equation (1) we get

$$\frac{N}{A} = \sum_i g_i e^{-\beta E_i} = Z \quad \dots(2)$$

Where Z is called partition function

Hence: Partition function, $Z = \sum_i g_i e^{-\beta E_i} \quad \dots(3)$

(b) **Relation with Thermodynamic Quantities:**

(i) **With Entropy (S)**: The relation between entropy and the maximum thermodynamic probability W is given by

$$S = k \log W \quad \dots(1)$$

The total number of molecules for a classical system

$$N = \sum_i n_i$$

We know

$$W = N! \prod \frac{g_i^{n_i}}{n_i!} \quad \dots(2)$$

Where g_i represent cells of i^{th} compartment.

Taking logarithm both sides, we have

$$\log W = \log N! + \sum_i (n_i \log g_i - \log n_i!)$$

Using Sterling formula,

$$\log n! = n \log n - n, \text{ we get}$$

$$\log W = N \log N - N + \sum_i (n_i \log g_i - n_i \log n_i + n_i) \quad \dots(3)$$

According to Maxwell-Boltzmann distribution law,

$$\begin{aligned} n_i &= g_i e^{-\alpha} \cdot e^{-\beta E_i} \\ &= g_i A e^{-\beta E_i} \end{aligned}$$

Substituting n_i in eq. (3)

$$\begin{aligned} \log W &= N \log N - N + \sum_i [n_i \log g_i - n_i \log (g_i A e^{-\beta E_i}) + n_i] \\ &= N \log N - N + \sum_i n_i \log g_i - \sum_i n_i \log g_i - \sum_i n_i \log A + \sum_i n_i \beta E_i + \sum_i n_i \end{aligned}$$

On putting

$$\sum_i n_i = N \quad \text{(The total number of molecules)}$$

$$\sum_i n_i E_i = E \quad \text{(Total energy of gas molecules)}$$

$$\log W = N \log N - N - \sum_i n_i \log A + \beta E + N$$

$$= N \log N - \sum_i n_i \log A + \beta E$$

$$= N \log N - N \log A + \beta E$$

$$\log W = N \log \frac{N}{A} + \beta E$$

$$= N \log Z + \beta E \quad \dots(4) \quad \left[\because \frac{N}{A} = Z, \text{ partition function} \right]$$

Substituting equation (4) in equation (1), we have

$$S = k \log W$$

$$= kN \log Z + k\beta E$$

$$= kN \log Z + k \frac{1}{KT} \cdot E$$

$$S = kN \log Z + \frac{E}{T} \quad \dots(5)$$

But we know, energy for an ideal gas

$$E = \frac{3}{2} NkT$$

Putting in equation (5), we get

$$S = kN \log Z + \frac{3}{2} Nk$$

This equation represent entropy of the system of ideal gas molecules.

(ii) Relation of partition function (Z) with Helmholtz free energy (F) :

Helmholtz free energy (F) is given as

$$F = E - TS$$

$$= E - T \left(kN \log Z + \frac{E}{T} \right) \quad [\text{Using eq. (5)}]$$

$$= E - NkT \log Z - E$$

$$F = -NkT \log Z$$

(iii) Relation of partition function (Z) with total Energy E :

Consider a system having N particles and average energy is given as

$$\bar{E} = \frac{E}{N} = \frac{\sum_i n_i E_i}{\sum_i n_i}$$

$$= \frac{\sum_i g_i A e^{-\beta E_i} \cdot E_i}{\sum_i g_i A e^{-\beta E_i}}$$

$$\bar{E} = \frac{\sum_i g_i E_i e^{-\beta E_i}}{Z} \quad \left[\because Z = \sum_i g_i e^{-\beta E_i} \right]$$

For a case of isothermal isochoric transformation we can write

$$\left(\frac{\partial Z}{\partial T} \right)_V = \sum_i g_i \times \frac{E_i}{kT^2} \times e^{-\frac{E_i}{kT}}$$

$$= \frac{1}{kT^2} \times \sum_i g_i e^{-E_i/kT} \times E_i$$

$$kT^2 \left(\frac{\partial Z}{\partial T} \right)_V = \sum_i g_i E_i e^{-E_i/kT} = Z \bar{E}$$

or

$$\bar{E} = \frac{kT^2 \left(\frac{\partial Z}{\partial T} \right)_V}{Z}$$

Multiplying both side by N, we get

$$N \bar{E} = \frac{NkT^2 \left(\frac{\partial Z}{\partial T} \right)_V}{Z}$$

The total energy E is given by

$$E = N \bar{E} = \frac{NkT^2 \left(\frac{\partial Z}{\partial T} \right)_V}{Z}$$

$$E = NkT^2 \left[\frac{\partial}{\partial T} (\log Z) \right]_V$$

(iv) Relation of partition function (Z) with Enthalpy (H) :

Enthalpy can be given as

$$H = E + PV = E + RT$$

$$H = NkKT^2 \left[\frac{\partial}{\partial T} (\log Z) \right]_V + RT$$

(v) Relation of partition function (Z) with pressure (P) of gas :

Pressure is given as

$$P = \left(\frac{-\partial F}{\partial V} \right)_V$$

$$P = NkT \left[\frac{\partial}{\partial V} (\log Z) \right]_V$$

(vi) Relation of partition function (Z) with specific heat at constant volume C_V :

Specific heat is given as

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

$$= \frac{\partial}{\partial T} \left[NkT^2 \left\{ \frac{\partial}{\partial T} \log Z \right\} \right]$$

$$C_V = Nk \left[2T \frac{\partial}{\partial T} (\log Z) + T^2 \frac{\partial}{\partial T^2} (\log Z) \right]_V$$

MULTIPLE CHOICE QUESTIONS

Q 1.01. The probability of drawing a queen of hearts out of a well shuffled pack of cards is :

(a) $\frac{4}{52}$

(b) $\frac{52}{4}$

(c) $\frac{1}{52}$

(d) $\frac{2}{52}$

Q 1.02. A card is drawn out of a well shuffled pack of cards. The probability that it is either a king or ace is given by :

- (a) $\frac{8}{13}$ (b) $\frac{4}{13}$
(c) $\frac{1}{13}$ (d) $\frac{2}{13}$

Q 1.03. A pair of dice is thrown simultaneously. The probability of showing up a sum of 8 is :

- (a) $\frac{4}{36}$ (b) $\frac{5}{36}$
(c) $\frac{2}{36}$ (d) $\frac{1}{36}$

Q 1.04. If p_1 and p_2 be the probabilities of two independent events, then the probability of the two events to take place simultaneously is :

- (a) $p_1 + p_2$ (b) p_1/p_2
(c) $p_1 - p_2$ (d) $p_1 p_2$

Q 1.05. The value of the probability of any event cannot be :

- (a) 1 (b) $\frac{1}{2}$
(c) zero (d) negative.

Q 1.06. The thermodynamic probability of a macrostate depends upon the constraints on the system :

- (a) True (b) False

Q 1.07. The probability of occurrence of anyone of the microstates of a system is :

- (a) equal to the probability of corresponding macrostate
(b) called thermodynamic probability
(c) same
(d) zero.

Q 1.08. 8 particles are to be distributed in 2 compartments. There is no restriction on the number of particles that can go into either of the compartments. The number of microstates is :

- (a) 2 (b) 4
(c) 16 (d) 256.

Q 1.09. A system consists of 5 distinguishable particles to be distributed in two equal sized compartments. The thermodynamic probability of the macrostate (2, 3) is :

- (a) 5 (b) 10
(c) 15 (d) 25.

Q 1.10. Behaviour of a system can be described from the knowledge of its :

- (a) microstate in which it exists (b) number of microstate
(c) temperature of the system (d) none of these.

Q 1.11. The number of most probable macrostates for a system consisting of odd number of particles is :

- (a) 3 (b) 1
(c) 2 (d) 4.

Q 1.12. The probability of occurrence of the independent events is equal to their :

- (a) sum (b) difference
(c) product (d) ratio.

ANSWERS

- 1.01. (c) 1.02. (d) 1.03. (b) 1.04. (d) 1.05. (d) 1.06. (a)
1.07. (c) 1.08. (d) 1.09. (b) 1.10. (a) 1.11. (c) 1.12. (c).

SHORT ANSWER QUESTIONS

Q. 1. What is the probability of an event ?

Ans. The probability of a certain event is 1.

Q. 2. What is the probability of a random event ?

Ans. The probability of a random event is $\frac{1}{2}$.

Q. 3. What is the probability of an impossible event ?

Ans. The probability of an impossible event is 0.

Q. 4. What are the limits of variation of probability. ?

Or

What is the range of probability (P) of an event ?

Ans. The probability varies from 0 to 1. It is zero for the event that can never occur and 1 for event that is sure to occur.

Q. 5. What is the meaning of the principle of equal a priori probability ?

Ans. The assumption of equal probability for the event that are equally likely to occur is called the principle of equal a priori probability. e.g. when we toss a coin the probability of getting a head or tail is equal.

Q. 6. What are microscopic and macroscopic systems ?

Ans. Microscopic system. A system consisting of a few particles is called microscopic system e.g. electron, proton, atom, molecule etc.

Macroscopic system. A system consisting of very large number of particles is called macroscopic system e.g. drop of water (10^{20} molecules), 1 cc of hydrogen atom at N.T.P. (10^{19} molecules).

Q. 7. What is thermodynamic probability ?

Or

What is thermodynamic probability ? What is its minimum value ?

Ans. The number of microstates in a macrostate is called the thermodynamic probability of that macrostate. Its minimum value is 1.

Q. 8. Distinguish between a microstate and a macrostate.

Or

Explain the difference between a macrostate and microstate ?

Ans. Distinction between a microstate and a macrostate

Macrostate	Microstate
1. It is general distribution of particles of the system. 2. It gives information about the number of particles to be placed in a given number of compartments.	1. It is particular distribution of the particles of the system. 2. It gives the description of the particles to be placed in different compartments (i.e. which particles in which compartment).

Q. 9. Write down the various microstates and macrostates for system of 2-distinguishable particles distributed in 2-compartments.

Ans. Two distinct particles in two equal sized compartments :

Compt. I	Compt. II	No. of microstates in a macrostate	Macrostates
ab	—	m_1] 1	(2, 0)
a	b	m_2] 2	(1, 1)
b	a	m_3] 2	(0, 2)
—	ab	m_4] 1	

So, there are 2^2 microstates and $(2 + 1)$ macrostates.

Q. 10. Explain the difference between macrostate and a microstate with the help of an example.

Ans. **Microstate** is the distinct state of the particles of a system.

Macrostate is the arrangement of the particles of a system without distinguishing them from one another.

For example, if two distinguishable particles a and b are distributed in two compartments, then four distinct arrangements are $(ab, \times), (a, b), (b, a), (\times, ab)$, these are four microstates. And if two particles are to be distributed in two compartments without distinguishing the particles, then three states $(2, 0), (1, 1), (0, 2)$ are three macrostates.

Q. 11. How is the number of macrostates and microstates related to each other when the particles are indistinguishable?

Ans. For indistinguishable particles, the number of microstates is equal to the number of macrostates. That is, each macrostate has only microstate.

Q. 12. What is meant by (i) meaningful and (ii) meaningless arrangements?

Ans. (i) An arrangement is called *meaningful*, if it is in some way different from the other arrangements. For example, when three distinguishable particles, a, b and c are placed one after the other, then we get following arrangements :

$abc, bca, cab.$

All the three arrangements are meaningful, because they differ from one another in some way.

(ii) An arrangement is said to be *meaningless*, if it is similar to any other arrangement. For example, three distinguishable particles, a, b, c can be arranged themselves as follows :

$abc, bca, cab.$

However, when the particles are indistinguishable, we can replace b as well as c by a . So, the possible arrangements are :

aaa, aaa, aaa

Thus, out of the three arrangements, only one is meaningful while the others are meaningless.

Q. 13. What are the factors that determine the thermodynamic probability of a macrostate?

Ans. The thermodynamic probability of a macrostate depends upon the following factors :

- Distinguishable or indistinguishable nature of the particles.
- Constraints on the system.
- Number of compartments into which the space is divided.
- Number of cells into which each compartment of the space is divided.

Q. 14. What is meant by the most probable macrostate of a system?

Ans. Most probable macrostate is that state whose probability is maximum.

Since probability of a macrostate is proportional to its thermodynamic probability, hence most propable state has the highest thermodynamic probability.

Again, thermodynamic probability is equal to the number of microstates in the macrostate. Therefore, most probable macrostate is that which has maximum number of microstates. It is found that when n particles are to be distributed in two compartments, the most probable state is that in which each

compartment has $\frac{n}{2}$ particles. That is, in such a case, most probable macrostate is $\left(\frac{n}{2}, \frac{n}{2}\right)$.

Q. 15. What is the role played by the most probable state in determining the behaviour of a dynamic system?

Ans. For a system consisting of a large number of particles, the probability of deviation from the most probable state decreases very rapidly. As a result, we conclude that for systems consisting of large number of particles, the deviation from the most probable state is highly improbable. That is, appreciable deviation rarely occurs. So, most of the time the system stays in the most probable state.

Consider such a dynamic system in equilibrium. If the system is disturbed, it again tends to go towards the equilibrium state because the probability of staying in the disturbed state is very small. It means, that the behaviour of the system in general represents its properties in the most probable state. Then, most probable state helps us to deduce the properties or behaviour of the system in equilibrium state.

Q. 16. In how many ways 5 particles can be distributed in 2 compartments?

Ans. $2^5 = 32$.

Q. 17. Explain the necessity of introducing the concept of a cell.

Ans. If we have a system consisting of different compartments of unequal sizes, then the a priori probability of the particles going into a compartment is not equal, so to remove this difficulty, the concept of cell is used.

Q. 18. Explain the term constraint on a system.

Ans. Constraints are the set of conditions that must be obeyed by the system. For example, when n particles are distributed in two compartments, then constraint on the system

is :

$$n_1 + n_2 = n,$$

where n_1 is the number of particles in one compartment and n_2 that in the other.

Q. 19. What is the value of (i) nP_n (ii) nC_n (iii) $0!$ (iv) $1!$?

Ans. (i) $n!$ (ii) 1 (iii) 1 (iv) 1.

Q. 20. A pair of six faced dice are thrown simultaneously. What is the probability that both of them have their face 2 up ?

Ans. Number of possible events = 6

$$\text{Probability of the first dice falling with its face 2 up} = \frac{1}{6}$$

$$\text{Probability of the second dice falling with its face 2 up} = \frac{1}{6}$$

$$\therefore \text{Probability of both the dice falling with their face 2 up} = \frac{1}{6} \times \frac{1}{6} = \frac{1}{36}.$$

Q. 21. Show that the probability of a microstate corresponding to distribution of N -particles in two identical compartments is $\frac{1}{2^N}$.

Or

Calculate the probability of a microstate corresponding to distribution of N -particles in two identical compartments ?

Ans. In general, the total number of microstates for N -particles distributed in k -compartments is k^N .

So, number of microstates for N -particles distributed in two compartments = 2^N

Hence, probability of a microstate corresponding to distribution of N distinguishable particles in the compartments = $\frac{1}{2^N}$.

QUESTIONS

1. Define the meaning of the terms macrostate and microstate.
2. Taking the case of n particles distributed in 2 compartments, discuss the variation of probability of a macrostate on account of a small deviation from the state of maximum probability. Also plot your observations.
3. Derive an expression for the number of meaningful ways of arranging n distinguishable balls in k compartments of a box such that n_1 balls go into the first compartment, n_2 in the second compartment and so on.
4. Derive the expression :

$$P_x = P_{\max} e^{-\frac{f^2 n}{2}}$$

for a macrostate having a deviation x from the most probable macrostate for a distribution of n distinguishable particles in two identical compartments.

5. Explain that when n is very large, the system lies in the most probable macrostate.
6. What is the probability of an event ? A large number (n) of particles are distributed in two compartments of equal a priori probability. Discuss analytically the variation of probability of macrostate on account of small deviation from the state of maximum probability.
7. Evaluate number of microstates, macrostates and thermodynamic probability for the distribution of four distinguishable particles in two compartments of equal size.

8. Use the expression $\frac{P_x}{P_m} = e^{-\frac{f^2 n}{2}}$ to explain that as n increases, the probability of a macrostate

falls off, more and more rapidly even for a straight deviation w.r.t. the most probable macrostate.

9. Explain the stable equilibrium of a dynamic system having a large number of particles.
10. How do you define the most probable macrostate ? What is the role played by it in determining the behaviour of a system in equilibrium ?
11. Discuss in detail the distribution of four different particles in two identical compartments and tabulate the results.
12. What is the meaning and importance of the principle of equal a priori probability in statistical physics ?
13. What is the principle of equal a priori probability ?
14. Discuss thermodynamic probability.
15. Define thermodynamic probability and show that probability of a macrostate is proportional to its thermodynamic probability.
16. Explain the concept of macrostate, microstate and thermodynamic probability of microstate. What is the relation between thermodynamic probability and probability of a macrostate ?
17. What is meant by the term thermodynamic probability of a macrostate ? Show that all the microstates of a system have the equal a priori probability and the probability of a macrostate is directly proportional to the thermodynamic probability.
18. Define Microstate, Macrostate and Thermodynamical Probability and give their interrelation.
19. What is meant by microstate, macrostate and thermodynamic probability of statistical system ? Illustrate by arranging four particles into two compartments.
20. What is Thermodynamic Probability for distributing n distinguishable particles in two compartments. Find the probability for a macrostate and most probable macrostate.
21. Define thermodynamic probability for ' n ' distinguishable particles to be distributed in two compartments, prove that thermodynamic probability of macrostate ($n_1 + n_2$) is :

$$W(n_1, n_2) = \frac{n!}{n_1! n_2!} \text{ where } n = n_1 + n_2$$

22. Show that the probability of a microstate corresponding to distribution of n -particles in two compartments is $\frac{1}{2^n}$.
23. Write down in a tabular form the various microstates and macrostates of a system of 3-particles arranged in 3-compartments assuming the particles to be :
(i) distinguishable (ii) indistinguishable.

24. Explain the concepts of (i) micro and macrostates (ii) thermodynamic probability (iii) constraints on a system.
25. Suppose n -particles are to be distributed in two compartments with equal a priori probability. Find an expression for the thermodynamic probability of a macrostate slightly different from the most probable state.
26. For ' n ' distinguishable particles to be distributed in two compartments, prove that thermodynamic probability of macrostate (n_1, n_2) is :

$$W(n_1, n_2) = \frac{n!}{n_1! n_2!}, \text{ where } n = n_1 + n_2$$

27. Calculate the percentage error made in using the Stirling formula $\ln n! = n \ln n - n$, when $n = 5$.
[36.35%]
28. Prove that for a dynamic system, the fraction of the total time spent in any particular macrostate is proportional to the thermodynamic probability of that state.
29. Prove that the probability of a macrostate is equal to the product of a thermodynamic probability of a macrostate and the probability of a microstate.
30. Discuss the distribution of n distinguishable particles in k compartments which are further sub-divided into cells of equal a priori probability.
31. Derive an expression for the probability of a macrostate corresponding to N distinguishable particles in k compartments of different sizes.
32. Define a microstate and a macrostate.
33. What is the difference between a microstate and macrostate?
34. What is the difference between static and dynamic equilibrium?
35. (a) Explain the effect of constraints on the system.
(b) Show that probability $P(r, n-r)$ of a macrostate ($r, n-r$) is maximum when $r = n/2$, where

$$P(r, n-r) = \frac{n!}{r!(n-r)!} \frac{1}{2^n}$$

NUMERICAL PROBLEMS

1. Calculate the probability of drawing a king out of a well shuffled pack of cards. [Ans. $\frac{1}{13}$]
2. Calculate the probability of drawing a queen of hearts out of a well shuffled pack of cards. [Ans. $\frac{1}{52}$]
3. A card is drawn out of a well shuffled pack of cards. Calculate the probability that it is
(a) either a king or an ace (b) either king or ace of hearts. [Ans. (a) $\frac{2}{13}$ (b) $\frac{1}{26}$]
4. If a pair of dice is thrown simultaneously, calculate the probability of showing up a sum of :
(a) 8 (b) 10 (c) 12. [Ans. (a) $\frac{5}{36}$ (b) $\frac{1}{12}$ (c) $\frac{1}{36}$]

5. A pair of six faced dice with faces marked 1 to 6 is thrown. What is the probability that the sum of the numbers which shows up is 7? [Ans. $\frac{1}{6}$]

6. 2000 coins are thrown simultaneously. How many of them are likely to fall with their heads upwards? [Ans. 1000]

7. A dice is to be thrown 7200 times. How many times one may expect the face 1 to show up? [Ans. 1200]

8. A six faced die is thrown along with a coin. Calculate the probability that the dice falls with its face 3 upwards and the coin falls with its tail upwards. [Ans. $\frac{1}{12}$]

$$\text{Hint : } P_1 (\text{dice}) = \frac{1}{6} \text{ and } P_2 (\text{coin}) = \frac{1}{2}$$

9. Two six faced dice are thrown simultaneously. What is the probability that none of the two dice falls with face numbered 6 upwards? [Ans. $\frac{25}{36}$]

$$\text{Hint : } P_1 = \frac{5}{6}, P_2 = \frac{5}{6}$$

10. Two six faced dice are thrown simultaneously. What is the probability that one dice shows the face 6 and the other does not? [Ans. $\frac{5}{36}$]

$$\text{Hint : } P_1 = \frac{1}{6}, P_2 = \frac{5}{6}$$

11. A box is divided into 20 equal sized compartments. 5 balls are thrown into the box. Each ball has equal a priori probability of entering any one of the compartments. Calculate the probability for the third compartment to contain (i) none of the balls (ii) 1 ball (iii) 2 balls (iv) 3 balls (v) 4 balls (vi) all the 5 balls.

$$\text{Ans. (i) } \left(\frac{19}{20}\right)^5 \quad \text{(ii) } \left(\frac{1}{20}\right) \times \left(\frac{19}{20}\right)^4 \quad \text{(iii) } \left(\frac{1}{20}\right)^2 \times \left(\frac{19}{20}\right)^3$$

$$\text{(iv) } \left(\frac{1}{20}\right)^3 \times \left(\frac{19}{20}\right)^2 \quad \text{(v) } \left(\frac{1}{20}\right)^4 \times \left(\frac{19}{20}\right) \quad \text{(vi) } \left(\frac{1}{20}\right)^5$$

12. 20 particles are to be distributed in 2 compartments. Calculate the thermodynamic probability of the state (4, 16). The particles are distinguishable. [Ans. 48, 45]
13. In a system of 8 distinguishable particles distributed in 2 equal sized compartments, calculate the thermodynamical probability of the macrostate (2, 6). [Ans. 28]
14. 8 distinguishable particles are to be distributed in two compartments of 'equal a priori probability.' Calculate the total number of microstates of the system. What is the number of microstates in the most probable macrostate? [Ans. 256, 70]

2

UNIT

KINETIC THEORY OF GASES, MOLECULAR COLLISIONS AND EQUIPARTITION LAW

2.1. MAXWELL'S DISTRIBUTION OF MOLECULAR VELOCITIES IN AN IDEAL GAS

According to kinetic theory, a gas is made of very large number of molecules which are always in a state of motion. They are frequently colliding with one another and also with the walls of the containing vessel. Hence their speeds and direction of motion are changing. We may, therefore, conclude that at any time, molecules of all possible velocities are present in the gas. However, the value of the root mean square velocity of the gas molecules remains unchanged at a given temperature.

Maxwell considered the distribution of velocities among the molecules of the gas. He made the following assumptions :

1. The gas consists of molecules with all possible velocities between 0 and ∞ .
2. When the gas is in the steady state, its density remains, on the average, uniform throughout.
3. Though the velocities of individual molecules are changing, but definite number of molecules have velocities between definite ranges.

2.2. MAXWELL'S SPEED DISTRIBUTION LAW

In a gas, the speed of a molecule varies between 0 and ∞ . If n_u is the number of molecules having velocity (or speed) u , then n_u is given by

$$n_u = n a e^{-bu^2} = n \sqrt{\frac{b}{H}} e^{-bu^2} \quad \dots(2.2.1)$$

where b is a constant and is given by

$$b = \frac{m}{2kT}$$

Using eq. 2.2.1, we can determine the number of molecules per unit volume having speed between c and $c + dc$, where

$$c^2 = u^2 + v^2 + w^2 \quad \dots(2.2.2)$$

Let us consider the volume element in spherical polar coordinates (r, θ, ϕ) . The volume of this element is given by

$$dn \times c \, d\theta \times c \sin \theta \, d\phi = c^2 \sin \theta \, dc \, d\theta \, d\phi$$

The number of molecules per unit volume having velocity components lying between u and $u + du$, v and $v + dv$, w and $w + dw$ is given by

$$dn = n a^3 e^{-b(u^2 + v^2 + w^2)} du \, dv \, dw \quad \dots(2.2.3)$$

To obtain the number of molecules having speed between c and $c + dc$, replace $u^2 + v^2 + w^2 = c^2$

$$du \, dv \, dw = c^2 \sin \theta \, dc \, d\theta \, d\phi \quad \dots(2.2.4)$$

and integrate the expression for all values of θ and ϕ . Thus, we have

$$dn_c = n a^3 e^{-bc^2} c^2 dc \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi$$

$$dn_c = 4\pi n a^3 e^{-bc^2} c^2 dc \quad \dots(2.2.5)$$

The speed c is independent of θ and ϕ . Putting the values of constants a and b as $\sqrt{\frac{m}{2\pi kT}}$ and

$\frac{m}{2kT}$, we get

$$dn_c = 4\pi n \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}} dc$$

which is known as Maxwell's distribution law for speeds of molecules in gas. It applies to monoatomic gases and for the translational motion for diatomic and polyatomic gases.

The probability that its speed lies between c and $c + dc$.

$$\frac{dn_c}{n} = P(c) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}} dc \quad \dots(2.2.6)$$

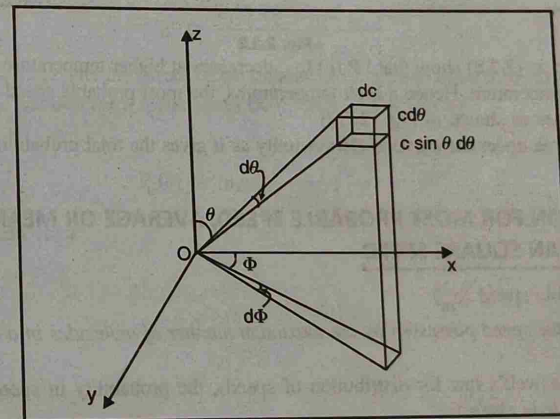


Fig. 2.2.1

Discussion of the Maxwellian Speed Distribution Law

(i) The probability function for a molecule to have speed c is given by

$$P(c) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}} \quad \dots(2.2.7)$$

When

$$c = 0, P(c) = 0,$$

thus, the probability of a molecule having zero speed is zero.

(ii) At low values of c , when $\frac{mc^2}{2kT} < 1$, then $e^{-\frac{mc^2}{2kT}} = 1$

$$P(c) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} c^2, \quad \dots(2.2.8)$$

This shows that $P(c) \propto c^2$, therefore, $P(c)$ increases with the increase in value of c ; reaches a maximum value at a particular value of c equal to c_m , called most probable speed. When c is further increased the function $P(c)$ behaves as $e^{-\frac{mc^2}{2kT}}$ and falls exponentially.

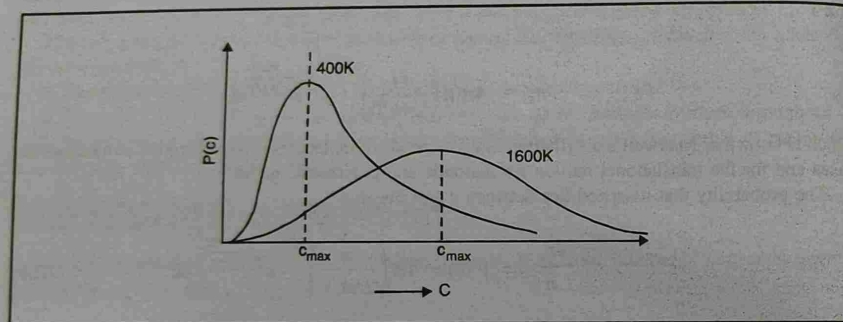


Fig. 2.2.2

(iii) This equation (2.2.8) shows that $P(c)_{\max}$ decreases at higher temperature and $c_{\max}$ increases with increase of temperature. Hence at high temperatures, the most probable speed $c_{\max}$ increases and peak value decreases as shown in Fig. (2.2.2)

(iv) The total area under the curve is always unity as it gives the total probability for all values of c from 0 to ∞ .

2.3. EXPRESSION FOR MOST PROBABLE SPEED, AVERAGE OR MEAN SPEED AND ROOT MEAN SQUARE SPEED

(i) Most probable speed (c_m)

It is defined as the speed possessed by the maximum number of molecules in a sample at a given temperature.

According to Maxwell's law for distribution of speeds, the probability in speed having velocity between c and $c + dc$ is given by

$$\frac{dn_c}{n} = P(c) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}}$$

Differentiating both sides w.r.t. c , we get

$$\frac{d}{dc} P(c) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{d}{dc} \left[c^2 e^{-\frac{mc^2}{2kT}} \right]$$

At most probable speed $P(c)$ is maximum

$$\text{So } \frac{d}{dc} P(c) = 0 \text{ and } c = c_m$$

$$\text{So } 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \left[2c_m e^{-\frac{mc_m^2}{2kT}} + c_m^2 e^{-\frac{mc_m^2}{2kT}} \left(-\frac{2mc_m}{2kT} \right) \right] = 0$$

$$\text{or } 2c_m e^{-\frac{mc_m^2}{2kT}} \left[1 - \frac{mc_m^2}{2kT} \right] = 0$$

$$\text{or } 1 - \frac{mc_m^2}{2kT} = 0$$

$$\text{or } \frac{mc_m^2}{2kT} = 1$$

$$\text{or } c_m = \sqrt{\frac{2kT}{m}} = 1.41 \sqrt{\frac{kT}{m}} \quad \dots(2.3.1)$$

(ii) Mean or Average speed $\bar{c}$. It is defined as the ratio of the sum of the individual speeds of the molecules to the number of molecules

$$\bar{c} = \frac{c_1 + c_2 + \dots + c_n}{n}$$

where $c_1, c_2, c_3, \dots, c_n$ are the speeds of the individual molecules and n is the number of molecules.

The probability function for a molecule to have speed c is given by

$$P(c) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}}$$

Average or mean value

$$\bar{c} = \int_0^{\infty} c P(c) dc$$

$$= \int_0^{\infty} c^3 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mc^2}{2kT}} dc$$

$$\text{Using the integral, } \int_0^{\infty} c^3 e^{-\frac{mc^2}{2kT}} dc = \frac{1}{2 \left(\frac{m}{2kT} \right)^2}$$

we get

$$\begin{aligned}\bar{c} &= 4\pi \frac{m^{3/2}}{(2\pi kT)^{3/2}} \times \frac{1}{2} \left(\frac{2kT}{m} \right)^2 \\ &= \frac{2\pi m^{3/2}}{\pi \sqrt{\pi} (2kT)^{3/2}} \times \frac{(2kT)^2}{m^2} \\ &= \frac{8kT}{\pi m} = 1.59 \sqrt{\frac{kT}{m}} \quad \dots(2.3.2)\end{aligned}$$

(iii) **Root Mean square speed** $|\bar{c}|$ or (c_{rms}) . It is defined as the square root of mean of the square of the speed of all the molecules.

The mean square speed is given by

$$c_{rms} = |\bar{c}^2| = \int_0^\infty c^2 P(c) dc$$

or

$$|\bar{c}^2| = \int_0^\infty c^2 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}} dc$$

$$\text{Using the integral } \int_0^\infty c^4 e^{-\frac{mc^2}{2kT}} dc = \frac{3}{8} \sqrt{\frac{\pi}{\left(\frac{m}{2kT} \right)^5}}$$

$$|\bar{c}^2| = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \cdot \frac{3}{8} \frac{\sqrt{\pi}}{\left(\frac{m}{2kT} \right)^{5/2}}$$

$$= 4\pi \frac{m^{3/2}}{\pi \sqrt{\pi} (2kT)^{3/2}} \cdot \frac{3}{8} \sqrt{\pi} \left(\frac{2kT}{m} \right)^{5/2}$$

or

$$|\bar{c}^2| = \frac{3kT}{m}$$

$$|\bar{c}| = \sqrt{\frac{3kT}{m}} \quad \dots(2.3.3)$$

where $|\bar{c}|$ is called root mean square speed.

Example 2.1 Calculate root mean square velocity of hydrogen at 27°C . Also find most probable velocity. Given $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$ and mass of hydrogen molecule $= 3.34 \times 10^{-27} \text{ kg}$.

Solution. Given

$$T = 27 + 273 = 300 \text{ K}$$

$$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

$$m = 3.34 \times 10^{-27} \text{ kg}$$

$\therefore$ Root mean square velocity of hydrogen molecule

$$|\bar{c}| = \sqrt{\frac{3kT}{m}}$$

$$= \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 300}{3.34 \times 10^{-27}}} = 1.928 \times 10^3 \text{ ms}^{-1}$$

The most probable velocity

$$c_{max} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2 \times 1.38 \times 10^{-23} \times 300}{3.34 \times 10^{-27}}} = 1.574 \times 10^3 \text{ ms}^{-1}$$

2.4. EXPERIMENTAL VERIFICATION OF VELOCITY DISTRIBUTION

Zartman and Ko (1934) performed an experiment to study the distribution of velocity. The apparatus consists of an oven with an opening at A. S_1 and S_2 are two parallel slits. A drum D can be rotated about an axis passing through O. P is a glass surface on which a beam of silver atoms will get deposited (Fig. 2.4.1)

Metallic silver is melted in the oven. A beam of silver atoms is ejected through A. The drum D is rotated with a speed of 6000 r.p.m. approximately. When the drum is stationary, the silver atoms get deposited at the same point on the glass plate. When the drum is rotated, a fine beam of silver molecules enters through the slit S_2 . Molecules with very high speeds reach the plate P first i.e. on the right end of P and molecules with very low speed reach the other end of the plane. After a short time, sufficient quantity of silver is deposited on the plate P. Using a spectro photometer, the relative intensity of silver on the plate P is studied and this represents the velocity distribution of the molecules. The graph representing the number of molecules and velocity agrees with Maxwell's distribution of velocity.

In 1947, Estermann, Simoson and Stern designed a more precise apparatus to study the velocity distribution.

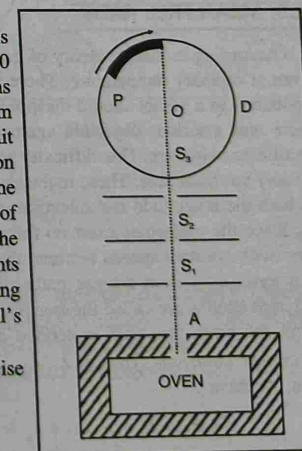


Fig. 2.4.1

Cesium atoms from the oven emerge from the opening A (Fig. 2.4.2) S is a slit and D is hot tungsten wire. The whole apparatus is enclosed in an evacuated chamber (pressure 10^{-8} mm of Hg). The opening A and the slit S are horizontal. In the absence of a gravitational field, the path is a parabola. The atoms going along the path 3 do not reach the wire. The atoms going along the paths 1 and 2 reach at D_1 and D_2 respectively. The velocity of atoms in path 1 is higher than the path 2.

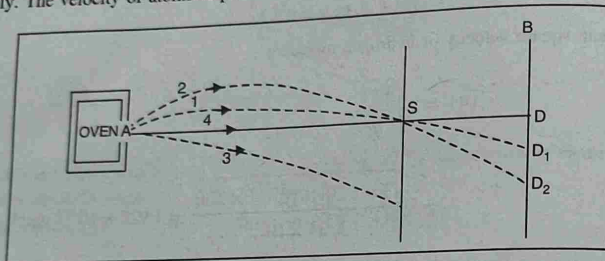


Fig. 2.4.2

When cesium atoms strike the wire they get ionized and re-evaporate. They are collected by a negatively charged detecting cylinder surrounding the tungsten wire. The magnitude of the detector indicates the intensity of the atoms at various positions. The detector can be moved to different positions of the wire. The atoms reaching at D_1 have higher velocity than those reaching at D_2 . The vertical height of the detector represents the magnitude of the velocity and the ionization current indicates the number of atoms making the wire in a particular point. A graph is drawn between the ionization current along the y-axis and the vertical height (speed of the atoms) of the detector along the x-axis. The velocity distribution is found to be in agreement with Maxwellian distribution law of velocity.

2.5. MEAN FREE PATH

According to kinetic theory of gases, the molecules of a gas are moving with very large velocities even at ordinary temperature. There is no force to restrain their motion and hence the gaseous mass contained in a vessel should disappear in no time which is contrary to the actual observations. Thus, there was a serious objection against the assumption that the molecules of a gas move with large rectilinear velocities. This difficulty was solved by Clausius who assumed, the molecules of a gas have a small but finite size. These molecules collide with one another after short interval resulting a change in both the magnitude and direction of the velocities of the molecules.

Since the molecules exert no force on one another except during collision, they move in straight lines with constant speeds between the two successive collisions. Thus, the path of a single molecule is a series of a short zig-zag paths of different lengths as shown in the Fig. 2.5.1. These paths of different lengths are called the free path of the molecules and their mean path is called mean free path. Thus, the mean free path is defined as the average distance traversed by a molecule between two successive collisions. Thus, if $\lambda_1, \lambda_2, \dots, \lambda_n$ are the successive free paths travelled in total time t , then, we have

$$\lambda_1 + \lambda_2 + \dots + \lambda_n = \bar{v} t$$

where $\bar{v}$ is the average speed of molecule.

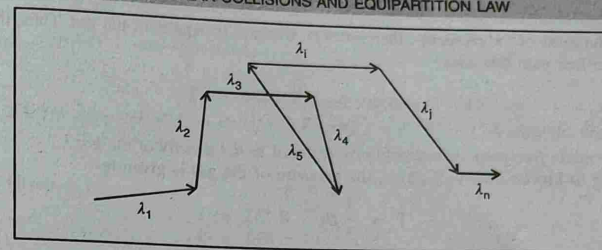


Fig. 2.5.1

If N is the total number of collision suffered i.e. the free paths traversed in time t and λ is the mean free path, then we have

$$\lambda = \frac{\lambda_1 + \lambda_2 + \dots + \lambda_n}{N} = \frac{\bar{v} t}{N}$$

Expression for mean free path

Let us consider a gas having n molecules per unit volume. Let us assume that only one molecule which is under consideration is in motion while all the others are at rest. If σ is the diameter of each molecule, then the moving molecule will collide with all those molecules, whose centres lie within a distance σ from its centre as shown in Fig. 2.5.2. If v is the velocity of the moving molecule, then in one second, it will collide with all the molecules whose centres lie in a cylinder of radius σ and length v i.e. within volume $\pi \sigma^2 v$.

Thus, the number of collisions made by the molecules in one second

$$N = \pi \sigma^2 v n$$

where n is number of molecules per unit volume.

As the distance traversed by the molecules in one sec is v , therefore, the mean free path is given by

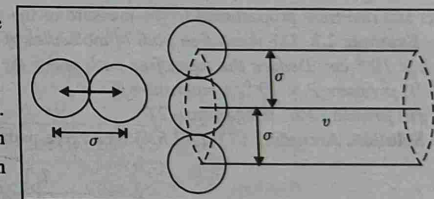


Fig. 2.5.2

$$\lambda = \frac{\text{Total distance traversed in one sec}}{\text{Number of collisions suffered by the molecules in one sec}}$$

$$= \frac{v}{\pi \sigma^2 v n} = \frac{1}{\pi \sigma^2 n} \quad \dots(2.5.1)$$

This expression has been derived by assuming that only one molecule under consideration is moving while all others are at rest which do not represent the actual state of affairs. Therefore, Maxwell assumed the realistic assumption that all the molecules are moving with all possible velocities in all possible directions and found the results by applying distribution law of molecular speeds. The exact results obtained by him is

$$\lambda = \frac{1}{\sqrt{2}(\pi \sigma^2 n)} \quad \dots(2.5.2)$$

If m is the mass of the molecule, then $mn = \rho$, where ρ is density of the gas. Thus, the expression for the mean free path becomes

$$\lambda = \frac{m}{\sqrt{2}(\pi \sigma^2 \rho)} \quad \dots(2.5.3)$$

Thus, the mean free path is inversely proportional to the density of the gas. According to kinetic theory of gases, the pressure of the gas is given by

$$P = \frac{1}{3} \rho \bar{v}^2$$

where $\bar{v}^2$ is mean square speed of the molecules.

But $\bar{v}^2 = \frac{3kT}{m}$, where k is Boltzmann constant and T is absolute temperature.

$$\therefore P = \frac{1}{3} \rho \frac{3kT}{m}$$

$$\text{or} \quad \frac{m}{\rho} = \frac{kT}{P}$$

Using this value in eq. (2.5.3), we have

$$\lambda = \frac{kT}{\sqrt{2}(\pi \sigma^2 P)} \quad \dots(2.5.4)$$

This is expression for the mean free path in terms of absolute temperature and pressure of the gas. According to this relation, the mean free path is directly proportional to the absolute temperature of the gas and inversely proportional to the pressure of the gas.

Example 2.2. The mean free path of molecules of a certain gas at pressure P and temperature T is 2×10^{-5} cm. Deduce the mean free path under the following conditions :

(i) pressure $P \times 10^{-6}$, temperature T

(ii) pressure $P/2$, temperature $2T$.

Solution. According to Eq. (2.5.4) mean free path at pressure P and temperature T is given by

$$\lambda = \frac{kT}{\sqrt{2}(\pi \sigma^2 P)}$$

(i) The mean free path at $P \times 10^{-6}$ and temperature T will be

$$\lambda_1 = \frac{kT}{\sqrt{2}(\pi \sigma^2 P \times 10^{-6})}$$

$$\therefore \frac{\lambda_1}{\lambda} = 10^6, \text{ and } \lambda_1 = 10^6 \lambda$$

$$\text{or} \quad \lambda_1 = 10^6 \times 2 \times 10^{-5} \text{ cm} = 20 \text{ cm}$$

(ii) The mean free path at pressure $\frac{P}{2}$ and temperature $2T$ will be

$$\lambda_2 = \frac{k \cdot 2T}{\sqrt{2} \pi \sigma^2 \left(\frac{P}{2}\right)} = \frac{4kT}{\sqrt{2} \pi \sigma^2 P}$$

$$\therefore \frac{\lambda_2}{\lambda} = 4$$

$$\lambda_2 = 4 \times \lambda = 4 \times 2 \times 10^{-5} = 8 \times 10^{-5} \text{ cm}$$

Example 2.3. The diameter of the molecule of a gas is 2×10^{-10} m. Calculate the mean free path at NTP.

Solution. Given,

$$\sigma = 2 \times 10^{-10} \text{ m}$$

$$T = 273 \text{ K}$$

$$P = 1.01 \times 10^5 \text{ Nm}^{-2}$$

$$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

Since

$$\lambda = \frac{kT}{\sqrt{2}(\pi \sigma^2 P)} = \frac{1.38 \times 10^{-23} \times 273}{\sqrt{2} \times 3.14 \times 4 \times 10^{-20} \times 1.01 \times 10^5}$$

$$= 2.1 \times 10^{-7} \text{ m Ans.}$$

Example 2.4. Calculate the mean free path and collision frequency of air molecules at 0°C and 1 atmosphere pressure.

Given $\sigma = 2 \times 10^{-10}$ m, $n = 3 \times 10^{25}$ molecules m^{-3} , $\bar{v} = 10^7 \text{ ms}^{-1}$.

Solution. Using the relation,

$$\lambda = \frac{1}{\sqrt{2} \pi n \sigma^2}$$

we get

$$\lambda = \frac{1}{\sqrt{2} \times 3.142 \times 3 \times 10^{25} \times 4 \times 10^{-20}}$$

$$\lambda = 2 \times 10^{-7} \text{ m}$$

$$\text{Collision frequency} = \frac{\bar{v}}{\lambda} = \frac{10^7}{2 \times 10^{-7}} = 5 \times 10^{13} \text{ Hz.}$$

2.6. TRANSPORT PHENOMENON IN GASES

From kinetic theory of gases, we find that the molecules of a gas are in continuous random motion moving with different speeds in all possible directions. Hence they carry mass, momentum and energy from one region to another. If the volume of the containing vessel is small the gas might be in equilibrium, but for large volume, the temperature and pressure may not be the same at all points so the gas is not in equilibrium state and hence there is transportation of mass or velocity and momentum or energy from one region to another.

Those phenomena which can be explained on the basis of molecular motion are called transport phenomena.

The transport phenomena are the results of the natural law that energy system in nature tends to attain the state of equilibrium, if allowed to do. In gases, the following three cases may happen :

(i) The molecules of a gas in different layers may be moving with different momentum. They will attain the state of equilibrium, if the momentum is transported from one layer to another. This phenomenon is termed as **viscosity**.

(ii) The molecules of a gas in different layers may be having different temperatures. So that equilibrium state is attained, heat energy will be transported from one layer to another. This phenomenon is described as **thermal conduction**.

(iii) The molecular concentration in different layers may be different. In order to attain the state of equilibrium, the molecules and hence the mass will diffuse from one layer to another. This phenomenon is called **diffusion**.

2.7. VISCOSITY (TRANSPORT OF MOMENTUM)

Consider a gas flowing in the form of layers parallel to XY-plane along the direction OX [Fig. 2.7.1]. The velocity of the gas layer in contact with XY-plane is zero. Let $\frac{dv}{dz}$ be velocity gradient along OZ. If v is velocity of the layer A, then velocity of layer B (at a distance λ above A) will be $v + \lambda \frac{dv}{dz}$ while that of the layer C (at a distance λ below A) will be $v - \lambda \frac{dv}{dz}$.

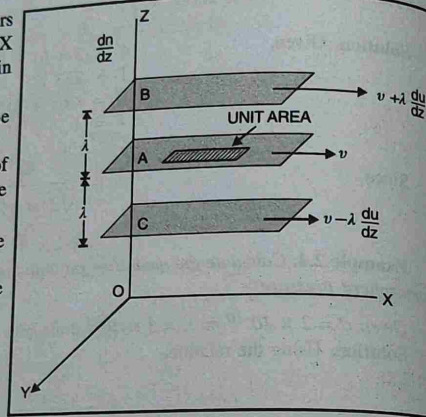


Fig. 2.7.1

Let n be number of molecules per unit volume of the gas and $\bar{v}$ is the average speed of the molecules.

Since the molecules have a tendency to move in all the directions i.e. the probability of the existence of molecules along any of three co-ordinate axes is the same.

Let $\frac{n}{3}$ molecules are moving along each of the three directions x, y, z .

$\therefore$ Number of molecules moving along z -axis $= \frac{n}{3}$.

Out of these, $\frac{n}{6}$ are moving downward and $\frac{n}{6}$ are moving upward.

$\therefore$ Number of molecules crossing the plane A upward or downward per second

$$= \frac{\frac{n}{6} \bar{v}}{1} = \frac{1}{6} n \bar{v}$$

If m is the mass of each molecule, then

$$\text{Momentum of each molecule at plane A} = m \left(v + \lambda \frac{dv}{dz} \right)$$

$$\text{Momentum of each molecule at plane C} = m \left(v - \lambda \frac{dv}{dz} \right)$$

$\therefore$ Momentum carried by the molecules from layer B to layer A per unit per unit area per second.

$$= \frac{1}{6} m n \bar{v} \left(v + \lambda \frac{dv}{dz} \right)$$

and momentum carried by the molecules from layer A to layer C per unit area per second

$$= \frac{1}{6} m n \bar{v} \left(v - \lambda \frac{dv}{dz} \right)$$

So, net momentum transferred in the downward direction per unit area per unit time of layer A

$$= \frac{1}{6} m n \bar{v} \left[\left(v + \lambda \frac{dv}{dz} \right) - \left(v - \lambda \frac{dv}{dz} \right) \right] \\ = \frac{1}{3} m n \bar{v} \lambda \frac{dv}{dz} \quad \dots(2.7.1)$$

This is rate of change of momentum and is force and we are considering unit area, so this is the viscous force acting on a unit area of a layer A. So

$$F = \frac{1}{3} m n \bar{v} \lambda \frac{dv}{dz} \quad \dots(2.7.2)$$

According to Newton, the viscous force acting on the unit area is given by

$$F = \eta \frac{dv}{dz} \quad \dots(2.7.3)$$

Here, η is coefficient of viscosity of the gas.

From equations (2.7.2) and (2.7.3), we have

$$\eta \frac{dv}{dz} = \frac{1}{3} m n \bar{v} \lambda \frac{dv}{dz}$$

or

$$\eta = \frac{1}{3} m n \bar{v} \lambda$$

Also,

$$m n = \rho, \text{ density of the gas} \quad \dots(2.7.4)$$

Therefore,

$$\eta = \frac{1}{3} \rho \bar{v} \lambda \quad \dots(2.7.5)$$

Discussion. The average velocity and the mean free path of a gas molecule are given by

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \quad \dots(2.7.6)$$

and

$$\lambda = \frac{1}{\sqrt{2} \pi n \sigma^2} \quad \dots(2.7.7)$$

Putting Eq. (2.7.7) and Eq. (2.7.4) in Eq. (2.7.5), we get

$$\eta = \frac{m \bar{v}}{3\sqrt{2} \pi n \sigma^2} \quad \dots(2.7.8)$$

Putting Eq. (2.7.6) and Eq. (2.7.7) in Eq. (2.7.5), we get

$$\eta = \frac{1}{3} m n \sqrt{\frac{8kT}{\pi m}} \cdot \frac{1}{\sqrt{2} \pi n \sigma^2} \quad \dots(2.7.9)$$

$$\eta = \frac{2}{3\sigma^2} \sqrt{\frac{kmT}{\pi}} \quad \dots(2.7.10)$$

From this equation, we find that

(i) **Effect of mass of gas molecule**

as $\eta \propto \sqrt{m}$ the coefficient of viscosity of a gas varies directly as the square root of the mass of the gas molecule. Therefore, value of η for a lighter gas will be lesser than that for a heavier gas.

(ii) **Effect of temperature of the gas**

as $\eta \propto \sqrt{T}$ the coefficient of viscosity of a gas varies directly as the square root of the absolute temperature of the gas. In fact, η is found to vary as T^x , where x lies between 0.6 and 1.0.

(iii) **Effect of molecular diameter**

As $\eta \propto \frac{1}{\sigma^2}$, the coefficient of viscosity of a gas varies inversely as the square of the molecular diameter.

(iv) **Effect of pressure**

The coefficient of viscosity is independent of pressure of the gas. The reason is that density of a gas is directly proportional to the pressure ($\rho \propto P$) while mean free path is inversely proportional to the pressure ($\lambda \propto \frac{1}{P}$) and, therefore, the factor $\rho \lambda$ in equation (2.7.5) will be independent of pressure.

The coefficient of viscosity is found to be independent of pressure over a wide range. At very low pressures only the viscous force depends on the pressure.

2.8. THERMAL CONDUCTION (TRANSPORT OF HEAT ENERGY)

Consider a gas at rest in the form of layers parallel to XY plane [Fig. 2.8.1]. Suppose a

temperature gradient $\frac{dT}{dz}$ exists along OZ.

Let θ be temperature of gas molecules in a layer A. The temperature of gas molecules in layer B (at a distance λ above it) will be

$T + \lambda \frac{dT}{dz}$ and that of layer C (at a distance

λ below it) will be $T - \lambda \frac{dT}{dz}$. Due to temperature difference heat energy will flow from layer B to layer C.

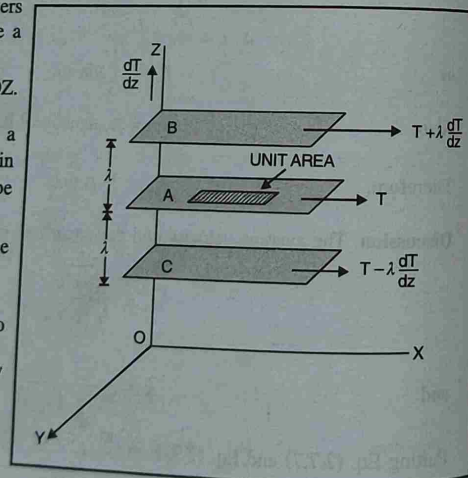


Fig. 2.8.1

Let n be number of molecules per unit volume of the gas and $\bar{v}$ is the average speed of the molecules.

Since the molecules have the tendency to move in all directions i.e. the probability of the existence of the molecules along any of the three axes is same. Let us assume that $\frac{n}{3}$ molecules are moving along each of the three directions x , y and z .

$$\therefore \text{Number of molecules moving along } z\text{-axis} = \frac{n}{3}$$

Out of these, $\frac{n}{6}$ are moving downwards and $\frac{n}{6}$ are moving upward.

$\therefore$ Number of molecules crossing the plane A upward or downward per second

$$= \frac{n\bar{v}}{6} = \frac{1}{6} n \bar{v}$$

If m is the mass of each molecule, then amount of heat carried by the molecules from layer B to layer C per unit area per second

$$= \frac{1}{6} mn \bar{v} C_v \left[T + \lambda \frac{dT}{dz} \right]$$

and amount of heat carried by the molecules from layer A to layer C per unit area per second

$$= \frac{1}{6} mn \bar{v} C_v \left[T - \lambda \frac{dT}{dz} \right]$$

So net amount of heat energy transferred in the downward direction per unit area per unit time of layer A,

$$\frac{dQ}{dt} = \frac{1}{6} mn \bar{v} C_v \left[\left(T + \lambda \frac{dT}{dz} \right) - \left(T - \lambda \frac{dT}{dz} \right) \right]$$

or

$$\frac{dQ}{dt} = \frac{1}{3} mn \bar{v} \lambda C_v \frac{dT}{dz} \quad \dots(2.8.1)$$

Since amount of heat energy transferred across two layers per unit area per unit time is given by

$$\frac{dQ}{dt} = K \frac{dT}{dz} \quad \dots(2.8.2)$$

where K is the coefficient of thermal conductivity.

From Eq. (2.8.1) and Eq. (2.8.2), we have

$$K = \frac{1}{3} mn \bar{v} \lambda C_v \quad \dots(2.8.3)$$

This is the expression for thermal conductivity of the gas.

Discussion. The average velocity $\bar{v}$ and the mean-free path of a gas molecule are given by

$$\bar{v} = \sqrt{\frac{8kT}{m}} \quad \dots(2.8.4)$$

and

$$\lambda = \frac{1}{\sqrt{2\pi n \sigma^2}} \quad \dots(2.8.5)$$

Putting these values of $\bar{v}$ and λ in Eq. (2.8.3), we get

$$K = \frac{1}{3} m n \sqrt{\frac{8kT}{m}} \frac{1}{\sqrt{2\pi n \sigma^2}} C_v$$

or

$$K = \frac{2}{3\sigma^2} \sqrt{\frac{kmT}{\pi^3}} C_v \quad \dots(2.8.6)$$

Since thermal conductivity η is given by

$$\eta = \frac{2}{3\sigma^2} \sqrt{\frac{kmT}{\pi^3}} \quad \dots(2.8.7)$$

So

$$K = \eta C_v$$

From Eq. (2.8.6) we find that coefficient of thermal conductivity is :

- directly proportional to square root of the mass of the molecule.
- directly proportional to the square root of the absolute temperature of the gas.
- inversely proportional to the square of the molecular diameter and
- independent of the pressure of the gas.

2.9. DIFFUSION (TRANSPORT OF MASS)

Consider a gas in the form of layers parallel to XY-plane. Let n be the concentration (number of molecules) per unit volume) of the molecules in layer A and a

concentration gradient equal to $\frac{dn}{dz}$ exist

along OZ [Fig. 2.9.1]. The concentration of molecules in layer B (at a distance λ above

it) will be $n + \lambda \frac{dn}{dz}$ and that in layer C (at a

distance λ below it) will be $n - \lambda \frac{dn}{dz}$. Due to difference in concentration of molecules in layers B and C, molecules will cross from layer B to layer C.

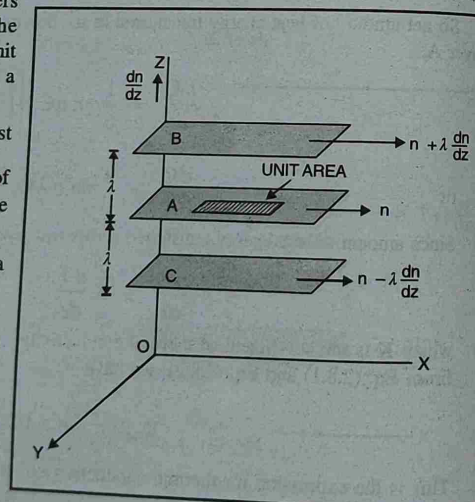


Fig. 2.9.1

Since the molecules have tendency to move in all directions i.e. probability of the existence of molecules along any of three coordinates is same. Let us assume that $\frac{1}{3}$ rd molecules moving along each of the three directions x, y, z .

$\therefore$ Number of molecules moving along z -axis = $\frac{1}{3}$.

Out of these, $\frac{1}{6}$ th are moving downward and $\frac{1}{6}$ th are moving upward.

If $\bar{v}$ is the average speed of the molecules, then

Number of molecules crossing the plane A upwards or downwards per second = $\frac{1}{6} \bar{v}$.

$\therefore$ Number of molecules crossing the plane B downwards per unit area per second

$$= \frac{1}{6} \bar{v} \left(n + \lambda \frac{dn}{dz} \right)$$

and number of molecules crossing the plane B upwards per unit area per second

$$= \frac{1}{6} \bar{v} \left(n - \lambda \frac{dn}{dz} \right)$$

$\therefore$ Net number of molecules crossing unit area of the plane A in the downward direction per unit area per unit time.

$$\frac{dM}{dt} = \frac{1}{6} \bar{v} \left[\left(n + \lambda \frac{dn}{dz} \right) - \left(n - \lambda \frac{dn}{dz} \right) \right]$$

$$\frac{dM}{dt} = \frac{1}{3} \bar{v} \lambda \frac{dn}{dz} \quad \dots(2.9.1)$$

The rate of flow of molecules across any plane per unit area per unit time is given by

$$\frac{dM}{dt} = D \frac{dn}{dz} \quad \dots(2.9.2)$$

where D is called the coefficient of inter-diffusion for two gases and coefficient of self-diffusion for the same gas.

From Eq. (2.9.1) and Eq. (2.9.2), we have

$$D = \frac{1}{3} \bar{v} \lambda \quad \dots(2.9.3)$$

This is the expression for diffusion coefficient.

Discussion

Since,

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

and

$$\bar{\lambda} = \frac{1}{\sqrt{2\pi}\sigma^2 n}$$

Equation (2.9.3) becomes

$$D = \frac{1}{3} \sqrt{\frac{8kT}{\pi m}} \cdot \frac{1}{\sqrt{2\pi}\sigma^2 n}$$

Since,

$$n = \frac{P}{kT}$$

$$D = \frac{1}{2} \sqrt{\frac{8kT}{\pi m}} \cdot \frac{1}{\sqrt{2\pi}\sigma^2 n}$$

$$D = \frac{2}{3} \left(\frac{k}{\pi}\right)^{\frac{3}{2}} \frac{T^{\frac{3}{2}}}{m^{\frac{1}{2}} \sigma^2 P}$$

or

$$D = \frac{2}{3\sigma^2 \sqrt{m} P} \left(\frac{kT}{\pi}\right)^{\frac{3}{2}}$$

From this equation, it follows that

(i) as $D \propto \frac{1}{\sqrt{m}}$, the coefficient of diffusion of a gas is inversely proportional to square root of the mass of the gas molecules.

(ii) as $D \propto T^{\frac{3}{2}}$, the coefficient of diffusion of a gas is directly proportional to three half power of the absolute temperature of the gas.

Experimentally, it has been found that $D \propto T^x$, where x varies between 1.75 to 2.0.

(iii) as $D \propto \frac{1}{\sigma^2}$, the coefficient of diffusion of a gas is inversely proportional to square of the molecular diameter and

(iv) as $D \propto \frac{1}{P}$, the coefficient of diffusion of a gas is inversely proportional to the pressure of the gas.

2.10. RELATION BETWEEN η , K AND D

The mathematical expression for coefficient of viscosity (η), coefficient of thermal conductivity (K) and coefficient of diffusion (D) of a gas are given by

$$\eta = \frac{2}{3\sigma^2} \sqrt{\frac{kmT}{\pi^3}} \quad \dots (2.10.1)$$

$$K = \frac{2}{3\sigma^2} \sqrt{\frac{kmT}{\pi^3}} C_v \quad \dots (2.10.2)$$

and

$$D = \frac{2}{3\sigma^2 \sqrt{m} P} \left(\frac{kT}{\pi}\right)^{\frac{3}{2}}$$

or

$$D = \frac{2}{3\sigma^2 P} \sqrt{\frac{k^3 T^3}{\pi^3 m}}$$

Since

$$P = n kT$$

$\therefore$

$$D = \frac{2}{3\sigma^2 n} \sqrt{\frac{kT}{\pi^3 m}} \quad \dots (2.10.3)$$

From Eq. (2.10.1) and Eq. (2.10.2), we have

$$\frac{K}{\eta} = C_v$$

or

$$K = \eta C_v$$

From Eq. (2.10.1) and Eq. (2.10.3), we have

$$\frac{D}{\eta} = \frac{1}{mn}$$

But $mn = \rho$, the density of the gas

$\therefore$

$$\frac{D}{\eta} = \rho$$

or

$$D = \eta \rho \quad \dots (2.10.5)$$

From Eq. (2.10.4) and Eq. (2.10.5) we have

$$\eta = \frac{K}{C_v} = \frac{D}{\rho} \quad \dots (2.10.6)$$

Eq. (2.10.6) give relation between η , K and D .

Example 2.5. The viscosity of oxygen at a temperature 27°C is 200 micropoise. Calculate the diameter of molecules of the gas. Avogadro number is 6.023×10^{23} and molecular weight of oxygen is 32, $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$.

Solution. The coefficient of viscosity is given by

$$\eta = \frac{1}{3} mn \bar{v} \bar{\lambda}$$

And

$$\lambda = \frac{1}{\sqrt{2\pi}\sigma^2 n}$$

$$\eta = \frac{m\bar{v}}{3\sqrt{2\pi}\sigma^2}$$

 $\therefore$

$$\sigma^2 = \frac{m\bar{v}}{3\sqrt{2\pi}\eta}$$

or

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

But

$$\sigma^2 = \frac{m}{3\sqrt{2\pi}\eta} \sqrt{\frac{8kT}{\pi m}}$$

 $\therefore$

$$\sigma^2 = \frac{1}{3\sqrt{2\pi}\eta} \sqrt{\frac{8mkT}{\pi}}$$

or

$$\text{Here } \eta = 200 \text{ micro poise} = 200 \times 10^{-6} \text{ poise} = 200 \times 10^{-5} \text{ Nm}^{-2} \text{ s}$$

$$m = \frac{M}{N} = \frac{32 \times 10^{-3}}{6.023 \times 10^{23}} \text{ kg}$$

$$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

$$T = 27^\circ\text{C} = 300 \text{ K}$$

 $\therefore$

$$\sigma^2 = \frac{1}{3 \times 4.14 \times 3.142 \times 200 \times 10^{-5}} \times \sqrt{\frac{8 \times 32 \times 10^{-3} \times 1.38 \times 10^{-23} \times 300}{6.02 \times 10^{23} \times 3.142}}$$

Solving, we get

$$\sigma = 3.968 \times 10^{-8} \text{ m.}$$

2.11. BROWNIAN MOTION

Brownian motion is the random movement of particles in a fluid due to their collisions with other atoms or molecules. This phenomenon was first discovered by Brown in 1827. He was examining the aqueous suspension of fine **inanimate** (dead or lifeless) spores using a high power microscope. He observed that the spores were moving in a random manner. It also has been observed that when a colloidal solution be examined under highly magnifying microscope, the suspended particles appear like stars of light moving to and fro, rapidly and continuously in random manner. Every particle in solution moves in all directions irregularly as shown in Fig. 2.11.1.

This continuous, spontaneous and irregular motion is called Brownian motion.

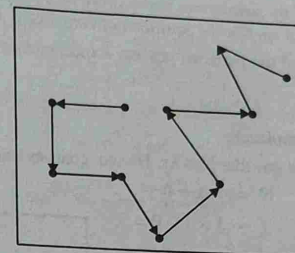


Fig. 2.11.1. Brownian Motion

It has been verified by different experiments that the motion of the suspended particles is not due to chemical behaviour or electrical nature. On increasing the temperature of the liquid, the motion of suspended particles become more vigorous. The motion of particles also depend upon the size. The smaller the size of molecules, the more irregular motion it requires.

The Brownian motion may be explained, if the suspended particles are considered as buoys (**floating bodies**) in a sea of molecules. The thermal energy of the solution is shared among all the suspended

particles and the average translation kinetic energy of each particle is $\frac{3}{2}kT$. Due to impacts of molecules from all sides, a molecule experiences a resultant force in a certain direction. When the size of molecule is large, the force due to impacts get balanced from all sides hence the motion is less agitated. Whereas the force for smaller molecules are unbalanced and the motion is more agitated. Brownian motion is the basic assumption of kinetic theory of gases. Transport phenomenon in gases, molecular speed etc. can be significantly explained using concept of Brownian motion.

2.12. DEGREES OF FREEDOM

The total number of independent quantities or coordinates required to describe the configuration of a dynamic system is called its degrees of freedom.

(i) A particle moving along a straight line can be described by its displacement along the axis of motion, so it has one degree of freedom.

(ii) A particle moving in a plane can be described by its displacement along two axis, so it has two degrees of freedom.

(iii) Similarly, a particle moving in space has three degrees of freedom.

To find degrees of freedom

In the above cases, we have considered a particle as a point mass which cannot undergo rotation. But a particle of finite mass can have translational as well as rotational motion and rotational motion can also be described by three independent coordinates, hence a rigid body has three degrees of freedom due to translational motion and three degree of freedom due to rotational motion i.e. total six degrees of freedom.

Let us now consider a system of two free particles, each particle has three degrees of freedom, so the system will have six degrees of freedom in all. If the particles are not free but move in space such that distance between them always remains constant, then co-ordinates required to describe the system is therefore five. Thus we can generalise the observation that the number of degrees of freedom of a

dynamic system can be obtained by subtracting the number of independent relations from the total number of coordinates required to specify the positions of constituent particles of the system.

If a system has N particles and the particles possess k independent relations between them, then number of degrees of freedom,

$$f = 3N - k.$$

e.g. (i) For monoatomic gas molecule

The molecule of a monoatomic gas like Ne, Ar, He etc. consists only of one atom.

i.e. $N = 1, k = 0$

$\therefore f = 3 \times 1 - 0 = 3$

i.e. a monoatomic gas molecule possesses 3-degrees of freedom.

(ii) For diatomic gas molecule

The molecule of diatomic gas like H_2 , O_2 , N_2 etc. has two atoms in it. (Fig. 2.11.2). This molecule has three degrees of freedom due to translational motion about its centre of mass and the molecule can rotate about the axis OY and OZ axis both perpendicular to each other i.e. two degrees of freedom due to rotational motion making the total $3 + 2 = 5$.

Also if we put

$$N = 2, k = 1$$

$$f = 3 \times 2 - 1 = 5$$

i.e. a diatomic gas molecule possesses 5 degrees of freedom.

(iii) For triatomic gas molecule

The molecule of a triatomic gas like SO_2 , H_2S , etc. has three atoms in it.

(a) In a linear molecule

Here

$$N = 3, k = 2 \text{ [Fig. 2.12.2]}$$

$\therefore$

$$f = 3 \times 3 - 2 = 7$$

(b) In a non-linear molecule

Here

$$N = 3, k = 3 \text{ [Fig. 2.12.3]}$$

$\therefore$

$$f = 3 \times 3 - 3 = 6$$

It may be noted that at temperature (≈ 5000 K) when vibrational motion excited up*. The diatomic (or polyatomic) gas molecule will possess vibrational degrees of freedom (2-degrees of freedom for diatomic and two or more degrees of freedom for polyatomic gas molecule depending upon whether linear or non-linear molecule).

2.13. LAW OF EQUIPARTITION OF ENERGY

It states that, for any system in thermal equilibrium, the total energy is equally distributed among all the degrees of freedom and energy associated with each degree of freedom is $\frac{1}{2}kT$.

According to the kinetic theory of gases, the mean kinetic energy of a molecule at temperature T given by

The molecules of Cl_2 gas possess vibrational degrees of freedom even at room temperature.

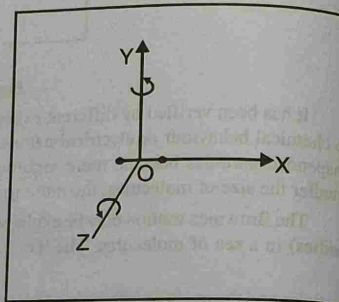


Fig. 2.12.1.

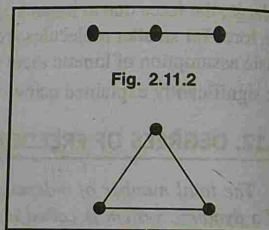


Fig. 2.12.3.

$$\frac{1}{2}mc^2 = \frac{3}{2}kT$$

But

$$c^2 = u^2 + v^2 + w^2$$

As x, y, z are all equivalent, mean square velocities along the three axes are equal.

So

$$u^2 = v^2 = w^2$$

$\therefore$

$$\frac{1}{2}mu^2 = \frac{1}{2}mv^2 = \frac{1}{2}mw^2$$

or

$$\frac{1}{2}mc^2 = 3 \left[\frac{1}{2}mu^2 \right] = 3 \left[\frac{1}{2}mv^2 \right] = 3 \left[\frac{1}{2}mw^2 \right] = \frac{3}{2}kT$$

So we have

$$\frac{1}{2}mu^2 = \frac{1}{2}kT$$

$$\frac{1}{2}mv^2 = \frac{1}{2}kT$$

$$\frac{1}{2}mw^2 = \frac{1}{2}kT$$

Therefore, the kinetic energy associated with each degree of freedom = $\frac{1}{2}kT$.

Thus, the energy associated with each degree of freedom (whether translatory or rotatory) is $\frac{1}{2}kT$.

2.14. SPECIFIC HEAT OF GASES

Specific heat of a substance is defined as the amount of heat required to raise the temperature of unit mass of substance through 1°C (or 1 K).

Generally, we take one mole of a substance in all chemical processes and the specific heat for one mole is called molar specific heat. **Molar specific heat of a substance** is defined as the amount of heat required to raise the temperature of one mole of the substance through 1°C (or 1 K).

These definitions are true for all gases. But when a gas is heated, there is an appreciable change in its pressure and volume. The physical condition under which heat is supplied i.e. at constant volume or constant pressure determines specific heat of the gas. It is because of this reason that a gas has two specific heats.

1. Molar Specific Heat at a Constant Volume (C_v). It is defined as the amount of heat required to raise the temperature of one mole of a gas through 1 K, when its volume is kept constant. It is denoted by C_v and is measured in $\text{J mole}^{-1} \text{K}^{-1}$.

2. Molar Specific Heat at Constant Pressure (C_p). It is defined as the amount of heat required to raise the temperature of one mole of a gas through 1 K, keeping its pressure constant. It is denoted by C_p and is measured in $\text{J mole}^{-1} \text{K}^{-1}$.

2.15. SPECIFIC HEAT OF MONO, DIA AND TRI-ATOMIC GAS

Consider one mole of a gas. Let each gas molecule possess f degrees of freedom. As one mole of gas contains N molecules (N is Avogadro's number.)

$\therefore$ Total degrees of freedom of the system = Nf

If T is the temperature of the system, then from law of equipartition of energy, the amount of energy associated with each degree of freedom is $\frac{1}{2}kT$.

$\therefore$ Total energy of the system,

$$U = Nf \left(\frac{1}{2}kT \right)$$

or

$$U = \frac{f}{2}RT$$

where $Nk = R$ is the gas constant for one mole of the gas.
The mole specific heat at constant volume is given by

$$C_v = \frac{dU}{dT} = \frac{d}{dT} \left[\frac{f}{2}RT \right]$$

or

$$C_v = \frac{f}{2}R \quad \dots(2.15.1)$$

For an ideal gas, specific heat at constant pressure is given by

$$C_p = C_v + R$$

$\therefore$

$$C_p = \frac{f}{2}R + R$$

or

$$C_p = \left(1 + \frac{f}{2} \right) R \quad \dots(2.15.2)$$

And the ratio of two specific heats of the gas is given by

$$\gamma = \frac{C_p}{C_v} = \frac{\left(1 + \frac{f}{2} \right) R}{\frac{f}{2}R}$$

or

$$\gamma = 1 + \frac{2}{f} \quad \dots(2.15.3)$$

For Eqs. (2.15.1), (2.15.2) and (2.15.3), we can calculate the molar specific heat of mono, dia and tri-atomic gases.

(i) **Molar specific heat of a monoatomic gas.** The molecules of monoatomic gases such as He, Ar, Ne etc. are single atoms. So the molecule of a monoatomic gas has *three* degrees of freedom of translational motion.

i.e.

From Eq. (i),

$$f = 3$$

Molar specific heat at constant volume,

$$C_v = \frac{f}{2}R$$

or

$$C_v = \frac{3}{2}R$$

From Eq. (ii),

Molar specific heat at constant pressure,

$$C_p = \left(1 + \frac{f}{2} \right) R = \left(1 + \frac{3}{2} \right) R$$

$$C_p = \frac{5}{2}R$$

From Eq. (iii),

Ratio of two specific heats of the gas,

$$\gamma = 1 + \frac{2}{f} = \left(1 + \frac{2}{3} \right)$$

or

$$\gamma = \frac{5}{3} = 1.67$$

(ii) **Molar specific heat of a diatomic gas.** The molecules of diatomic gases such as H_2 , O_2 , N_2 , CO etc., have two atoms each.

At ordinary temperature (250 K to 750 K), the molecule of a diatomic gas possesses 3 degrees of freedom corresponding to translational motion and 2 degrees of freedom corresponding to rotational motion. So total degrees of freedom is 5.

i.e.

$$f = 5$$

From Eq. (i),

Molar specific heat at constant volume,

$$C_v = \frac{f}{2}R$$

or

$$C_v = \frac{5}{2}R$$

From Eq. (ii),

Molar specific heat at constant pressure,

$$C_p = \left(1 + \frac{f}{2} \right) R = \left(1 + \frac{5}{2} \right) R$$

or

$$C_p = \frac{7}{2}R$$

From Eq. (iii),

Ratio of two specific heats of the gas,

$$\gamma = 1 + \frac{2}{f} = 1 + \frac{2}{5}$$

$$\gamma = \frac{7}{5} = 1.4$$

At high temperature. The diatomic gas molecule possesses additional two degrees of freedom corresponding to vibrational motion.

So

$$f = 7$$

So

$$C_v = \frac{f}{2}R = \frac{7}{2}R$$

$$C_p = \left(1 + \frac{f}{2}\right)R = \left(1 + \frac{7}{2}\right)R = \frac{9}{2}R$$

and

$$\gamma = 1 + \frac{2}{f} = 1 + \frac{2}{7} = \frac{9}{7} = 1.28$$

(iii) **Molar specific heat of triatomic gas.** The molecules of triatomic gases such as CO_2 , SO_2 , H_2S etc. have three atoms each.

For non-linear molecule, the triatomic molecule possesses 6 degrees of freedom i.e.

$$f = 6$$

So

$$C_v = \frac{f}{2}R = \frac{6}{2}R = 3R$$

$$C_p = \left(1 + \frac{f}{2}\right)R = \left(1 + \frac{6}{2}\right)R = 4R$$

and

$$\gamma = 1 + \frac{2}{f} = 1 + \frac{2}{6} = \frac{4}{3} = 1.33$$

For linear molecule, the triatomic molecule possesses 7 degrees of freedom. i.e.

$$f = 7$$

So

$$C_v = \frac{f}{2}R = \frac{7}{2}R$$

$$C_p = \left(1 + \frac{f}{2}\right)R = \left(1 + \frac{7}{2}\right)R = \frac{9}{2}R$$

and

$$\gamma = 1 + \frac{2}{f} = 1 + \frac{2}{7} = \frac{9}{7} = 1.28$$

2.16. VARIATION OF C_v OF A DIATOMIC GAS WITH TEMPERATURE

The molar specific heats of a gas are expected to be independent of temperature. The observation is found to be true for monoatomic gases only. For diatomic gases, the molar specific heat at constant volume changes remarkably with changes in temperature.

Fig. 2.16.1 shows the variation of C_v with temperature in case of hydrogen gas. As a long range of temperature has to be covered, the temperature has been plotted on logarithmic scale.

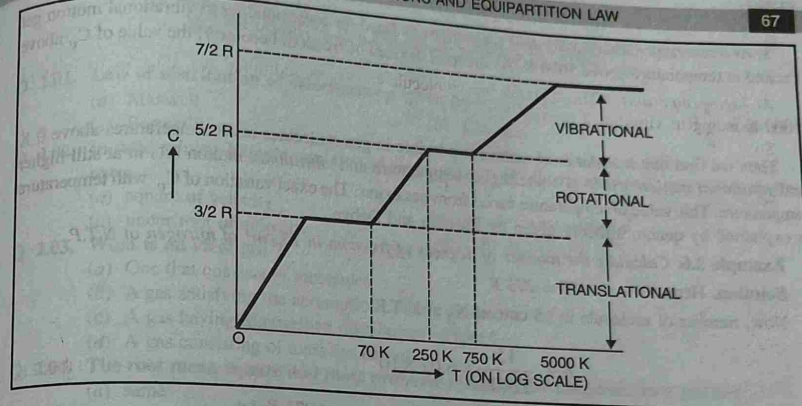


Fig. 2.16.1

It follows from the graph that for H_2 gas :

- (i) $C_v = \frac{3}{2}R$, for temperature of the gas below 70 K.
- (ii) $C_v = \frac{5}{2}R$, for temperature of the gas between 250 K and 750 K.
- (iii) $C_v = \frac{7}{2}R$, for temperature of the gas above 5000 K.

In other words, the molar specific heat of H_2 gas at constant volume which is expected to have a constant value of $\frac{5}{2}R$, varies between $\frac{3}{2}R$ to $\frac{7}{2}R$ with temperature.

Explanation

The molar specific heat of a gas at constant volume is

$$C_v = \frac{f}{2}R$$

1. At temperature below 70 K. At such low temperature, the H_2 molecule neither possesses degrees of freedom corresponding to rotational motion and nor corresponding to vibrational motion. It possesses only 3 degrees of freedom corresponding to translatory motion and hence, C_v is equal to $\frac{3}{2}R$.
2. At temperature between 250 K and 750 K. In this temperature range, H_2 gas molecule possesses 3 degrees of freedom corresponding to translatory motion and 2 degrees of freedom corresponding to rotational motion. As the total degrees of freedom is $3 + 2 = 5$, it possesses C_v equal to $\frac{5}{2}R$.

3. At temperature above 5000 K. Two degrees of freedom corresponding to vibrational motion get excited at temperature above 5000 K. As the total degrees of freedom become 7, the value of C_v above 5000 K is $\frac{7}{2}R$.

Thus we find that *translational motion* is possible in gas molecules at all temperatures above 0 K and *rotational motion* sets in at some higher temperature and *vibrational motion* sets in at still higher temperature. This value of temperature varies from gas to gas. The exact variation of C_v with temperature is explained by quantum theory given by Einstein and Debye.

Example 2.6. Calculate the number of degrees of freedom in 15 cm³ of nitrogen at N.T.P.

Solution. Here $T = 273$ K

Now, number of molecule in 15 cm³ of N₂ at N.T.P.

$$n = \frac{15}{22400} \times 6.02 \times 10^{23}$$

A diatomic gas molecule possesses 5 degrees of freedom at 273 K i.e.

$$f = 5$$

$$\therefore \text{Total degrees of freedom of the gas} = nf = \frac{15}{22400} \times 6.02 \times 10^{23} \times 5$$

$$= 2.016 \times 10^{21}$$

Example 2.7. Find the average kinetic energy of a gas molecule at 20°C according to kinetic theory. Boltzmann's constant, $k = 1.38 \times 10^{-23}$ J molecule⁻¹ K⁻¹.

Solution. Here,

$$T = 20 + 273 = 293 \text{ K}$$

$$k = 1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$$

1. Monoatomic gas. A monoatomic gas molecule possesses three degrees of freedom at all temperatures i.e.,

$$f = 3$$

$\therefore$ K.E. of a monoatomic gas molecule

$$= f \times \frac{1}{2} kT$$

$$= 3 \times \frac{1}{2} \times 1.38 \times 10^{-23} \times 293$$

$$= 6.065 \times 10^{-21} \text{ J}$$

2. Diatomic gas. A diatomic gas molecule will possess 5 degrees of freedom at 293 K i.e.

$$f = 5$$

$\therefore$ K.E. of a diatomic gas molecule

$$= f \times \frac{1}{2} kT$$

$$= 5 \times \frac{1}{2} \times 1.38 \times 10^{-23} \times 293$$

$$= 10.108 \times 10^{-21} \text{ J}$$

MULTIPLE CHOICE QUESTIONS

Q. 2.01. Law of distribution of velocities was given by :

- (a) Maxwell
- (b) Clausius
- (c) Bernoulli
- (d) Dalton.

Q. 2.02. In determining Kinetic equation of gases velocity of all molecules are not equal so we use :

- (a) square of velocity
- (b) mean square velocity
- (c) under root of velocity
- (d) cube of velocity.

Q. 2.03. What is an ideal gas ?

- (a) One that consists of molecules.
- (b) A gas satisfying the assumptions of kinetic theory.
- (c) A gas having Maxwellian distribution of speed.
- (d) A gas consisting of massless particles.

Q. 2.04. The root mean square and most probable speed of the molecules in a gas are

- (a) same
- (b) different
- (c) cannot say
- (d) depends on nature of gas.

Q. 2.05. If the rms velocity of a gas is v , then

- (a) $v^2 T = \text{constant}$
- (b) $\frac{v^2}{T} = \text{constant}$
- (c) $vT^2 = \text{constant}$
- (d) v is independent of T .

$$\text{Hint. } v^2 = \frac{3kT}{m}$$

$$\therefore \frac{v^2}{T} = \text{constant.}$$

Q. 2.06. The rms speeds of molecules of ideal gases at the same temperature are :

- (a) the same
- (b) directly proportional to the molecular weight
- (c) inversely proportional to the square root of molecular weight
- (d) inversely proportional to the molecular weight.

Q. 2.07. The ratio of rms velocity of O₃ and O₂ is :

- (a) 1 : 1
- (b) 3 : 2
- (c) 2 : 3
- (d) $\sqrt{2} : \sqrt{3}$.

Q. 2.08. Which of the following gases possesses maximum rms velocity, all being at the same temperature :

- (a) oxygen
- (b) air
- (c) CO₂
- (d) hydrogen.

Q. 2.09. Unit of thermal conductivity is

- (a) W/s/m/k
- (b) JK⁻¹
- (c) mK⁻¹
- (d) Js⁻¹ m⁻¹ K⁻¹.

Q. 2.10. Viscosity is the transfer of :

- (a) energy
- (b) mass
- (c) momentum
- (d) force.

Q. 2.11. Which of the following does not require bulk motion ?
 (a) viscosity (b) conduction
 (c) diffusion (d) none of these.

Q. 2.12. The molar specific heat of a diatomic gas at high temperature is :

- (a) $\frac{5}{2}R$ (b) $\frac{7}{2}R$
 (c) $\frac{3}{2}R$ (d) $\frac{9}{2}R$

ANSWERS

- 2.01. (a) 2.02. (b) 2.03. (b) 2.04. (b) 2.05. (b) 2.06. (c)
 2.07. (d) 2.08. (c) 2.09. (d) 2.10. (c) 2.11. (c) 2.12. (d)

SHORT ANSWER QUESTIONS

Q. 1. Why very long mean free paths are not possible for molecules of a gas ?

Ans. The number of molecules of a gas is very large and they are moving in all possible directions. During their random motion, they collide with other molecules. As the total number of molecules is very large, so, the frequency of collisions suffered by a molecule is very high. Hence a molecule travels very small distance between two successive collisions i.e. free path and hence mean free path of the molecule is very small. In other words, very long free paths are not possible for the molecules of a gas.

Q. 2. How does mean free path depend on density of a gas ?

Ans. The mean free path of a molecule of a gas is given by

$$\lambda = \frac{1}{\sqrt{2} \pi n \sigma^2} \quad \dots(i)$$

If m is the mass of molecule, then

$\rho = mn$, the density of the gas.

$$\therefore n = \frac{\rho}{m} \quad \dots(ii)$$

Putting (ii) in (i), we get

$$\lambda = \frac{m}{\sqrt{2} \pi \rho \sigma^2}$$

$$\text{or } \lambda \propto \frac{1}{\rho}$$

i.e. smaller the density of the gas, greater is the value of λ .

Q. 3. What assumption is made while finding the expression, $\lambda = \frac{1}{\pi n \sigma^2}$?

Ans. The derivation of this formula, $\lambda = \frac{1}{\pi n \sigma^2}$ is based on the assumption that only one molecule under consideration is moving while all other molecules are at rest, which is not true.

Q. 4. Distinguish between collision number and collision frequency.
 Ans.

Collision number	Collision frequency
It is the number of collisions made per second by a particular molecule with other molecules.	It is the total number of collisions of all the molecules per second in a unit volume.

Q. 5. Temperature remaining constant, show that λ for a gas is independent of pressure of the gas.

Ans. Since $\lambda = \frac{1}{\sqrt{2} \pi \rho \lambda} \quad \dots(i)$

At constant temperature,

$$\rho \propto P$$

and

$$\lambda \propto \frac{1}{P}$$

$\therefore$ the factor $\rho \lambda$ in Eq. (i) is independent of pressure.

Q. 6. Why are viscosity, thermal conductivity and diffusion called transport phenomenon ?

Ans. Those phenomenon which can be explained on the basis of molecular motion are called transport phenomenon. If a gas is not in steady state any one of the following three cases may arise :

- Transfer of momentum from faster moving layer of a fluid to slower moving fluids. This is responsible for viscosity of fluids.
- Transfer of mass from one region of higher concentration to one of lower concentration. This is responsible for diffusion of a gas.
- Transfer of heat energy from higher temperature to lower temperature. This is responsible for conduction of a gas.

Q. 7. In what manner does η depend on temperature of the gas ?

Ans. The coefficient of viscosity η is given as

$$\eta = \frac{1}{3} m n \bar{v} \lambda$$

and

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

$$\therefore \eta = \frac{1}{3} m n \sqrt{\frac{8kT}{\pi m}} \lambda$$

$$\text{i.e. } \eta \propto \sqrt{T}$$

Thus η is directly proportional to square root of absolute temperature.

Q. 8. Is there any relation between mass of the molecule of a gas and coefficient of diffusion of the gas ?

Ans. The coefficient of diffusion D is given by

$$D = \frac{1}{3} \bar{v} \lambda$$

Since

$$\bar{v} \propto \frac{1}{\sqrt{\rho}}$$

 $\therefore$

$$D \propto \frac{1}{\sqrt{\rho}}$$

or

$$D \propto \frac{1}{\sqrt{m n}}$$

or

$$D \propto \frac{1}{\sqrt{m}}$$

Q. 9. What is the effect of temperature on the mean free path of gas molecules ?

Ans. The mean free path of a gas molecule can be put in the form,

$$\bar{\lambda} = \frac{kT}{\sqrt{2} \pi d^2 P}$$

Therefore, the mean free path of a gas molecule is directly proportional to the temperature of the gas.

Q. 10. How does conduction differ from diffusion ?

Ans. Conduction and diffusion, both are transport phenomenon. But whereas in conduction heat energy is transported, it is mass which is transported in diffusion.

Q. 11. A vessel is filled with a mixture of two different gases. Will the mean kinetic energy per molecule of both the gases be equal ?

Ans. Yes. This is because the mean kinetic energy per molecule, i.e. $\frac{3}{2} kT$ depends only upon temperature.

QUESTIONS

1. Derive Maxwell's speed distribution law.
2. Derive expression for most probable speed.
3. Derive expression for mean and root mean square speed.
4. Explain experimental verification of velocity distribution.
5. If n is the number of molecules per unit volume and σ is the diameter of a molecule, show that the mean free path,

$$\lambda = \frac{1}{\sqrt{2} \pi n \sigma^2}$$

6. Explain mean free path of a gas molecule. Find an expression for it, stating clearly the assumptions used.
7. Shows that the mean free path of a molecule is inversely proportional to the pressure of the gas.
8. Derive an expression for the mean free path of a gas. What is the effect of temperature and pressure on the mean free path ?
9. What do you mean by mean free path ? Show that the mean free path is equal to $\frac{kT}{\sqrt{2} \pi P \sigma^2}$, where the letters have their usual meanings.

10. Explain mean free path and show that it varies inversely with its density.
11. What is mean free path of the molecules of a gas ? Derive an expression for it in terms of diameter of a molecule per unit of a gas. How does it vary with temperature and pressure ?
12. What are transport phenomena in gases ? Discuss its effects of pressure and temperature on the viscosity of gases.
13. Explain viscosity of a gas as a transport phenomenon. How does the viscosity of a gas vary with temperature ? Explain qualitatively.
14. Derive the relation $\eta = \frac{1}{3} \bar{v} \rho \lambda$ for a gas. Here η is coefficient of viscosity, $\bar{v}$ is mean molecular velocity and λ is mean free path.
15. What are transport phenomena in gases ? Explain diffusion on the phenomenon of molecular collision.
16. Derive the relation $\frac{K}{\eta C_v} = 1$ for a gas, where K is coefficient of thermal conductivity, η is coefficient of viscosity and C_v is molar specific heat at constant volume.

NUMERICAL PROBLEMS

1. Calculate the diameter of a molecule of benzene if $n = 2.79 \times 10^{25}$ molecules m^{-3} and mean free path λ for benzene = 2.2×10^{-8} m. [Ans. 6 Å]
2. Calculate the mean free path of a gas molecule if number of molecules per m^3 is 3×10^{25} and diameter of the molecule is 2 Å. [Ans. 1.88×10^{-7} m]
3. How many collisions per second does each molecule of a gas make when average speed of molecule is $5 \times 10^{-6} \text{ ms}^{-1}$ and mean free path is 3.2×10^{-5} m. [Ans. 1.563×10^7]
4. At what pressure will the mean free path of nitrogen gas molecule be 1 Å at a temperature of 27°C ? Given, the molecular diameter = 3.74×10^{-10} m. Assume the behaviour of the gas to be ideal. [Ans. $6.67 \times 10^7 \text{ N m}^{-2}$]
5. Calculate the mean free path of O_2 molecule at NTP. Molecular diameter of O_2 is 2 Å. [Ans. 2.09×10^{-7} m]
6. Calculate the molecular diameter of a chlorine molecule at 25°C and 1 atmosphere pressure. The coefficient of viscosity of chlorine is 1.47×10^{-3} decapoise. [Ans. 4.24×10^{-10} m]
7. The viscosity of a gas at a temperature of 16°C is 169 micropoise. Calculate the diameter of the molecule of the gas. Given Avogadro number, $N = 6.02 \times 10^{23}$, molecular weight of oxygen = 32 and Boltzmann's constant, $k = 1.38 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1}$. [Ans. 1.84×10^{-10} m]

CLASSICAL STATISTICS

3.1. PHASE SPACE

Position space

It was explained in the previous chapter that systems of particles can be of two types : *static* and *dynamic*. For describing a **static system** we need to know the position co-ordinates of the different particles. These co-ordinates do not change with time. *The space in which the state of the constituent particles of a system can be described in terms of position co-ordinates is called position space.* As we need three co-ordinates to identify its position in the space, so, if a system consists of n particles, then we need $3n$ position co-ordinates to describe the system. Since we need three co-ordinates to identify the position of a particle, therefore the position space is said to be three dimensional.

Momentum space

The particles of a **dynamic system** are always in motion. At any instant, the position of each particle can be identified in terms of its 3 position co-ordinates in the position space. However, the position co-ordinates of the particles of the dynamic system change with time. So, we need to know the instantaneous position co-ordinates. Also, each particle possesses an instantaneous momentum, which can be resolved into three components. The momentum of the particle may also change with time. Thus, to describe the dynamic behaviour of the system, we need to know 3 momentum co-ordinates of each particle. *The space in which the dynamic state of the constituent particles of a system can be described in terms of the momentum co-ordinates is called momentum space.* If a system consists of n particles then we need $3n$ momentum co-ordinates to describe the dynamic behaviour of the system. Like position space, the momentum space is also three dimensional.

Phase space

The complete description of the dynamic behaviour of a system needs the knowledge of 3 position co-ordinates (say x , y and z) and 3 momentum co-ordinates (say p_x , p_y and p_z). *The space in which the state of the constituent particles of a system can be described in terms of position and momentum co-ordinates is called phase space.* It is a six dimensional space. So if a system consists of n particles then we need $6n$ co-ordinates to describe the behaviour of the system in the phase space.

Available volume

Suppose, we consider an elementary cubical part of the position space bounded by the sides, Δx , Δy , Δz . Then the volume of the position space element is given by :

$$\Delta V = \Delta x, \Delta y, \Delta z$$

Similarly, if we consider an elementary cubical part of the momentum space bounded by the sides Δp_x , Δp_y and Δp_z , then the volume of the momentum space element is given by :

$$\Delta \tau = \Delta p_x \Delta p_y \Delta p_z$$

The product of the volume element in the position space and that in the momentum space is called available volume. If we denote it by $\Delta \Gamma$, then

$$\Delta \Gamma = \Delta V \Delta \tau$$

or
This is the volume of the elementary phase space.
Generally, we write it as h_0^3 . Thus :

$$h_0^3 = \Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z$$

The dimensional formula of $h_0 = [M L^2 T^{-1}]$

The unit of h_0 = length $\times$ momentum

$$= \frac{\text{length}}{\text{time}} \times \text{time} \times \text{mass} \times \text{velocity}$$

$$= \text{velocity} \times \text{time} \times \text{mass} \times \text{velocity}$$

$$= \text{mass} \times \text{velocity}^2 \times \text{time} = (\text{kg m}^2 \text{s}^{-2}) \text{s}$$

$$= \text{Js}$$

That is, the unit of h_0 is 'joule second'. The actual significance of writing the unit in this form will be clear in the later sections.

3.2. DIVISION OF PHASE SPACE INTO COMPARTMENTS AND CELLS

In the previous chapter, we have considered the division of a box into compartments and then the compartments were divided into cells. That, in fact, referred to the division of position space into compartments and cells. It was suggested there that the compartments may be of different sizes. But each cell should be of the same size. So, different compartments may contain different number of cells. The distribution of particles in the box, then, could be studied in terms of the distribution of the particles in the cells and compartments. But, division of position space into compartments and cells can help in the study of static systems only.

For studying the dynamic systems, we have introduced the concept of phase space. We can divide the phase space into compartments and cells in the same way as we do for the position space of a box. For this purpose, we assume that available volume of each cell of the phase space is h_0^3 . It has already been explained that the unit of h_0 is joule second. Therefore, all particles possessing a given amount of energy at a particular instant are consigned to a particular cell. Also, the unit of h_0 can be written as $(\text{kg m s}^{-1}) \text{m}$, which is the unit of momentum multiplied by the unit of distance. Hence, all the particles possessing a given amount of momentum at a particular location can be consigned to one cell.

Each compartment can contain different number of cells. Therefore, compartments correspond to different energy intervals or momentum intervals. Thus, by dividing the phase space of a system into compartments and cells we can analyse the distribution of energy or momentum among the particles.

Suppose, we divide the phase space of a system in k compartments. Let at any instant the number of particles in the different compartments be $n_1, n_2, n_3, \dots, n_k$. Then the macrostate of the system can be denoted as $(n_1, n_2, n_3, \dots, n_k)$. The dynamic system continuously goes from one macrostate to another. Therefore, the values of $n_1, n_2, \dots, n_k$ etc. continuously change with time. However, the systems spend maximum time in the most probable state. Therefore, we can study the behaviour of the system by analysing the distribution of its phase space into the most probable state. That is the main problem we are going to encounter in statistical physics.

Occupation index

Each compartment of the phase space can contain different number of particles, which depends on the nature of the system itself. Suppose a compartment contains n_i particles and it can be divided in g_i

cells. Then n_i/g_i is called occupation index. It is the number of particles per unit cell.

3.3. NUMBER OF THE PHASE SPACE CELLS IN THE MOMENTUM INTERVAL p AND $p + dp$

Let the number of the phase space cells per unit momentum interval = g_p .
Then the number of cells in the interval p and $p + dp = g_p dp$.

Here we wish to obtain an expression for $g_p dp$.

By definition,

$$g_p dp = \frac{[\text{Volume of phase space corresponding to momentum interval } p \text{ and } p + dp]}{\text{Volume of each phase space cell}}$$

$$\text{or } g_p dp = \frac{\iiint dx dy dz \iiint dp_x dp_y dp_z}{h_0^3}$$

where h_0^3 is the available volume of each cell of the phase space.

$$\text{i.e. } g_p dp = \frac{V \iiint dp_x dp_y dp_z}{h_0^3} \quad \dots(1)$$

where V is the volume occupied by the system in position space

and $\iiint dp_x dp_y dp_z$ represents the volume of the momentum space corresponding to the momentum interval p and $p + dp$.

If we draw two concentric spheres, with origin O as the centre and radii p and $p + dp$ respectively (Fig. 3.3.1), then the volume of the momentum space between these two spheres will correspond to the momentum interval p and $p + dp$.

Accordingly, we get :

$$\iiint dp_x dp_y dp_z = [\text{Volume of sphere of radius } (p + dp) - \text{Volume of sphere of radius } p]$$

$$= \frac{4}{3}\pi (p + dp)^3 - \frac{4}{3}\pi p^3$$

$$= \frac{4}{3}\pi [p^3 + (dp)^3 + 3p dp (p + dp) - p^3]$$

Neglecting the terms involving second and higher powers of dp , we get

$$\iiint dp_x dp_y dp_z = 4\pi p^2 dp$$

Substituting in (1), we obtain the required expression

$$g_p dp = \frac{V \times 4\pi p^2 dp}{h_0^3} \Rightarrow g_p dp = \frac{4\pi V}{h_0^3} p^2 dp \quad \dots(3.3.1)$$

This gives the number of the phase space cells in the momentum interval p and $p + dp$.

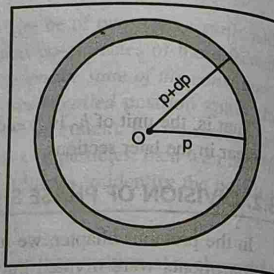


Fig. 3.3.1

Example 3.1. Find the number of phase space cells in the energy interval E and $E + dE$.

Solution. The number of phase space cells in the momentum interval p and $p + dp$ is given by :

$$g_p dp = \frac{V \times 4\pi p^2 dp}{h_0^3}$$

...(i)

The ideal particles possess only kinetic energy.

$$\text{Since } E = \frac{p^2}{2m}$$

$$\text{or } p^2 = 2mE.$$

$$\text{and } 2p dp = 2m dE.$$

$$dp = \frac{m}{p} dE = \frac{m}{\sqrt{2mE}} dE$$

Substituting in equation (i), the number of the phase space cells in the energy interval E and $E + dE$ is given by

$$g_E dE = \frac{V \times 4\pi (2mE) \frac{m}{\sqrt{2mE}} dE}{h_0^3}$$

$$g_E dE = \frac{V \times 4\pi \sqrt{2mE} m dE}{h_0^3}$$

$$= \frac{4\pi\sqrt{2} V}{h_0^3} m^{3/2} E^{1/2} dE$$

3.4. APPLICATIONS OF PHASE SPACE

(i) One-Dimensional Harmonic Oscillator

Let us consider a linear simple harmonic oscillator having mass m and oscillating freely with frequency ν . We want to calculate the number of phase cells in the energy range from 0 to E . Suppose the phase diagram of harmonic oscillator have one position coordinate x and one momentum coordinate p . So it may be called as p, x plane. At any instant, the total energy E of the oscillator will be the sum of potential energy and kinetic energy.

$$\text{Total Energy (E)} = P.E + K.E.$$

$$= \frac{1}{2} kx^2 + \frac{1}{2} mv^2$$

$$= \frac{1}{2} kx^2 + \frac{1}{2} \frac{m^2 v^2}{m}$$

$$E = \frac{1}{2} kx^2 + \frac{1}{2} \frac{p^2}{m}$$

$$2E = kx^2 + \frac{p^2}{m}$$

Now, Dividing by 2E,

$$1 = \frac{x^2}{2E/k} + \frac{p^2}{2mE} \quad \dots(1)$$

$$\therefore \frac{x^2}{a^2} + \frac{p^2}{b^2} = 1 \quad \left[\begin{array}{l} \text{where } a^2 = \frac{2E}{k} \\ b^2 = 2mE \end{array} \right]$$

This equation (1) represent an ellipse with semi major axis $a = \sqrt{\frac{2E}{k}}$ and semi-minor axis $b = \sqrt{2mE}$ in the x, y phase diagram (Fig. 3.4.1).

The phase space area of the oscillator having the energy between 0 to E is $A = \pi ab$ i.e.

$$\pi ab = \pi \sqrt{\frac{2E}{k}} \cdot \sqrt{2mE} = 2\pi E \sqrt{\frac{m}{k}} \quad \dots(2)$$

We know the frequency ν of the oscillator is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \dots(3) \text{ [k is called force constant]}$$

Using eq. (2) and (3), the area of phase space is

$$= 2\pi E \times \frac{1}{2\pi\nu} = \frac{E}{\nu}$$

Now, number of phase cells = $\frac{\text{area of phase space}}{\text{area of phase cell}}$

$$\phi(E) = \frac{E/\nu}{h_0}$$

or

$$\phi(E) = \frac{E}{h_0 \nu}$$

Energy will be

$$E = h_0 \nu \phi(E)$$

Number of phase space cell can take integral values i.e.

$$\phi(E) = 0, 1, 2, \dots, n$$

As energy occurs in discrete states.

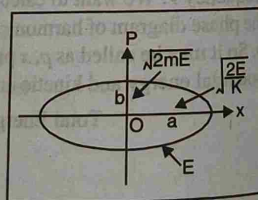


Fig. 3.4.1.

(ii) A Free particle. In order to calculate number of phase cells in the given energy range for three dimensional free particle, we consider a phase space representing a single particle of mass m in a volume V . The microstate of a particle can be specified by three position coordinates x, y, z and three momentum coordinates P_x, P_y, P_z .

The Volume of one phase cell in phase space is given as

$$\delta x \delta y \delta z \delta P_x \delta P_y \delta P_z = h^3$$

Now, total volume of phase space is

...(1)

$$V_{\text{phase}} = \iiint dx dy dz dP_x dP_y dP_z$$

$$= V \iiint dP_x dP_y dP_z \quad \dots(2)$$

$$\text{where } \iiint dx dy dz = V$$

The energy range is considered from 0 to E. So the possible values of momentum will be from 0 to p . The momentum space is like a sphere of radius p .

Volume of momentum space is

$$\iiint dP_x dP_y dP_z = \frac{4}{3} \pi p_{\text{max}}^3 \quad \dots(3)$$

The energy E of a free particle is only kinetic, so we can write

$$E = \frac{p^2}{2m}$$

or

$$p_{\text{max}}^2 = 2mE$$

Putting in eq. (3), we get

$$\iiint dP_x dP_y dP_z = \frac{4}{3} \pi (2mE)^{3/2} \quad \dots(4)$$

Using eq. (4) in eq. (2)

The volume of phase space

$$V_{\text{phase}} = V \left[\frac{4}{3} \pi (2mE)^{3/2} \right]$$

Now, the number of phase cells will be

$$\phi(E) = \frac{\text{Volume of phase space}}{\text{Volume of one cell}}$$

$$= V \left[\frac{4}{3} \pi (2mE)^{3/2} \right] \times \frac{1}{h^3}$$

$$\phi(E) = \frac{4\pi V}{3h^3} \times (2mE)^{3/2}$$

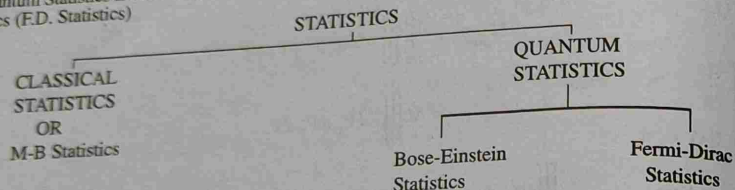
3.5. THREE KINDS OF STATISTICS

The study of statistical mechanics is divided into two branches :

- (a) Classical statistics
- (b) Quantum statistics

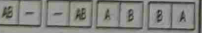
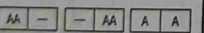
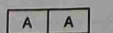
Classical statistics is also called Maxwell-Boltzmann statistics or M.B. Statistics, as it is based on Maxwell laws of distribution of molecules and Boltzmann's Theorem.

Quantum Statistics is of two types, namely Bose-Einstein's statistics (B.E. Statistics) and Fermi-Dirac Statistics (F.D. Statistics)



The Main Differences in Three Statistics

The main points of difference in the three statistics can be tabulated as given below :

S. NO.	POINT OF DIFFERENCE	CLASSICAL OR M-B STATISTICS	BOSE-EINSTEIN STATISTICS	FERMI-DIRAC STATISTICS
1.	Particles	Particles are distinguishable	Particles are indistinguishable	Particles are indistinguishable.
2.	Size of Phase-space cell	The size of phase-space cell can be as small as we require.	The size of the phase-space cell can not be less than h^3 (where h is Planck's constant)	The size cannot be less than h^3 .
3.	Number of cells	If n_i be the number of particles and g_i the number of cells then $g_i \gg n_i$ so $\frac{n_i}{g_i} < 1$ Thus number of cells can be made as large as possible $[\frac{n_i}{g_i}]$ is called occupation index]	The number of cells is less than or comparable to the number of particles $g_i \leq n_i$ $\frac{n_i}{g_i} \geq 1$	The number of cells has to be greater or equal to the number of particles $g_i \geq n_i$ so $\frac{n_i}{g_i} \leq 1$
4.	Restriction on Particles	No Restriction	No Restriction	Restriction due to Pauli's Exclusion Principle.
5.	Two Particle distribution	 The particles are distinguishable and can be arranged in 4 ways.	 The particles are indistinguishable and can be arranged in three ways.	 No two particles can occupy the same cell. Hence only one arrangement.

3.6. BASIC APPROACH IN THREE STATISTICS

The basic approach in the three kinds of statistics i.e. M.B., B.E. and F.D. statistics is essentially the same. Due to different assumptions, when the same approach is applied to a system, the different results are obtained.

(i) In each case, we search for the equilibrium state of a system—In a dynamical system consisting of large number of particles, there are very large number of macrostates. When a system is in equilibrium, then it exists only in the most probable state. From the assumptions of a given kind of statistics, we calculate the thermodynamical probability (W) for any given macrostate. For this state (macro) to represent the most probable state of the system, W must be maximum. For all natural systems, the thermodynamic probability W is a very large number. We therefore, deal with $\ln W$ instead of W . Since for most probable state W is maximum, therefore,

$$d(\ln W) = 0 \quad \dots(3.6.1)$$

(ii) In any system consisting of given number ' n ' of particles having total energy u , the quantities n and u remain constant. Consider a system whose total energy is divided into the energy intervals from 0 to u_k into large number of k intervals numbered as 1, 2, 3, ..., i , ..., k . Let $n_1, n_2, \dots, n_3, \dots, n_k$ represent the number of particles in the energy intervals 1, 2, 3, ..., i , ..., k respectively in the most probable or equilibrium state and mean energies of the particles in these intervals be $u_1, u_2, u_3, \dots, u_i, \dots, u_k$ respectively.

$$n = n_1 + n_2 + n_3 + \dots + n_i + \dots + n_k$$

$$= \sum_{i=1}^k n_i$$

As n is constant, therefore

$$dn = \sum_i dn_i = 0 \quad \dots(3.6.2)$$

Similarly,

$$u = n_1 u_1 + n_2 u_2 + \dots + n_i u_i + \dots + n_k u_k$$

$$= \sum_{i=1}^k u_i n_i$$

Since u is constant, therefore

$$du = \sum_{i=1}^k [u_i dn_i] = 0. \quad \dots(3.6.3)$$

The three equations (3.6.1), (3.6.2) and (3.6.3) must be satisfied by the system irrespective of the kind of statistics to be applied. These three conditions are incorporated in a single equation derived as follows :

Multiplying Eq. (3.6.2) by $-\alpha$ and Eq. (3.6.3) by $-\beta$ and adding to Eq. (3.6.1), we get :

$$d(\ln W) - \alpha \sum_i dn_i - \beta \sum_i u_i dn_i = 0, \quad \dots(3.6.4)$$

where α, β are arbitrary constants. (This is called the method of Lagrangian multipliers.)

From Eq. (3.6.4), we have

$$d(\ln W) = \alpha \sum_i dn_i + \beta \sum_i u_i dn_i = 0.$$

...(3.6.5)

or

$$d(\ln W) = \sum_i (\alpha + \beta u_i) dn_i = 0.$$

Eq. (3.6.5) is solved to obtain the distribution law for a given kind of statistics. This is the Basic equation which is used in all the three kinds of statistics.

3.7. MAXWELL-BOLTZMANN STATISTICS

The simplest many particle system is a sample of ideal gas. By definition, the molecules of a perfect gas are assumed to be point particles having no long range interparticle force between them. The particles may continuously collide with each other as well as with the walls of the containing vessel. The distribution of energy, momentum or velocities among the particles of such a system can be studied statistically. The statistical distribution laws applicable to them were obtained by Maxwell and Boltzmann and we call the statistical method of analysing such a system as Maxwell-Boltzmann statistics. It is often abbreviated as MB statistics. It is also called classical statistics.

Assumptions of MB statistics

The Maxwell Boltzmann statistics is based on the following assumptions :

1. The available volume of the phase space cell can be as small as we desire and may even approach to zero.

2. The phase space can be divided into a very large number of cells.

3. Any number of particles can occupy a phase space cell.

4. The particles of the system are distinguishable.

Size of the phase space cell

In classical physics, the molecules are assumed to be point masses. So, in principle, their volume should tend to zero. Hence, the phase space cell, which is required to house a particle, can also be assumed to have available volume as small as we desire, even that tending to zero. Accordingly the phase space can be divided into a very large number of cells.

Also, the particles being point masses, in any cell of finite size, any number of particles can be housed. This justifies the first three assumptions of MB statistics.

Identical but distinguishable particles

All molecules of the gas sample are assumed to be identical. Yet they are supposed to be distinguishable. This is made possible by dividing the phase space into so large number of the phase cells that each cell contains either one particle or none. Thus, although the particles are identical yet we can distinguish them by the cells they occupy.

3.8. MAXWELL-BOLTZMANN DISTRIBUTION LAW

Consider an isolated sample of an ideal gas. Let it consist of n molecules and let its volume be V . It is a dynamic system. All particles are in random motion, continuously colliding with each other as well as with the walls of the containing vessel. But, the system being isolated, its energy must remain constant with time. Let the energy of the system be denoted by u . We can divide the energy into k intervals, where k is very large. Let the mean energy of the different intervals be denoted by $u_1, u_2, u_3, \dots, u_k$ respectively. Each molecule of the system must have energy corresponding to one of the above mentioned k intervals. If the number of particles in the energy intervals denoted by mean values $u_1,$

$u_2, u_3, \dots, u_k$ etc. be $n_1, n_2, n_3, \dots, n_k$ respectively, then :

$$u = \sum_{i=1}^{i=k} n_i u_i$$

...(i)

Also,

$$n = \sum_{i=1}^{i=k} n_i$$

...(ii)

The equations (i) and (ii) specify the constraints on the system, which may be restated as follows :

(i) Total number of particles is equal to n , that is :

$$n = \sum_{i=1}^{i=k} n_i = \text{constant}$$

$$\therefore \quad dn = \sum_{i=1}^{i=k} dn_i = 0$$

....(iii)

(ii) Total energy of the system is equal to u , that is :

$$u = \sum_{i=1}^{i=k} u_i n_i = \text{constant}$$

$$\therefore \quad du = \sum_{i=1}^{i=k} u_i dn_i = 0$$

....(iv)

Here u_i , the energy in the i th interval (compartment) is also a constant.

Since the system must satisfy both the relations given by the equations (iii) and (iv), therefore we can write* :

$$\sum_{i=1}^{i=k} [\alpha dn_i + \beta u_i dn_i] = 0$$

or

$$\sum_{i=1}^{i=k} (\alpha + \beta u_i) dn_i = 0$$

...(v)

Here α and β are the constants, whose values are to be determined.

The distribution of n particles among k energy intervals is similar to the distribution of n particles in k compartments of a box. We suppose that each energy interval is further divided into cells. Let $g_1, g_2, g_3, \dots, g_k$ be the numbers of cells in the corresponding energy intervals. The thermodynamic probability of the macrostate $(n_1, n_2, n_3, \dots, n_k)$ is then given by :

$$W(n_1, n_2, n_3, \dots, n_k) = n! \prod_{i=1}^{i=k} \frac{(g_i)^{n_i}}{n_i!} = W(\text{say})$$

(Refer to section 3.16)

Taking natural logarithms, we get

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

....(vi)

*This is known as the method of Lagrangian undetermined multipliers.

Note that $\prod (g_i)^{n_i} = (g_1)^{n_1} \times (g_2)^{n_2} \times (g_3)^{n_3} \times \dots \times (g_k)^{n_k}$

$$\therefore \ln \left[\prod (g_i)^{n_i} \right] = n_1 \ln g_1 + n_2 \ln g_2 + \dots$$

$$= \sum_{i=1}^{i=k} n_i \ln g_i$$

Applying Stirling formula * to the equation (vi), we get

$$\ln W = n \ln n - n + \sum_{i=1}^{i=k} n_i \ln g_i - \sum_{i=1}^{i=k} n_i \ln n_i + \sum_{i=1}^{i=k} n_i$$

Since $\sum_{i=1}^{i=k} n_i = n$, so on simplification, we get

$$\ln W = n \ln n + \sum_{i=1}^{i=k} n_i \ln g_i - \sum_{i=1}^{i=k} n_i \ln n_i \quad \dots(vii)$$

Now n and g_i and hence $\ln n$ and $\ln g_i$ are constant and for a system in equilibrium $\ln W$ is constant. $\therefore$ Differentiating on both sides, we get

$$0 = 0 + \sum_{i=1}^k dn_i \ln g_i - \sum_{i=1}^k \left[dn_i \ln n_i + n_i \frac{1}{n_i} dn_i \right]$$

$$0 = \sum_{i=1}^k dn_i \ln g_i - \sum_{i=1}^k dn_i \ln n_i - \sum_{i=1}^k dn_i$$

But $\sum_{i=1}^k dn_i = 0$

$$0 = \sum_{i=1}^k (\ln g_i - \ln n_i) dn_i \quad \dots(viii)$$

Subtracting (v) from (viii), we get :

$$\therefore 0 = \sum_{i=1}^{i=k} [\ln g_i - \ln n_i - \alpha - \beta u_i] dn_i$$

Because all values of dn_i are independent of each other, therefore, above equation is valid only when :

$$\ln g_i - \ln n_i - \alpha - \beta u_i = 0$$

* According to the Stirling formula $\ln(n!) = n \ln n - n$.

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

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

$$n_i = g_i e^{-\alpha} e^{-\beta u_i} \quad \dots(ix)$$

This is the expression for the Maxwell Boltzmann law of energy distribution. Values of α and β are determined from the conditions in which the system operates. Here $e^{-\beta u_i}$ is called Boltzmann factor

$\sum_{i=1}^{i=k} e^{-\beta u_i}$ is called partition function.

Evaluation of $e^{-\alpha}$ and $e^{-\beta u_i}$

Determination of $e^{-\alpha}$

Let n_p represent the number of molecules per unit momentum interval.

From equation (ix) we can write the number of molecules in the momentum interval p and $p + dp$ as :

$$n_p dp = g_p e^{-\alpha} e^{-\beta u_p} dp \quad \dots(x)$$

Here u_p is the kinetic energy of the molecules having momentum p .

Now $u_p = \frac{p^2}{2m}$, where m is the mass of the molecule.

$$\therefore n_p dp = g_p dp e^{-\alpha} e^{-\frac{\beta p^2}{2m}} \quad \dots(xi)$$

Note that $u_p = \frac{1}{2} m v^2 = \frac{m^2 v^2}{2m} = \frac{p^2}{2m}$

The number of the cells g_p in the momentum interval p and $(p + dp)$ is given by :

$$g_p dp = \frac{4\pi V}{h_0^3} p^2 dp$$

[Refer to equation (3.3.1)]

where V is the volume of the system in position space and h_0^3 is the available volume of the cell in the phase space.

Hence $n_p dp = \frac{4\pi V}{h_0^3} p^2 e^{-\alpha} e^{-\beta p^2 / 2m} dp \quad \dots(xii)$

If p_m be the maximum value of the momentum, then :

Total number of molecules, $n = \int_0^{p_m} n_p dp = \int_0^{\infty} n_p dp$

Since there are no molecules between p_m and ∞ so raising the limit from p_m to infinity does not affect the actual value of the integral.

Total number of molecules is given by :

$$n = \int_0^{\infty} n_p dp = \int_0^{\infty} \frac{4\pi V}{h_0^3} p^2 e^{-\alpha} e^{-\frac{\beta p^2}{2m}} dp.$$

So

$$n = \frac{4\pi V}{h_0^3} e^{-\alpha} \int_0^{\infty} p^2 e^{-\frac{\beta p^2}{2m}} dp. \quad \dots(xiii)$$

or

Using the standard integral,

$$\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4} \left(\frac{\pi}{a^3} \right)^{1/2}, \text{ we can write}$$

$$n = \frac{4\pi V}{h_0^3} e^{-\alpha} \left[\frac{1}{4} \left(\frac{\pi}{(\beta/2m)^3} \right)^{1/2} \right] = \frac{V}{h_0^3} e^{-\alpha} \left(\frac{2\pi m}{\beta} \right)^{3/2}$$

$$e^{-\alpha} = \frac{nh_0^3}{V} \left(\frac{\beta}{2\pi m} \right)^{3/2} \quad \dots(xiv)$$

Determination of β

Substituting the value of $e^{-\alpha}$ in equation (xii), we find

$$n_p dp = \frac{4\pi V}{h_0^3} p^2 \times \frac{nh_0^3}{V} \left(\frac{\beta}{2\pi m} \right)^{3/2} e^{-\frac{\beta p^2}{2m}} dp$$

or

$$n_p dp = 4\pi n \left(\frac{\beta}{2\pi m} \right)^{3/2} p^2 e^{-\frac{\beta p^2}{2m}} dp. \quad \dots(xv)$$

Now $p^2 = 2mu$.

$$\therefore 2p dp = 2m du \text{ or } dp = \frac{m du}{p} = \frac{m}{\sqrt{2mu}} du = \sqrt{\frac{m}{2u}} du$$

Substituting the values of p^2 and dp in equation (xv), we get the number of molecules in the energy interval u and $u + du$ as follows :

$$n_u du = 4\pi n \left(\frac{\beta}{2\pi m} \right)^{3/2} \times 2mu e^{-\beta u} \times \sqrt{\frac{m}{2u}} du$$

or

$$n_u du = \frac{2n}{\sqrt{\pi}} \sqrt{u} \beta^{3/2} e^{-\beta u} du \quad \dots(xvi)$$

For an ideal gas, each molecule possesses an average kinetic energy $\frac{3}{2} kT$, where k is Boltzmann constant and T is temperature in kelvin. Hence total energy of the system of n molecule is :

$$E = \int_0^{\infty} u n_u du = n \frac{3}{2} kT$$

or

$$\frac{3}{2} nkT = \frac{2n}{\sqrt{\pi}} \beta^{3/2} \int_0^{\infty} u^{3/2} e^{-\beta u} du$$

Using the standard integral,

$$\int_0^{\infty} x^{3/2} e^{-ax} dx = \frac{3}{4a^2} \sqrt{\frac{\pi}{a}}$$

$$\frac{3}{2} nkT = \frac{2n}{\sqrt{\pi}} \beta^{3/2} \times \frac{3}{4\beta^2} \sqrt{\frac{\pi}{\beta}}$$

or

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

That is,

$$\beta = \frac{1}{kT} \quad \dots(3.8.1)$$

Substituting the value of β in equation (xvi), we have

$$n_u du = \frac{2n}{\sqrt{\pi}} \sqrt{u} \frac{1}{(kT)^{3/2}} e^{-\frac{u}{kT}} du$$

or

$$n_u du = \frac{2\pi n}{(\pi kT)^{3/2}} \sqrt{u} e^{-\frac{u}{kT}} du \quad \dots(xvii)$$

This is the required expression for Maxwell Boltzmann energy distribution for an ideal gas. It gives the number of particles (molecules) having energy between u and $u + du$.

Expression for the distribution of speeds

Since

$$u = \frac{1}{2} mv^2,$$

$\therefore$

$$du = \frac{1}{2} m \times 2v dv = mv dv.$$

Substituting the values in equation (xvii), we find

$$n_v dv = \frac{2\pi n}{(\pi kT)^{3/2}} \left(\frac{1}{2} mv^2 \right)^{1/2} e^{-\frac{mv^2}{2kT}} \times mv dv$$

or

$$n_v dv = \sqrt{2\pi n} \left(\frac{m}{\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv \quad \dots(xviii)$$

This is the required expression for Maxwell Boltzmann distribution for molecular speeds. It gives the number of particles (molecules) having velocity (speed) within v and $v + dv$ for an ideal gas having n molecules at absolute temperature T .

The fraction of the molecules having speed between v and $v + dv$ is given by

$$\frac{n_v dv}{n} = \sqrt{2\pi} \left(\frac{m}{\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv$$

By definition it is the probability that a molecule will have speed between v and $v + dv$, i.e.

$$P(v) dv = \sqrt{2\pi} \left(\frac{m}{\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv.$$

The probability that a molecule will possess speed v i.e. the probability function $P(v)$ is given by

$$P(v) = \sqrt{2\pi} \left(\frac{m}{\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$

3.9. GRAPHICAL REPRESENTATION OF MAXWELL-BOLTZMANN DISTRIBUTION OF SPEEDS

The mathematical expression for the Maxwell Boltzmann distribution of speed in a sample of ideal gas is given by

$$n_v dv = \sqrt{2\pi n} \left(\frac{m}{\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv.$$

A plot of n_v , the number of molecules having speed v , against v is plotted as shown in the Fig. 3.9.1. The number of molecules $n_v dv$ having speeds between v and $v + dv$ is given by the area under the curve in the interval dv (shown shaded). The total area under the curve, given by summation of $n_v dv$ over all the possible speeds gives the number of molecules.

$$\int_0^{\infty} n_v dv = n.$$

The lower limit of integral reflects the fact that the speed of a molecule cannot be negative.

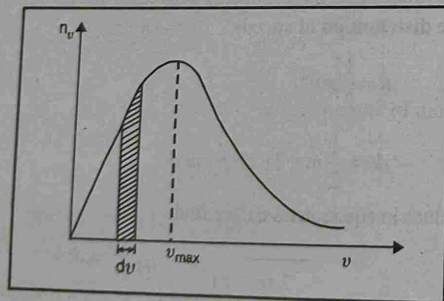


Fig. 3.9.1

(i) At low values of v , the exponential term $\exp\left(-\frac{mv^2}{kT}\right)$ becomes practically equal to one. So n_v

increases with increase in the value of v as n_v is proportional to v^2 . n_v reaches to its maximum value at a particular value of v equal to v_{max} , called the most probable speed v_p .

For large value of v , the exponential term dominates over v^2 , now n_v becomes proportional to $\exp\left(-\frac{mv^2}{kT}\right)$, and decreases with the increase in value v .

(ii) The distribution curve is asymmetrical about its peak. This is because the lowest possible speed of the molecules is zero but there is no limit to the highest speed of the molecule. Therefore the average speed $\bar{v}$ is slightly larger than the most probable speed v_m corresponding to the peak of the curve (Fig. 3.9.2). As such the area under the curve on the right side of the peak is larger than the area on the left side.

Effect of Temperature. The most probable speed v_m (as well as $\bar{v}$ and v_{rms}) increases in proportion to the square root of the absolute temperature of the gas. Hence the distribution curve broadens with rise in temperature. Since the area under the curve (which represents the total number of molecules in a gas) must remain unchanged, the curve becomes flattened as the temperature rises. This means that the number of molecules which have speeds greater than given speed increases, as shown in Fig. 3.9.2.

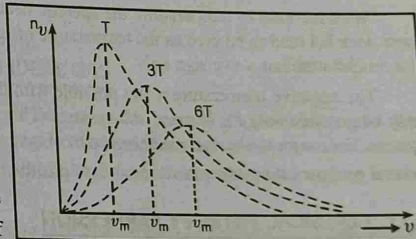


Fig. 3.9.2

Effect of Molecular mass. The most probable speed v_p ($\bar{v}$ and v_{rms}) being inversely proportional to $\sqrt{m}$, decreases with increasing molecular mass. Accordingly molecular speeds in hydrogen are on the whole greater than in oxygen at the same temperature as shown in the diagram.

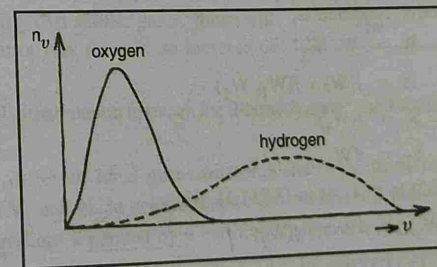


Fig. 3.9.3

3.10. NEGATIVE TEMPERATURE

Negative temperature may refer to temperatures that are expressed as negative numbers on Celsius or Fahrenheit scales, with values that are lower than the zero points of those scales but still higher than absolute zero. But according to laws of thermodynamics, there cannot be any temperature less than zero kelvin. In other words, a negative temperature is not possible on Kelvin's scale. This concept may be logically explained as :

If we consider negative temperature exists and is attainable, then let us assume the sink of a heat engine at some negative temperature, say $T_2 = -T_2$. The efficiency will be

$$\eta = 1 - \left(\frac{-T_2}{T_1} \right) = 1 + \frac{T_2}{T_1}$$

$$\eta > 1.$$

The efficiency of engine is greater than unity which is against the second law of thermodynamics and hence not possible. Hence we can conclude that the above obtained result violates the second law of thermodynamics. Hence the assumption made of negative temperature exists is not true. So there cannot be a negative temperature. We can say that a sink at absolute zero is unattainable, so an engine with 100% efficiency is not possible.

With increase in temperature, the specific heat of a substance decreases. However, the specific heat does not tend to be zero as the temperature of substance tends to infinity. This clearly shows that the temperature has a +ve sign only.

The negative temperature is not possible with the system as a whole. The negative temperatures may be possible only for isolated sub-systems. This sub-system is considered isolated from the main system. For example, the nucleus being a part of system, can have a negative temperature. But for all the normal purposes the temperature are always positive.

3.11. CLASSICAL ENTROPY EXPRESSION

In equilibrium position, both entropy and probability become maximum, thus Boltzmann concluded that entropy (S) is a function of probability (W).

$$\text{i.e. } S = f(W)$$

In order to find the nature of the function, let us consider two independent systems 1 and 2 having entropies S_1 and S_2 respectively. The entropy S of the two systems when taken together is given by

$$S = S_1 + S_2 \quad \dots(3.11.1)$$

If W_1 is the probability of 1 and W_2 is the probability of 2, then probability of finding both the systems at their respective condition is

$$W = W_1 W_2$$

$$\therefore S = f(W) = f(W_1, W_2) \quad \dots(3.11.2)$$

$$\therefore S_1 = f(W_1) \quad \dots(3.11.3)$$

$$\text{and } S_2 = f(W_2) \quad \dots(3.11.4)$$

Putting Eqs. (3.11.2) to (3.11.4) in (3.11.1), we get

$$f(W_1, W_2) = f(W_1) + f(W_2) \quad \dots(3.11.5)$$

Differentiating Eq. (3.11.5) partially w.r.t. W_1 and W_2 , we get

$$W_2 f(W_1, W_2) = f'(W_1)$$

$$W_2 f(W_1, W_2) = f'(W_1)$$

$$\therefore \frac{W_2}{W_1} = \frac{f'(W_1)}{f'(W_2)}$$

$$\text{or } W_1 f'(W_1) = W_2 f'(W_2) = \dots = k \text{ (a constant)}$$

$$\therefore f'(W_1) = \frac{k}{W_1}; f'(W_2) = \frac{k}{W_2}$$

Integrating, we get

$$f(W_1) = k \ln W_1 + C_1$$

$$\text{and } f(W_2) = k \ln W_2 + C_2$$

In general,

$$f(W) = k \ln W + C$$

$$\text{or } S = k \ln W + C$$

The value of constant C is found to be zero

$$\text{i.e. } C = 0$$

$$\therefore S = k \ln W$$

3.12. GIBBS PARADOX : ENTROPY OF AN IDEAL GAS

According to thermodynamics, the entropy of an irreversible process is greater than zero. We know diffusion is an irreversible process. When we mix two different gases the entropy increases because the diffusion takes place and we know diffusion is an irreversible process according to the thermodynamics.

Also when we mix two similar gases diffusion take place therefore the entropy of mixing two similar (indistinguishable) gases also increases.

But according to statistical mechanics, if the number of microstates increases, then the entropy increases because the number of increase of microstates means there is an increase of randomness and there is increase of entropy. In mixing of two different gases, new microstates arise so there is an increase of entropy.

But when we are mixing two similar gases, there will not be any increase of entropy as there is no increase of microstates.

So there is paradoxical phenomenon between the thermodynamics and statistical mechanics which is known as Gibbs Paradox.

Let us consider two different ideal gases (distinguishable) with number of particles N_1 in compartment A of volume V_1 and N_2 in compartment B of volume V_2 . These two gases are at same pressure and temperature and are separated by a partition as shown in Fig. 3.12.1. When partition is removed the gases will be mixed in a volume $V = V_1 + V_2$ at the same temperature.

The entropy of mixer increases. Since the process is irreversible. But when the gases are of same kind (indistinguishable) the change in entropy of mixture should be zero. But we found increase in entropy. This is in contradiction. Gibbs paradox is resolved by the concept of quantum mechanics.

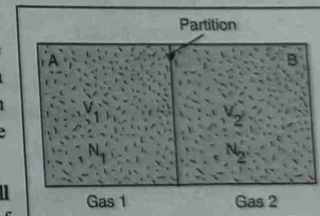


Fig. 3.12.1

Removal of paradox. In order to resolve this paradox, the expression for the Maxwell-Boltzmann count must be divided by $N!$. If N number of particles interchange their position, according to permutation it will be $N!$.

$$S = \frac{5}{2}NK - NK \log \left[\frac{N}{V} \left(\frac{h^2}{2\pi mKT} \right)^{3/2} \right] + k \log N!$$

In otherwords, we should subtract the term $K \log N!$ from this equation.

$$S = \frac{5}{2}Nk - Nk \log \left[\frac{N}{V} \left(\frac{h^2}{2\pi mKT} \right)^{3/2} \right]$$

In this way the paradox is resolved. This has been verified experimentally for a gas at high temperature also. This equation is also known as **Sackur Tetrode** equation.

MULTIPLE CHOICE QUESTIONS

- Q. 3.01. To describe a dynamic system we must have the knowledge of :
 (a) position space only
 (b) momentum space only
 (c) both position as well as momentum space
 (d) neither position nor momentum space.
- Q. 3.02. The minimum volume of an elementary cell in classical statistics is :
 (a) h^3
 (b) less than h^3
 (c) more than h^3
 (d) can have any arbitrary value.
- Q. 3.03. Select the correct statement, in Maxwell Boltzmann (MB) statistics, the particles are :
 (a) distinguishable
 (b) indistinguishable
 (c) partly distinguishable.
- Q. 3.04. There are seven particles and seven cells. In how many ways can they be arranged, assuming that the particles obey F-D statistics.
 (a) 1 way
 (b) 7 ways
 (c) 71 ways
 (d) 7⁷ ways.
- Q. 3.05. Pauli's exclusion principle is applicable to :
 (a) M.B
 (b) F.D.
 (c) B.E.
 (d) None.
- Q. 3.06. Hydrogen escapes faster from the earth's atmosphere than oxygen because :
 (a) hydrogen has higher most probable velocity than oxygen
 (b) hydrogen gets heated up faster than oxygen
 (c) hydrogen molecules possess less average kinetic energy than oxygen molecules
 (d) of some reason other than those mentioned above.
- Q. 3.07. Which one of the following is not a constraint on an isolated dynamic system in the state of equilibrium ?
 (a) Each cell is of the same size

- (b) The number of particles is constant
 (c) Total energy of the system is constant
 (d) None of the above.
- Q. 3.08. Which of the following is zero for a sample of gas molecules having Maxwellian distribution of speeds ?
 (a) Average velocity
 (c) Most probable velocity
 (b) Root mean square velocity
 (d) None of the above.
- Q. 3.09. Out of N particles in a gas, the number of particles having exactly the most probable speed is :
 (a) N
 (c) 0
 (b) $N/2$
 (d) ∞ .
- Q. 3.10. In which of the following, no phase space cell can contain more than one particle.
 (a) M-B statistics
 (c) F-D statistics
 (b) B-E statistics
 (d) None of these.
- Q. 3.11. For a gas at NTP which shall be maximum :
 (a) v_{av}
 (c) v_{mp}
 (b) v_{rms}
 (d) All of the above.

ANSWERS

- 3.01. (c) 3.02. (d) 3.03. (a) 3.04. (a) 3.05. (b) 3.06. (a)
 3.07. (a) 3.08. (a) 3.09. (c) 3.10. (c) 3.11. (b)

SHORT ANSWER QUESTIONS

Q. 1. What is meant by available volume ?

Ans. The product of volume in the position space and that in the momentum space is called available volume. The available volume of a system of particles may be written as :

$$\tau = \int \int \int dx \, dy \, dz \int \int \int dp_x \, dp_y \, dp_z.$$

Q. 2. In classical statistics, how can we treat the identical gas molecules as distinguishable from each other ?

Or

In classical statistics, what is the basis for treating identical gas molecules as distinguishable ?

Ans. In classical physics, there is no restriction on the size of the phase space cell. So, we can reduce its size to as small as we desire. Accordingly, the phase space may be divided into so large a number of cells that each cell contains either one molecule or none. And, the molecules can be distinguished by the cells they occupy, even though they may be identical to each other.

Q. 3. List the basic assumptions of Maxwell Boltzmann statistics.

Ans. Maxwell Boltzmann (MB) statistics is based on the following assumptions :

- The particles of the system are distinguishable.
- Available volume of the phase space cell can be as small as we desire and even approach zero.
- Any number of particles can occupy a phase space cell.
- The number of phase space cell is very-very large.

Q. 4. Why is the choice of the cell size immaterial in classical statistics ?

Ans. The available volume of the phase space cell is given by

$$d\tau = dx \, dy \, dz \, dp_x \, dp_y \, dp_z.$$

Since in classical physics the distance as well as momentum can have any small magnitude, even that tending to zero, therefore, the volume or the size of the phase space cell can be as small as we desire. Hence the choice of the cell size is immaterial in classical statistics.

Q. 5. What is the minimum size of a cell in classical statistics and quantum statistics ?

Ans. In classical physics, the phase space cell can be assumed to have available volume as small as we desire, even that tending to zero. Accordingly, the phase space can be divided into very large number of cells. In quantum mechanics the volume of elements cells in phase space can not be less than h^3 where h is Planck's constant.

Q. 6. What is the role of elementary cell in statistical physics ?

Or

What is the purpose of dividing phase space into cells ?

Ans. A dynamic system consisting of very larger number of particles spends most of its time in most probable state, also called equilibrium state. So, to study such a system, we study the most probable state of the system. The most probable state of the system is completely determined by the position and momentum co-ordinates of the particles. For this purpose we divide the phase space into compartments and each compartment may be divided into space cells. Each compartment represents momentum of energy interval. A number of particles can possess a given amount of energy and momentum at a particular instant. All these particles may be treated to be in one compartment. The compartments or intervals are of different sizes depending upon the magnitude or energy of momentum. Each compartment may be further divided into equal sized cells to house one or more particles. Then, the probability considerations of distributing n particles in k compartments of different sizes, each one of which is divided into $g_1, g_2, \dots$ cells can be used to solve the problem.

Q. 7. What is phase space ? How will you divide it into cells ?

Or

What is the concept of a phase space ? What is its dimensionality ?

Ans. Phase Space. The combination of position space and momentum space is called phase space. Phase space is a six dimensional space in which x, y, z, p_x, p_y, p_z represent mutually perpendicular directions.

A small volume element in phase space is denoted by $d\tau$ and is given by

$$d\tau = dx dy dz dp_x dp_y dp_z$$

or

$$d\tau = dV d\Gamma$$

Generally we write it as h_0^3 , so

$$h_0^3 = dx dy dz dp_x dp_y dp_z$$

h_0 has dimensions $[ML^2 T^{-1}]$ and its unit is Js.

Division of phase space into compartment and cells

We can divide the phase space into compartments and cells, and all particles possessing a given amount of energy at a particular instant are consigned to a particular cell, also all particles possessing a given amount of momentum at a particular location can be arranged to one cell.

Each compartment can contain different number of cells. Therefore, compartments correspond to different energy intervals on momentum intervals. Thus, by dividing the phase space of a system into compartments and cells we can analyse the distribution of energy or momentum among the particles.

Suppose, we divide the phase space of a system in k compartments. Let at any instant the number of particles in the different compartments be $n_1, n_2, n_3, \dots, n_k$. Then the macrostate of the system can

be denoted as $(n_1, n_2, n_3, \dots, n_k)$. The dynamic system continuously goes from one macrostate to another. Therefore, the values of $n_1, n_2, n_3, \dots, n_k$ etc. continuously change with time. However, the systems spend maximum time in the most probable state. Therefore, we can study the behaviour of the system by analysing the distribution of its phase space into the most probable state. That is the main problem we are going to encounter in statistical physics.

Q. 8. Explain what is phase space ?

Ans. See Q. No. 7.

Q. 9. What determines the distribution of molecular speeds in a perfect gas ?

Ans. $n_v d_v$ gives the number of molecules having speed v and $v + dv$ and is a function of temperature of the gas and molecular mass. Hence it determines the distribution of molecular speeds in a perfect gas.

Q. 10. When the temperature of the gas sample rises, how does the area under the v and n_v curve vary ?

Ans. It remains constant, because area under the v and n_v curve is equal to the number of molecules in the sample, which does not vary with temperature.

Q. 11. How does the fraction $n_v dv/n$ for the given value of v vary when the temperature rises ?

Ans. As the temperature rises, more and more molecules acquire higher speeds. So, the fraction $n_v dv/n$ for the given volume V goes on decreasing.

Q. 12. Explain the phenomenon of evaporation of liquids making use of the Maxwell Boltzmann law for the distribution of molecular speeds.

Ans. Evaporation from liquid surface. For leaving the liquid surface, a molecule must possess certain minimum velocity (kinetic energy). The average velocity of the molecules is less than this limit. However, according to Maxwellian distribution of molecular speeds, some molecules can possess very high velocities at all temperatures. If such molecules happen to be on the surface, they easily escape out. This is how evaporation takes place. This also explains how evaporation occurs at all temperatures.

Q. 13. Explain the escape of gases from the earth's atmosphere with the help of Maxwell Boltzmann law for the distribution of speeds.

Ans. Escape of gases from the earth's atmosphere. To escape from the gravitational pull of the earth, a body should possess a velocity equal to or greater than the escape velocity. In accordance with Maxwellian distribution of velocities, some molecules do possess very high velocities and they escape from the earth's atmosphere. (The phenomenon is similar to the evaporation of liquids).

Q. 14. What is the value of phase volume of a cell in classical statistics ?

Ans. In classical statistics, the phase volume can be reduced to any small size as we desire and can approach to zero in the limit, hence phase volume is entirely arbitrary in classical statistics.

QUESTIONS

- (a) Define phase space.
(b) What is the purpose of dividing phase space into cells ?
(c) What is the minimum size of a phase space cell in classical and quantum statistics ?
(d) Why is the choice of cell size immaterial as far as the classical statistics is concerned ?
- Compare MB, BE and FD statistics.
- Describe basic approach of three statistics.
- Define phase space and momentum space. Determine the number of phase space cells in the momentum interval p and $p + dp$. What is the minimum size of a phase space cell in classical and quantum statistics ?
- The Maxwellian distribution of speed v amongst n molecules per cm^3 enclosed in a chamber at

temperature T is given by $n_v dv = \sqrt{2\pi n} \left(\frac{m}{\pi k T} \right)^{3/2} e^{-\frac{mv^2}{2kT}} v^2 dv$

- (i) Draw a curve showing n_v against v at a given temperature T .
 (ii) Explain why the curve shows a peak.
 6. (a) What are the basic assumptions of three statistics?
 (b) Derive Maxwell-Boltzmann relation:

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

for the energy distribution of an ideal gas in equilibrium.

- Define Phase space. Obtain the number of phase space cells in the momentum interval dp .
- Treating an ideal gas as a system governed by classical statistics, derive the Maxwell Boltzmann distribution of molecular speeds.
- Derive M-B law for distribution of molecular speeds. Use this law to obtain an expression for the M.P. speeds of molecules.
- What is Maxwell-Boltzmann statistics? On What assumptions it is based? Using this statistics find the expression for distribution of molecular speeds.
- Explain the term phase space and its division into cells.
- Derive the Maxwell-Boltzmann law of distribution of molecular speeds by applying classical statistics.
- Explain the concept of phase-space.
- Define phase space cell and derive expression for the number of statistics.
- Describe briefly the experiment giving verification of M-B law of distribution of molecular speed.
- Explain the behaviour of Maxwell distribution of molecular speeds as a function of temperature.

NUMERICAL PROBLEM

- Discuss the distribution of 3-particles in 2-cells, assuming that they obey (i) M-B statistics (ii) B-E statistics and (iii) F-D statistics.
- Consider a system of large number of particles, each having mass of 0.1 g which are lying in a box at an equilibrium temperature 300 K. Find the probability that any one of the particles may spontaneously fly to a height of 1 Å (Assume that they obey M-B statistics).

$$\text{Ans. } k e^{-\frac{98}{9.14} \times 10^6}$$

Hint. In M-B statistics

$$P(v) = \sqrt{2\pi} \left(\frac{m}{\pi k T} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$

or
Here

$$P(v) = K e^{-\frac{u}{kT}}$$

$$u = mgh$$

$$P(v) = K e^{-\frac{mgh}{kT}}$$

4

UNIT

BOSE-EINSTEIN AND FERMI-DIRAC STATISTICS

4.1. LIMITATIONS OF MB STATISTICS—BIRTH OF QUANTUM STATISTICS

The Maxwell-Boltzmann statistics provides satisfactory explanation of the distribution of energy among the molecules of gas samples. However, there are other systems of particles such as photons in a constant temperature enclosure or free electrons in a piece of metal which, although have dynamic characteristics similar to that of gases, yet MB statistics fails to explain the energy distribution for them. The photons in a constant temperature enclosure are characterised by random motion and negligible interparticle interaction. Same is the case with the free electrons. It is because of this reason that sometimes we call them photons gas and electron gas. Why then, do the MB statistics fail to explain their energy distribution? The main reason for this limitation of the MB statistics lies in the fact that the system of photons and free electrons are subjected to certain constraints which are not applicable to the gas systems. By taking those constraints into account, two more statistics have been developed. They may be called non-classical statistics, because they are based on certain concepts, such as quantisation of energy, which have no place in classical physics.

Quantum Statistics

The non-classical statistics are generally called quantum statistics, because they are based on the concept of quantisation of energy. The quantum statistics are of two types:

- Bose-Einstein statistics and
- Fermi-Dirac statistics.

Bose-Einstein statistics

Bose, in the year 1924, deduced the Planck's law of radiations on the basis of statistical considerations different than those of MB statistics. In the same year, Einstein used the similar reasoning to explain the behaviour of gas molecules. Thus, Bose Einstein statistics (BE statistics) was born.

The basic assumptions of BE statistics are given below:

- The particles of the system are indistinguishable and identical.
- Available volume of the phase space cell cannot be less than h^3 , where h is Planck's constant.
- Any number of particles can occupy a phase space cell.
- The number of phase space cells is comparable with the number of particles. That is,

$$\text{occupation index } \frac{n_i}{g_i} \approx 1.$$

- The particles of the system under consideration do not obey the Pauli's exclusion principle.

Bosons

Bosons are the particles of a system whose energy spectra can be explained on the basis of BE statistics. Bosons do not obey Pauli's exclusion principle. That is, two or more particles can exist in the same energy level. The bosons have either zero or integral spin.

Examples of bosons are as under :

- K and π mesons (spin 0).
- Atoms like ${}^4\text{He}$, total spin of whose electrons, protons and neutrons is integral.
- Photons, that is quanta of light waves (spin 1).

Fermi-Dirac statistics

In the year 1926, Fermi and Dirac used the Pauli's exclusion principle to modify the BE statistics and successfully explained the behaviour of free electrons in metals. Thus, Fermi Dirac statistics (FD statistics) came into existence.

Following are the basic assumptions of FD statistics :

- The particles of the system are indistinguishable and identical.
- Available volume of the phase space cell cannot be less than h^3 where h is the Planck's constant.
- A phase space cell cannot contain more than one particle.
- The number of phase space cells is large as compared with the number of particles, such

that the occupation index $\frac{n_i}{g_i} \leq 1$.

- The particles of the system obey Pauli's exclusion principle.

Fermions

Fermions are the particles of a system whose energy distribution can be explained on the basis of FD statistics. Fermions obey Pauli's exclusion principle. That is, two or more particles cannot exist in the same energy level. The fermions have half integral spin.

Examples of fermions are (i) electrons (ii) positrons (iii) neutrons (iv) protons and (v) atoms like ${}^3\text{He}$.

4.2. DISTRIBUTION OF PARTICLES ACCORDING TO MB, BE AND FD STATISTICS

The MB, BE and FD statistics are applicable under different sets of constraints as regards the following :

- The distinguishable or indistinguishable nature of molecules, and
- The number of particles that can occupy a cell.

Therefore, the distribution of particles into cells will also be different for the three statistics. Let us explain it with an example.

Suppose, we wish to distribute the two particles in three cells. It can be done as described below :

MB statistics

In it the particles are distinguishable. Let they be designated as 'a' and 'b'. Also, more than one particle can occupy the same cell. So the possible microstates are :

(ab, 0, 0); (0, ab, 0); (0, 0, ab); (a, b, 0); (0, a, b); (a, 0, b); (b, 0, a); (0, b, a); (b, a, 0). That is, in all nine microstates are possible.

BE statistics

In it the particles are indistinguishable. Let they be a and a. Also, more than one particle can occupy the same cell. So, the possible microstates are :

(aa, 0, 0); (0, aa, 0); (0, 0, aa); (a, a, 0); (0, a, a); (a, 0, a).

That is, in all six microstates are possible :

FD statistics

In it the particles are indistinguishable and one cell cannot contain more than one particle. So, the possible microstates are :

(a, a, 0); (0, a, a); (a, 0, a).

That is, in all three microstates are possible.

Example 4.1. Write the accessible microstates for distributing 4 particles in 2 cells according to the MB, BE and FD statistics.

Solution.

MB statistics. Let the particles be designated as a, b, c and d. Then the accessible macrostates are as follows :

(4, 0) $\rightarrow$ (abcd, 0)

(3, 1) $\rightarrow$ (abc, d), (bcd, a), (cda, c), (dab, c)

(2, 2) $\rightarrow$ (ab, cd), (ac, bd), (ad, bc), (bd, ac), (cd, ab) (bc, ad)

(1, 3) $\rightarrow$ (d, abc), (a, bcd), (b, cda), (c, dab)

(0, 4) $\rightarrow$ (c, abcd)

That is, in all 16 microstates are possible.

BE statistics

Let each particle be designated as 'a'. Then the two accessible microstates are as follows :

(4, 0) $\rightarrow$ (aaaa, 0)

(3, 1) $\rightarrow$ (aaa, a)

(2, 2) $\rightarrow$ (aa, aa)

(1, 3) $\rightarrow$ (a, aaa)

(0, 4) $\rightarrow$ (0, aaaa)

That is, in all five microstates are possible.

FD statistics

Here no cell can occupy more than two particles. But we have 4 particles and 2 cells. Therefore, the FD distribution is not possible, because there have to be at the best two particles in each cell which is not permissible. So, the number of accessible microstates is zero.

Example 4.2. What are the number of ways to arrange two particles 'a' and 'b' into three energy states according to Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics ?

Solution.

MB Statistics.

The particles are distinguishable and there is no restriction on the particle to enter into any energy state. Hence there are nine possible arrangements as shown in table 4.1.

Table 4.1

1st energy state	ab	-	-	a	-	a	b	-	b
2nd energy state	-	ab	-	b	a	-	-	b	a
3rd energy state	-	-	ab	a	b	b	a	a	-

BE statistics

The particles are indistinguishable. Let us denote both of them by 'a'. There is no restriction on the particle to enter into any energy state. Hence there are six possible arrangements as shown in table 4.2.

Table 4.2

1st energy state	aa	-	-	a	-	a
2nd energy state	-	aa	-	a	a	-
3rd energy state	-	-	aa	-	a	a

FD statistics

The particles are indistinguishable. Let us denote both of them by 'a'. They obey Pauli's exclusion principle and so one energy state can occupy one particle. Hence there are three possible arrangements as shown in table 4.3.

Table 4.3

1st energy state	a	-	a
2nd energy state	a	a	-
3rd energy state	-	a	a

Example 4.3. Discuss the distribution of three particles in three cells assuming that they obey

- (i) M-B statistics (ii) B-E statistics (iii) F-D statistics.

Solution. (i) In M-B statistics all three particles are distinguishable. Let us call them a, b and c. Since there is no restriction on the particles to enter a given cell, so 27 arrangements are possible as shown in table (4.4).

Table 4.4

Cell	c c b	b a a	c b a	x x x	c b a	a c b c a b	x x x	c a b c a b	x	x	abc
1st											
2nd	b a a	c c b	x x x	c b a	a b c a b c	x x x	c a b c a b	b a c	x	a b c	x
3rd	a b c	a b c	a b c a b c	a b c a b c	x x x	b a c	b a c	x x x	abc	x	x

(ii) In B-E statistics, all the particles are indistinguishable. Let us denote them by dots (.). Also there is no restriction on the particles to enter a given cell, so 10 arrangements are possible as shown in table 4.5).

Table 4.5

Cells	.	.	.	x	x	.	.	.	.	.	.
1st	.	.	.	x	x	.	.	.	.	.	.
2nd	x	.	.	x	.	.	.	x	.	x	.
3rd	x	x	.	.	x	.	.	x	.	.	.

(iii) In F-D statistics, all the particles are indistinguishable. Let us denote them by dots (.) and there is restriction on the particles that only one particle can enter into one cell, so 3-arrangements are possible as shown in table (4.6).

Table 4.6

Cell	.
1st	.
2nd	.
3rd	.

4.3. SIZE OF THE PHASE SPACE CELL IN QUANTUM STATISTICS

According to the uncertainty principle, the product of the uncertainties in the measurement of the position and momentum cannot be less than 'h', where h is the Planck's constant. That is :

$$\Delta x \Delta p_x \geq h.$$

Therefore :

$$\text{Available volume } \Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z = h^3.$$

That is, the size of the phase space cell cannot be less than h. Since BE and FD statistics are based on the Planck's quantum hypothesis, so for applying them, we cannot assume the size of the phase space cell less than h. Generally, we assume it to be equal to h.

4.4. IN THE QUANTUM STATISTICS, THE PARTICLES OF THE SYSTEM CANNOT BE DISTINGUISHED FROM EACH OTHER

In classical statistics, the size of the cell can be as small as we desire. So, the number of the phase space cells can be made very, very large as compared to the number of the particles and the chance of one cell containing more than one particle is negligible. And although each particle is identical to the other particle, yet it can be distinguished from the other in terms of the cell it occupies.

In quantum statistics, the size of the phase space cell cannot be smaller than h. Therefore, the number of the phase space cells may be comparable with the number of particles. So, one cell may contain one or more than one particles and hence the particle cannot be distinguished by the cell it occupies.

4.5. BOSE-EINSTEIN DISTRIBUTION LAW

Consider a system of n bosons (particles obeying BE statistics) and k compartments. Let $g_1, g_2, \dots, g_k$ be the number of cells in the compartment numbered 1, 2, ..., k respectively.

The system operates under the following two constraints :

(i) Total number of particles is constant and is equal to n

$$\text{i.e. } n_1 + n_2 + n_3 + \dots + n_k = n$$

or

$$\sum_{i=1}^{i=k} n_i = n = \text{a constant}$$

$$\therefore \sum_{i=1}^{i=k} dn_i = 0$$

... (4.5.1)

(ii) Total energy of the system is constant
i.e. $n_1 u_1 + n_2 u_2 + \dots + n_k u_k = a$ constant

or $\sum_{i=1}^k n_i u_i = a$ constant

$$\therefore \sum_{i=1}^k u_i dn_i = 0 \quad \dots(4.5.2)$$

Consider i th compartment having g_i cells. Let there be n_i indistinguishable particles in g_i cells. So there are $(g_i - 1)$ partitions and $(n_i + g_i - 1)$ objects. And $(n_i + g_i - 1)$ objects can be arranged among themselves in $(n_i + g_i - 1)!$ ways and n_i indistinguishable particles can be permuted among themselves in $n_i!$ ways and are meaningless. Similarly $(g_i - 1)$ partitions can be permuted among themselves in $(g_i - 1)!$ ways and are meaningless.

Also, the total number of arrangements = meaningful arrangements $\times$ meaningless arrangements.
That is,

$$\left[\frac{\text{Meaningful}}{\text{arrangements}} \right] = \frac{\text{Total number of arrangements}}{\text{Meaningless arrangements}}$$

Hence, total numbers of meaningful ways of distributing n_i particles in g_i cells according to the assumption of the statistics are :

$$\text{or } W_i = \frac{(n_i + g_i - 1)!}{(g_i - 1)! (n_i)!}$$

Here W_i gives the thermodynamic probability of distributing n_i particles in g_i cells. The thermodynamic probability of distributing n particles in k compartments is :

$$W = W_1 \times W_2 \times W_3 \times \dots \times W_i \times \dots \times W_k = \prod_{i=1}^k W_i \quad \dots(4.5.3)$$

$$\text{or } W = \prod_{i=1}^k \frac{(n_i + g_i - 1)!}{(g_i - 1)! (n_i)!} \quad \dots(4.5.3)$$

Taking natural logarithm on both sides, we find :

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

Applying Stirling formula, we get

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

or

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

Differentiating and noting that g_i is constant, we get :

$$d(\ln W) = \sum_{i=1}^k \left\{ (n_i + g_i - 1) \times \frac{1}{(n_i + g_i - 1)} dn_i + dn_i \ln(n_i + g_i - 1) - \left\{ n_i \times \frac{1}{n_i} dn_i + dn_i (\ln n_i) \right\} \right\}$$

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

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

Since n_i is very very large as compared to 1, therefore, 1 can be neglected as compared to $n_i + g_i$.
That is, we can write $(n_i + g_i - 1) \cong (n_i + g_i)$

$$\text{Hence } d(\ln W) = \sum_{i=1}^k [\ln(n_i + g_i) - \ln(n_i)] dn_i \quad \dots(4.5.4)$$

In the most probable state, the value of thermodynamic probability is maximum. Therefore $d(\ln W) = 0$

$$\text{i.e. } \sum_{i=1}^k [\ln(n_i + g_i) - \ln(n_i)] dn_i = 0 \quad \dots(4.5.5)$$

Now we use the Lagrangian method of undetermined multipliers. Multiplying the equation (4.5.1) by α , and the equation (4.5.2) by β and subtracting both from (4.5.5), we get :

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

$$\text{or } \sum_{i=1}^k \ln(n_i + g_i) - \ln n_i - \alpha - \beta u_i \} dn_i = 0 \quad \dots(4.5.6)$$

As the variation in dn_i for different compartments is independent of each other, therefore the above relation will be true only when :

$$\ln(n_i + g_i) - \ln(n_i) - \alpha - \beta u_i = 0$$

or

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

or

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

$\therefore$

$$n_i = \frac{g_i}{e^{\alpha} e^{\beta u_i} - 1} \quad \dots(4.5.7)$$

If n_u be the number of particles per unit energy interval corresponding to the mean energy of magnitude u , then :

$$n_u du = \frac{g_u}{e^{\alpha} e^{\beta u} - 1} du$$

where g_u is the number of energy levels corresponding to the mean energy state u .

It is found (from Eq. 4.7.1) that $\beta = \frac{1}{kT}$, where k is Boltzmann constant and T is temperature in kelvin. Therefore, we can write :

$$n_u du = \frac{g_u}{e^{\alpha} e^{u/kT} - 1} du \quad \dots(4.5.8)$$

This is the expression for Bose Einstein distribution law. It gives the distribution of energy among the bosons in the most probable state of the system.

Example 4.4. Find the number of meaningful ways of distributing 10 indistinguishable particles among 8 cells of equal a priori probability according to the assumptions of BE statistics.

Solution :

The number of meaningful ways of distributing the particles is given by :

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

Here

$$n_i = 10, g_i = 8.$$

$$W = \frac{(10 + 8 - 1)!}{10! (8 - 1)!} = \frac{17!}{10! 7!}$$

$$= 19448.$$

4.5.1. Thermodynamic functions of a completely degenerate Fermi—Dirac gas

In case of strong degeneracy at temperature T above absolute zero, The energy of fermi dirac gas can be written as :

$$E = \frac{3}{5} n u_f \left[1 + \frac{5}{12} \left(\frac{\pi K T}{u_f} \right)^2 - \dots \right] \quad \dots(1)$$

The corresponding pressure may be

$$P = \frac{2E}{3V}$$

$$P = \frac{2}{3} \left(\frac{n u_f}{V} \right) \left[1 + \frac{5}{12} \left(\frac{\pi K T}{u_f} \right)^2 - \dots \right] \quad \dots(2)$$

Thermal Capacity C_V . At such low temperature, the fermi dirac gas will have a thermal capacity given as :

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

$$\begin{aligned} &= \frac{\partial}{\partial T} \left[\frac{3}{5} n u_f \left\{ 1 + \frac{5}{12} \left(\frac{\pi K T}{u_f} \right)^2 - \dots \right\} \right] \\ &= n u_f \left(\frac{\pi K}{u_f} \right)^2 \frac{T}{2} - \dots \\ C_V &= \frac{n T}{2} (\pi K)^2 \frac{1}{u_f} - \dots \end{aligned} \quad \dots(3)$$

We know the fermi energy

$$u_f = \frac{h^2}{2m} \left(\frac{3n}{4\pi V g_s} \right)^{2/3} \quad [g \text{ is the spin degeneracy factor}]$$

Now

$$C_V = \frac{n T}{2} (\pi K)^2 \frac{1}{\frac{h^2}{2m} \left(\frac{3n}{4\pi V g_s} \right)^{2/3}}$$

$$C_V = \frac{n \pi^2 m K^2}{h^2} \left(\frac{4\pi V g_s}{3n} \right)^{2/3} T \quad \dots(4)$$

from this result, we can say that heat capacity per particle would be small for large densities $\left(\frac{n}{V} \right)$ and small particle mass m . If the particles are electrons then eq. (4) gives electronic specific heat. At ordinary temperature, the contribution to the specific heat of metals due to electrons will be negligible as compared to the contribution due to atoms because the atomic specific heat is proportional to T^3 . But at very low temperature electronic specific heat will be significant.

Entropy S can be obtained as :

$$S = \int_0^T \frac{C_V}{T} dT$$

$$= \int_0^T \frac{n \pi^2 m K^2 \left(\frac{4\pi V g_s}{3n} \right)^{2/3}}{h^2} T dT$$

$$S = \frac{n \pi^2 m K^2 \left(\frac{4\pi V g_s}{3n} \right)^{2/3}}{h^2} T$$

If we use equation (3) then entropy, can be :

$$S = \int_0^T \left[\frac{n u_f}{2} \left(\frac{\pi K}{u_f} \right)^2 - \dots \right] dT$$

$$= \frac{nu_f}{2} \left(\frac{\pi K}{u_f} \right)^2 T - \dots$$

$$S = \left(\frac{nu_f}{T} \right) \left\{ \frac{\pi^2}{2} \left(\frac{KT}{u_f} \right)^2 - \dots \right\}$$

Helmholtz Free Energy. It can be written as:

$F = E - TS$
 where E is the internal energy
 T Absolute temperature
 S Final entropy.

$$F = \frac{3}{5} nu_f \left[1 + \frac{5}{12} \left(\frac{\pi KT}{u_f} \right)^2 - \dots \right] - T \left(\frac{nu_f}{T} \right) \left\{ \frac{\pi^2}{2} \left(\frac{KT}{u_f} \right)^2 - \dots \right\}$$

$$= \frac{3}{5} nu_f + \frac{1}{4} \left(\frac{\pi KT}{u_f} \right)^2 \pi u_f - \frac{1}{2} \left(\frac{\pi KT}{u_f} \right)^2 nu_f$$

$$F = nu_f \left[\frac{3}{5} - \frac{1}{4} \left(\frac{\pi KT}{u_f} \right)^2 - \dots \right]$$

This is the expression for Helmholtz free energy.

4.6. BLACK BODY RADIATIONS

A body that absorbs all the radiations falling on it is called a perfectly black body or simply a black body. Thus, the absorptive power of a perfectly black body is 1. However, no such body exists in practice. The nearest practical approach to a black body is the surface coated with lamp black. However, its absorptive power is found to be 0.97 and not 1. It in fact, transmits most of the long wavelength infra red (thermal) radiations. A number of physicists in the 19th century attempted to design a perfectly black body. Prominent among them were Lummer, Pringsheim, Wien and Ferry. The simplest design for the perfectly black body was suggested by Ferry, the same is described below:

Ferry's black body consists of a hollow double walled metallic sphere, having a fine opening on one side as shown in fig. 4.6.1. The air from within the walls is evaporated to avoid losses of heat due to conduction, convection, etc. This helps in maintaining the temperature of the enclosure constant.

The inner wall of the enclosure is generally painted black. Just opposite to the opening O, a sharp edged conical projection P is fitted. This ensures that even a ray of light that may be incident normally at the surface just opposite to the opening O cannot return along the same path.

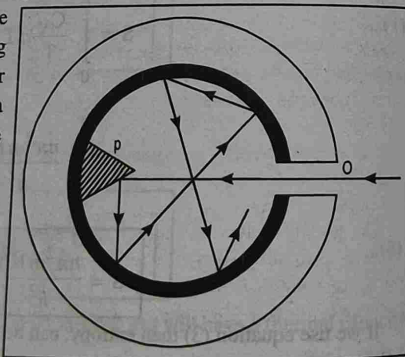


Fig. 4.6.1

When a ray of the radiations enters the enclosure through the opening O, it suffers multiple reflections as shown in Fig. 4.6.1. At every reflection, a part of the incident ray (say 97% of it) is absorbed. After a few reflections most of the incident ray is absorbed and ultimately whole of it is absorbed. The above process of absorption is independent of the wavelength of the incident radiations. Therefore, all the radiations entering the enclosure through the opening O are completely absorbed and hence the absorptive power of the enclosure is 1. By making the area of cross-section of the opening very very small, the chances of the radiations entering the enclosure to escape out are greatly reduced. The conical projection in front of the opening further helps in preventing the escape of the radiations entering through the opening. Thus, the enclosure behaves like a perfectly black body.

According to the Prevost's theory of the exchange of radiations, everybody at all temperatures above absolute zero both absorbs and emits radiations. So, the constant temperature enclosure of the above absolute zero should also emit all types of radiations. It is found that the radiations inside a constant temperature enclosure are homogeneous isotropic and depend only on the temperature. That is why, they are also called temperature radiations or complete (total) radiations emitted from the walls of the enclosure can escape out and the escaping radiations will have all the characteristics of the radiations inside the enclosure. That is, the nature of radiations will depend upon the temperature of the enclosure and not on the nature, shape or colour, etc. of the walls of the enclosure.

Photon gas

According to the Planck's quantum theory, the energy of radiations is quantised. The quanta of energy are usually called photons. The enclosure contains very large number of photons, moving at the velocity of light. The movement of the photons is random as is the case with gas molecules. Therefore, the radiations inside the enclosure is also known as "photon gas".

The particles or quanta of photon gas are indistinguishable. Their spin is 1. That is spin integral. So, they do not obey Pauli's exclusion principle. The size of the phase space cell cannot be less than the Planck's constant h . Any number of photons can be there in a particular level (phase space cell) of the given energy state. Thus, they satisfy the assumptions of the BE statistics. So BE statistics can be used to study the black body radiation.

Difference between Photons and Other Bosons

The rest mass of photon is zero. This is not the case with any other boson. So, the number of bosons in the photon gas is not limited. Unlike gas molecules, the photons are continuously emitted and absorbed by the walls of the enclosure. Although the total energy of the photon gas within the enclosure is constant yet the number of photons may vary. This implies that two or more photons may be absorbed at any instant and a single photon of equivalent energy may be emitted or vice versa. So, the photon gas does not obey the constancy of the particles and accordingly BE distribution formula need to be modified.

$$\text{Since } \sum dn_i \neq 0$$

$\therefore$ The multiplier α , corresponding to the constraint of constancy of particles in the derivation of the BE distribution law becomes zero.

Another difference is in the property of polarisation of the e.m. waves whose quanta the photons are. The photons have left handed and right handed polarisation. Accordingly, the system need to be treated as consisting of two sub-systems, one having the left handed polarised particles and the other having right handed polarised particles. Therefore, for obtaining the number of cells in a particular momentum interval, the volume of the position space gets doubled up.

Energy Distribution in the Spectrum of Black Body Radiations

The first ever analysis of the infra red spectrum was carried out by Langley, who studied the thermal radiations of the sun using a rock salt prism. However, the decisive analysis of the energy distribution in the spectrum of a black body radiation was carried out by Lummer and Pringsheim in the year 1899, using a fluorspar prism which is transparent to almost whole of the range of thermal radiations.

The experimental arrangement consisted of a carbon tube, which was heated electrically and was used as a source of black body radiations. A narrow beam of radiations was obtained using a fine slit S as shown in the fig. 4.6.2. The beam is rendered parallel by reflecting it from concave reflector (mirror) M_1 and is then incident on flint prism P, which disperses the thermal radiations. The dispersed radiations are focussed into a well defined spectrum with the help of another concave reflector (mirror) M. The thermal radiations of different wavelengths are brought to focus at different points and are studied with the help of bolometer*. By rotating the prism, the radiations of different wavelengths are incident on the bolometer and their radiant energy E_λ is measured. (In fact we measure the energy E corresponding to a small band of wave-length $d\lambda$ around λ and obtain E_λ using the relation $e_\lambda = E d\lambda$). Graphs are plotted between λ and E_λ for different temperatures (T_1, T_2, T_3, T_4) of the black body as shown in fig. 4.6.3. From the curves following conclusions can be drawn :

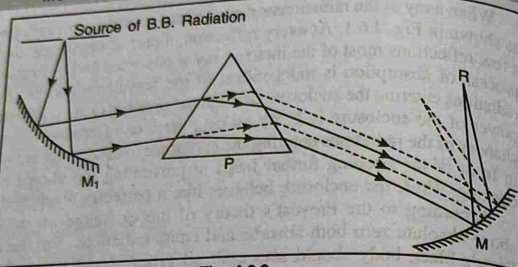


Fig. 4.6.2.

1. The general nature of the curves is same at all temperatures but the emissive power of the black body is greater at higher temperatures.
2. The distribution of energy among the various wavelengths is not uniform.
3. The amount of energy emitted per second increases for all wavelengths with the increase in temperature of the black body.
4. The amount of energy emitted per second by the black body is small both for short as well as long wavelength and most of the emission of radiations is confined to intermediate wavelengths.
5. Corresponding to every temperature of the black body there is a wavelength λ_m , for which the emissive power is highest.
6. The wavelength λ_m corresponding to maximum emission shifts towards shorter values as the temperature of the black body increases. (The dotted line in the figure joins the peaks of the various curves, which shows the trend in shifting of λ_m towards shorter values). It is found that λ_m is inversely proportional to the temperature in kelvin (T). That is

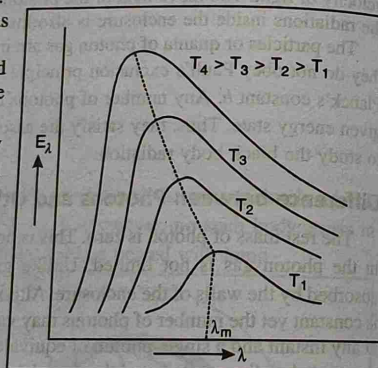


Fig. 4.6.3.

$\lambda_m T = \text{a constant}$. It is called Wiens Displacement law.

7. The total amount of the energy emitted per second by the black body within the wavelengths λ_1 and λ_2 is proportional to $\int_{\lambda_1}^{\lambda_2} E_\lambda d\lambda$. Here $\int_{\lambda_1}^{\lambda_2} E_\lambda d\lambda$ represents the area between the curve

*Bolometer is essentially a platinum resistance thermometer of low thermal capacity and high sensitivity. It is specifically modified to detect the thermal radiations. The term bolometer is derived from the Greek word bole meaning a ray.

and λ -axis. Hence total amount of energy emitted from the black body should be proportional to $\int_0^\infty E_\lambda d\lambda$. It is found proportional to the fourth power of the absolute temperature and is called Stefan's law.

4.7. APPLICATION OF B.E. STATISTICS TO PLANCK'S LAW FOR THE ENERGY DISTRIBUTION OF THE BLACK BODY RADIATIONS

Max Planck, in the year 1900, obtained the theoretical distribution for the black body radiations, on the basis of his quantum theory, which largely agreed with the experimentally observed energy distributions. Einstein, while analysing the photoelectric effect proposed the corpuscular nature of light in a form different than that suggested by Newton. He treated the packets of light energy as particles of energy $h\nu$, where h is Planck's constant and ν is the frequency of the radiations, and termed them as *photons*. Making use of this concept he successfully explained the phenomenon of photoelectric effect. Thus, the idea of photons got established in the scientific world.

Bose, in the year 1924 sent a paper to Einstein in which he proposed a new statistical theory, on the basis of which he was successful in deriving the Planck's law of radiations. This theory, as was already known is called Bose-Einstein statistics. To begin with, the only justification of the statistics proposed by Bose was that it could obtain the Planck's law. However, now it can be justified on the basis of quantum mechanics as well. Now, we consider the derivation of Planck's law from the BE distribution law, obtained in section 4.5.

Bose-Einstein energy distribution law gives the number of bosons n_u having the mean energy u as :

$$n_u du = \frac{g_u}{e^\alpha e^{u/kT} - 1} du \quad \dots(4.7.1)$$

Here g_u is the number of energy levels corresponding to the mean energy state u . In the statistical terminology, it gives the number of phase space cells corresponding to the mean energy level u and α is the multiplier connected with the constraint of constancy of number of particles in the system.

In case of photon gas, the rest mass of the particles is zero. Therefore their number as explained in section 4.6, is not constant as they are continuously emitted and absorbed by the walls of the enclosure.

That is $\sum_{i=1}^k n_i$ is not a constant.

Hence $\sum_{i=1}^k dn_i \neq 0$

This means that the constraint of constancy of number of particles does not apply to the photon gas. To take this fact into account we put $\alpha = 0$. Hence, the expression for the energy distribution becomes :

$$n_u du = \frac{g_u}{e^{u/kT} - 1} du \quad \dots(4.7.2)$$

The energy of the photons is quantised and the energy of a photon of frequency ν is given by

$u = hv$. Hence equation (4.7.2) can be written as :

$$n_v dv = \frac{g_v}{e^{hv/kT} - 1} dv \quad \dots(4.7.3)$$

This gives the number of photons or light waves having frequency between ν and $\nu + d\nu$. Also, the number of phase space cells corresponding to the momentum interval p and dp is :

$$g_p dp = \frac{4\pi V p^2}{h_0^3} dp \quad \dots(4.7.4)$$

where h_0 is the size of the phase space cell. In case of photon gas $h_0 = h$, where h is the Planck's constant ; therefore :

$$g_p dp = \frac{4\pi V p^2}{h^3} dp \quad \dots(4.7.4)$$

Due to their wave characteristics, photons have two types of polarization, which is termed as left handed polarisation and right handed polarisation respectively. These photons cannot be considered indistinguishable. So, as explained in section 4.6, the system may be considered to be made of two sub-systems each of volume V . Hence total volume of the system becomes $2V$ and equation (4.7.4) reduces to

$$g_p dp = \frac{8\pi V p^2}{h^3} dp \quad \dots(4.7.5)$$

Now, momentum of a photon is given by

$$p = \frac{hv}{c}$$

$$dp = \frac{h}{c} d\nu$$

Substituting in equation (4.7.5), we get :

$$g_v dv = \frac{8\pi V}{h^3} \times \left(\frac{hv}{c}\right)^2 \left(\frac{h}{c} d\nu\right) \quad \dots(4.7.6)$$

or

$$g_v dv = \frac{8\pi V \nu^2}{c^3} d\nu \quad \dots(4.7.6)$$

Substituting the value of g in Eq. (4.7.3), we get

$$n_v dv = \frac{8\pi V \nu^2}{c^3} \times \frac{1}{e^{hv/kT} - 1} dv \quad \dots(4.7.7)$$

Energy of the radiations between the frequency interval ν and $\nu + d\nu$ is :

$$u_v dv = [n_v dv] hv = \left[\frac{8\pi V \nu^2}{c^3} \times \frac{1}{e^{hv/kT} - 1} \right] hv$$

Therefore, the energy density of radiations between the frequency interval ν and $\nu + d\nu$ is :

$$E_v dv = u_v \frac{dv}{V} = \frac{8\pi h \nu^3}{c^3} \times \frac{1}{e^{hv/kT} - 1} dv \quad \dots(4.7.8)$$

This is the Planck's law in terms of frequency for the black body radiations.

Another form of the Planck's law

Since $\nu = \frac{c}{\lambda}$, where λ is the wavelength, therefore,

$$d\nu = -\frac{c}{\lambda^2} d\lambda$$

Hence, Planck's law for the energy density corresponding to the wavelength interval λ and $\lambda + d\lambda$ can be obtained by substituting the values of ν and $d\nu$ in the right hand side of equation (4.7.8)

$$E_\lambda d\lambda = \frac{8\pi h}{c^3} \times \frac{c^3}{\lambda^3} \times \frac{1}{e^{hc/\lambda kT} - 1} \left(\frac{c}{\lambda^2} d\lambda\right)$$

Negative sign with $\left(d\lambda \frac{c}{\lambda^2}\right)$ is omitted.

$$\therefore E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \times \frac{d\lambda}{e^{hc/\lambda kT} - 1} \quad \dots(4.7.9)$$

This is the Planck's law in terms of the wavelength of the radiations.

4.8. BOSE-EINSTEIN GAS

An assembly of indistinguishable elementary particles having zero or integral spin (i.e. bosons) is regarded as *Bose-Einstein gas*. Let us consider a perfect Bose-Einstein gas consisting of n bosons distributed among quantum states such that there are $n_1, n_2, \dots, n_i, \dots$ number of particles in quantum states whose approximate constant energies are $u_1, u_2, \dots, u_i, \dots$ respectively.

For a perfect Bose-Einstein gas, the most probable distribution is given by

$$n_i = \frac{g_i}{e^{\alpha} e^{\beta u_i} - 1} \quad \dots(4.8.1)$$

where g_i is the number of phase space cell in the i th compartment and is a measure of degeneracy. Since for an ideal gas, the interaction between its particles is considered to be entirely translational in character, hence the result obtained will be applicable to a monoatomic gas.

For convenience, let $e^{-\alpha} = A$

So Eq. (4.8.1) becomes

$$n_i = \frac{g_i}{A e^{\beta u_i} - 1}$$

Since

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

$\therefore$

$$n_i = \frac{g_i}{A^{-1} e^{\frac{u_i}{kT}} - 1} \quad \dots(4.8.7)$$

Since phase space cells according to the momentum interval p and $p + dp$ is given by

$$g_p dp = \frac{4\pi V p^2}{h_0^3} dp$$

where h_0 is the size of the phase space cell.

In case of Bose-Einstein gas $h_0 = h$ (Planck's constant)

$$g_p dp = \frac{4\pi V p^2}{h_0^3} dp \quad \dots(4.8.3)$$

From Eq. (4.8.2) for most probable distribution, the number of particles in the momentum range p and $p + dp$ is given by

$$dn_p = \frac{g_p dp}{A^{-1}e^{kT} - 1} \quad \dots(4.8.4)$$

Since momentum and energy are related by

$$u = \frac{p^2}{2m}$$

$$p^2 = 2mu$$

$$\text{or } 2p dp = 2m du$$

$$\text{or } dp = \frac{m du}{p} = \frac{m}{\sqrt{2mu}} du = \left(\frac{m}{2u}\right)^{1/2} du$$

So Eq. (4.8.3) becomes

$$dn_u = \frac{4\pi V (2mu)(m/2u)^{1/2} du}{h^3 \frac{u}{A^{-1}e^{kT} - 1}}$$

$$\text{or } dn_u = \frac{4\pi m V (2m)^{1/2} u^{1/2} du}{h^3 \left(\frac{u}{A^{-1}e^{kT} - 1} \right)} \quad \dots(4.8.5)$$

$$\text{Let } x = \frac{u}{kT} \quad \dots(4.8.6)$$

$$\therefore dx = \frac{du}{kT}$$

$$\therefore dn_u = \frac{4\pi m V (2m)^{1/2} (kT)^{1/2} kT dx}{h^3 (A^{-1}e^x - 1)}$$

$$dn_u = \frac{V}{h^3} (2\pi m kT)^{3/2} \cdot \frac{2}{\sqrt{\pi}} \frac{x^{1/2} dx}{(A^{-1}e^x - 1)} \quad \dots(4.8.7)$$

$\therefore$ Total number of particles is given by

$$n = \int dn_u = \frac{V}{h^3} (2\pi m kT)^{3/2} \left[\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{A^{-1}e^x - 1} \right]$$

or

$$n = \frac{V}{h^3} (2\pi m kT)^{3/2} F_1(\alpha) \quad \dots(4.8.8)$$

where

$$F_1(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{A^{-1}e^x - 1} \quad \dots(4.8.9)$$

And total energy of the system is given by

$$E = \int u dn(u) \quad (i)$$

Using Eq. (4.8.6), we get

$$E = \int kTx dn(u) \quad (ii)$$

Using Eq. (4.8.7), we get

$$E = \frac{V}{h^3} (2\pi m kT)^{3/2} kT \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{3/2} dx}{A^{-1}e^x - 1}$$

$$= \frac{3V}{2h^3} (2\pi m kT)^{3/2} kT \left[\frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2} dx}{A^{-1}e^x - 1} \right] \quad (i)$$

or

$$E = \frac{3V}{2h^3} (2\pi m kT)^{3/2} kT F_2(\alpha) \quad \dots(4.8.10)$$

where

$$F_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2} dx}{A^{-1}e^x - 1} \quad \dots(4.8.11)$$

Now let us evaluate the integrals $F_1(\alpha)$ and $F_2(\alpha)$.

For a Bose-Einstein system α should be positive otherwise the value of $n_i = g_i(A^{-1}e^{\beta u_i} - 1)^{-1}$ becomes negative at sufficient low energies, which is physically unacceptable.

When α is +ve, $A < 1$, and the integral $F_1(\alpha)$ is given by

$$F_1(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{A^{-1}e^x - 1} = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{A^{-1}e^x(1 - Ae^{-x})}$$

$$= \frac{2}{\sqrt{\pi}} \int_0^\infty Ax^{1/2} e^{-x} (1 - Ae^{-x})^{-1} dx$$

$$= \frac{2}{\sqrt{\pi}} \left[A \int_0^\infty x^{1/2} e^{-x} (1 + Ae^{-x} + A^2 e^{-2x} + \dots) dx \right]$$

or

$$F_1(\alpha) = \frac{2}{\sqrt{\pi}} \left[A \int_0^\infty x^{1/2} e^{-x} dx + A^2 \int_0^\infty x^{1/2} e^{-2x} dx + \dots \right]$$

$$= \frac{2}{\sqrt{\pi}} \left[\frac{\sqrt{\pi}}{2} \left(A + \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \dots \right) \right]$$

or

$$F_1(\alpha) = A + \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \dots \quad \dots(4.8.12)$$

Similarly

$$F_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2} dx}{A^{-1} e^x - 1}$$

$$= \frac{4}{3\sqrt{\pi}} \left[\frac{3\sqrt{\pi}}{4} \left(A + \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} + \dots \right) \right]$$

or

$$F_2(\alpha) = A + \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} + \dots \quad \dots(4.8.13)$$

Putting the value of $F_1(\alpha)$ and $F_2(\alpha)$ in Eq. (4.8.8) and Eq. (4.8.10), we get

$$n = \frac{V}{h^3} (2\pi mkT)^{3/2} \left[A + \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \dots \right] \quad \dots(4.8.14)$$

And

$$E = \frac{3V}{2h^3} (2\pi mkT)^{3/2} kT \left[A + \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} + \dots \right] \quad \dots(4.8.15)$$

Dividing Eq. (4.8.15) by (4.8.14), we get

$$\frac{E}{n} = \frac{3}{2} kT \left[A + \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} + \dots \right] \left[A + \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \dots \right]^{-1}$$

or

$$E = \frac{3nkT}{2} A \left[1 + \frac{A}{2^{5/2}} + \frac{A^2}{3^{5/2}} + \dots \right] A^{-1} \left[1 + \frac{A}{2^{3/2}} + \frac{A^2}{3^{3/2}} + \dots \right]^{-1}$$

$$= \frac{3nkT}{2} \left[1 + \frac{A}{2^{5/2}} + \frac{A^2}{3^{5/2}} + \dots \right] \left[1 - \frac{A}{2^{3/2}} - \frac{A^2}{3^{3/2}} - \dots \right]$$

$$= \frac{3nkT}{2} \left[1 + \frac{A}{2^{5/2}} + \frac{A^2}{3^{5/2}} - \frac{A}{2^{3/2}} - \frac{A^2}{3^{3/2}} - \dots \right]$$

or

$$E = \frac{3nkT}{2} \left[1 - \frac{A}{2^{5/2}} - \frac{A^2}{3^{5/2}} - \dots \right] \quad \dots(4.8.16)$$

4.9. MAXWELL-BOLTZMANN DISTRIBUTION AS A LIMITING CASE OF BOSE-EINSTEIN DISTRIBUTION

For a perfect Bose-Einstein gas, the most probable distribution is given by

$$n_i = \frac{g_i}{e^{\alpha} e^{\beta u_i} - 1} = \frac{g_i}{\frac{1}{A} e^{\beta u_i} - 1} \quad \dots(4.9.1) \quad [\because e^{-\alpha} = A]$$

If $A \ll 1$, then $\frac{1}{A} e^{\beta u_i} \gg 1$

$$n_i = \frac{g_i}{\frac{1}{A} e^{\beta u_i}}$$

Since

$$\frac{1}{A} = e^{\alpha}$$

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

This is *Maxwell-Boltzmann distribution*. Hence in the limiting case of $A \ll 1$, the Bose-Einstein distribution law reduces to Maxwell-Boltzmann distribution.

Also from Bose-Einstein gas, the energy of the system is given by

$$E = \frac{3nkT}{2} \left[1 - \frac{A}{2^{5/2}} - \frac{A}{3^{5/2}} - \dots \right]$$

Now for $A \ll 1$

$$E = \frac{3}{2} nkT \quad \dots(4.9.3)$$

This is Maxwell Boltzmann i.e. classical statistics.

4.10. DEGENERACY AND BOSE-EINSTEIN CONDENSATION

Degeneracy

For a perfect Bose-Einstein gas, the total number of particles n are given by

$$n = \frac{V}{h^3} (2\pi mkT)^{3/2} \left[A + \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \dots \right] \quad \dots(4.10.1)$$

If $A \ll 1$, then

$$n = \frac{V}{h^3} (2\pi mkT)^{3/2} A$$

or

$$A = \frac{n}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \quad \dots(4.10.2)$$

If n increases and (or T decreases), the value of A increases and there is deviations from the ideal gas behaviour. The deviations from perfect gas behaviour exhibited by Bose Einstein gas is termed as 'gas degeneracy.' The gas degeneracy is obviously a function of A called degeneracy parameter.

From equation (4.10.2), we find that the value of A depends upon number density, mass and temperature. Thus for particles of small mass at low temperatures and small volume, the degeneracy will be higher.

For lowest energy state, $A = 1$

$\because A = e^{-\alpha}$, and α can never be negative], So Eq. (4.10.1) becomes

$$n = \frac{V}{h^3} (2\pi mkT)^{3/2} \left[1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \dots \right]$$

$$= \frac{V}{h^3} (2\pi mkT)^{3/2} \times 2.612.$$

∴ Maximum value of particle density will be

$$\text{or } \left(\frac{n}{V}\right)_{\max} = \frac{(2\pi mkT)^{3/2}}{h^3} \times 2.612$$

If the temperature at this value of n/V is termed as T_0 called critical temperature, then

$$\frac{n}{V} = \frac{(2\pi mkT_0)^{3/2}}{h^3} \times 2.612 \quad \dots(4.10.3)$$

$$\text{or } T_0 = \left(\frac{n}{V \times 2.612} \right)^{2/3} \frac{h^3}{2\pi mk}$$

Thus T_0 is the temperature at which the degeneracy of energy levels starts. A graph between E and T is as shown in Fig. 4.10.1. From the graph we find that below T_0 the full line shows the relation between E and T of a degenerate gas, while the dotted line through the origin that of a non-degenerate gas.

The reason for gas degeneracy at low temperature (i.e. for $T < T_0$) is due to the fact that, while arriving at the Bose-Einstein distribution, we assumed the continuous distribution in place of discrete distribution due to closeness of energy levels and replaced the summation by integration. But at low temperature, the particles of Bose gas begin to crowd into lower energy level and the above condition is violated. So we must be careful in replacing the summation into integration while working at low temperature.

Bose Einstein condensation

The number of particles lying between energy range u and $u + du$ is given by (Eq. 4.9.5)

$$dn(u) = \frac{4\pi mV}{h^3} \cdot \frac{\sqrt{2mu}}{e^{\alpha+u/kT} - 1} du \quad \dots(4.10.4)$$

$$dn(u) = \frac{g(u)du}{e^{\alpha+u/kT} - 1}, \quad \dots(4.10.5)$$

where

$$g(u) = \frac{4\pi mV}{h^3} \sqrt{2mu}$$

For ground state, $u = u_0 = 0$, So $g(u) = 0$ but in reality $g(0) = 1$ because at $u = 0$, there is one state. So the above equation is unable to count the states at $u = 0$ which is called ground state and at low temperature a large number of particles occupy this ground state. The above distribution hold good if $u \neq 0$ because then $g(u) u \neq 0$. Hence we find that the above distribution given by

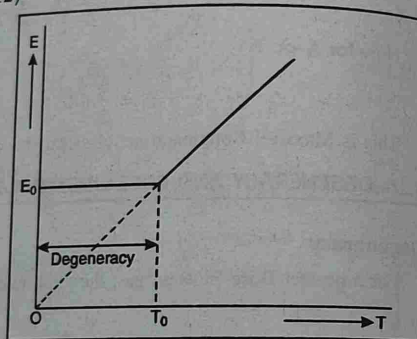


Fig. 4.10.1

Eq. (4.10.5) is applied for all states except ground state, and the ground state should be treated separately. For a single state, we write

$$n_i = \frac{g_i}{e^{\alpha+u_i/kT} - 1}$$

For ground state $u_i = u_0 = 0$ and $g_i = 1$

∴ Number of particles in ground state is given by

$$n_i = n_0 = \frac{1}{e^{\alpha} - 1}$$

∴ The total number of particle states may be written as

$$\begin{aligned} n &= n_0 + \int dn(u) \\ &= n_0 + \int_0^{\infty} \frac{4\pi mV}{h^3} \frac{\sqrt{2mu} du}{(e^{\alpha+u/kT} - 1)} \\ &= n_0 + n' \end{aligned} \quad \dots(4.10.6)$$

where

$$\text{Let } x = \frac{u}{kT}$$

So

$$u = kT x$$

or

$$du = kT dx$$

∴

$$\begin{aligned} n' &= \frac{4\pi mV}{h^3} \sqrt{2m} \int_0^{\infty} \frac{(kT)^{1/2} x^{1/2} kT dx}{e^{\alpha+x} - 1} \\ &= \frac{4\pi mV}{h^3} \sqrt{2m} (kT)^{3/2} \int_0^{\infty} \frac{x^{1/2} dx}{e^{\alpha+x} - 1} \end{aligned}$$

But

$$\int_0^{\infty} \frac{x^{1/2} dx}{e^{\alpha+x} - 1} = \frac{\sqrt{\pi}}{2} F_1(\alpha) \quad [\text{See Eq. 4.8.9}]$$

∴

$$n' = \frac{4\pi mV}{h^3} \sqrt{2m} (kT)^{3/2} \frac{\sqrt{\pi}}{2} F_1(\alpha)$$

or

$$n' = \frac{V (2\pi mk)^{3/2}}{h^3} T^{3/2} F_1(\alpha) \quad \dots(4.10.7)$$

At $T = T_0$

$$\frac{n}{V} = \frac{(2\pi mkT_0)^{3/2}}{h^3} \times 2.612 \quad [\text{See Eq. 4.10.3}]$$

$$\text{or } \frac{V(2\pi mk)^{3/2}}{h^3} = \frac{n}{2.612 T_0^{3/2}} \quad \dots(4.10.8)$$

$$\text{Since } F_1(\alpha) = A + \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} + \dots$$

For $A = 1$ and $\alpha = 0$,

$$F_1(0) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \dots = 2.612$$

$$\therefore \frac{V(2\pi mk)^{3/2}}{h^3} = \frac{n}{F_1(0) T_0^{3/2}} \quad \dots(4.10.9)$$

So Eq. (4.10.7) becomes

$$n' = n \left(\frac{T}{T_0} \right)^{3/2} \frac{F_1(\alpha)}{F_1(0)} \quad \dots(4.10.10)$$

$$\text{Since } \frac{F_1(\alpha)}{F_1(0)} < 1$$

So the value of n' given in Eq. (4.10.10) acquires its maximum value when $\alpha = 0$. Thus for $\alpha = 0$, the maximum number of particles occupying states above ground state is given by

$$n' = n \left(\frac{T}{T_0} \right)^{3/2} \quad (\text{for } T < T_0) \quad \dots(4.10.11)$$

and rest of particles are given by

$$\begin{aligned} n_0 &= n - n' \\ &= n - n \left(\frac{T}{T_0} \right)^{3/2} \\ &= n \left[1 - \left(\frac{T}{T_0} \right)^{3/2} \right], \quad (\text{for } T < T_0) \end{aligned} \quad \dots(4.10.12)$$

must condense into ground state.

Thus from equation 4.10.12 we find that on lowering the temperature of Bose-Einstein gas and at $T < T_0$ (critical temperature), the particles fall rapidly into the ground state. This is a sort of condensation into this state. This phenomenon of rapid increase of number of particles of ground state of a Bose-Einstein gas at a temperature below critical temperature T_0 is called the Bose-Einstein condensation. The temperature T_0 at which the Bose-Einstein condensation begins to occur depends upon the density of the gas. The critical temperature for helium is 3.12 K. Hence the condensation of helium starts at 2.19 K. which is very close to calculated value. Below 2.19 K helium behave like a super fluid. It is believed that the transition observed in liquid helium at 2.19 K is due to Bose Einstein condensation.

4.10.1. Property of Liquid Helium

Liquid helium. We can investigate the qualitative nature of the superfluid transition of liquid helium at 2.2 K. It is most significant application of Bose Einstein statistics. Ordinary helium consists of all the natural atoms of the isotope ${}^4\text{He}$ and the total angular momentum of these atoms is zero. Helium have important properties at low temperature.

1. At atmospheric pressure, helium gas condenses at 4.3 K into a liquid of very low density (0.124 gm/cm^3).
2. Further cooling to helium at about 0.82 K, it does not freeze. It remains liquid all the way down to absolute zero. The solid state of helium cannot form unless an external pressure of 23 atmosphere is applied on it. The phase diagram of helium is shown in Fig. 4.10.2.

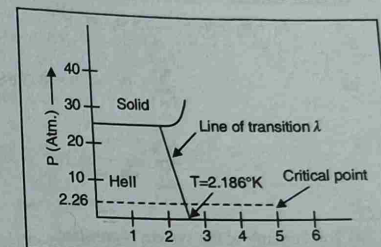


Fig. 4.10.2. Phase diagram of liquid helium

3. There is another phase transition of helium in liquid phase, called λ -transition. The liquid state of helium can have two phases He I and He II. K. Onnes found on liquefying the helium that at about 2.2 K, density increases abruptly upto maximum and then decreasing slightly thereafter. Investigations also revealed that the critical temperature is found at 2.186 K. Which represents a transition to a new state of matter known as liquid He II. It was also found that

- (a) The heat conductivity is very large of the order of 3.10^6 times greater.
- (b) The coefficient of viscosity gradually decreases as the temperature is lowered and approaching zero at absolute zero temperature.

- (c) Keesom measured the specific heat as shown in Fig. 4.10.3. It is discontinuous at 2.186 K. The shape of specific heat curve looks like the shape of letter λ . This peculiar transition is called λ -transition. The discontinuity temperature 2.186 K is called λ -point. Experimentally it was observed that at λ -point, Liquid He II state has no latent heat. The transition of He I $\rightarrow$ He II at T_λ is a second order transition. The transition temperature decreases as the pressure is increased, which can be seen by λ line transition in Fig. 4.10.3.

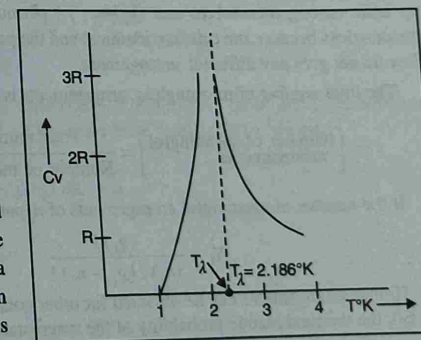


Fig. 4.10.3. Specific heat curve of liquid He

4.11. FERMI DIRAC DISTRIBUTION LAW

Consider a system of n fermions, (the particles obeying FD statistics). Let, in the most probable state, $n_1, n_2, n_3, \dots, n_k$ particles be possessing mean energies $u_1, u_2, u_3, \dots$ respectively. The phase space may be divided into k compartments each corresponding to one energy interval.

Thus, i th compartment contains u_i particles each possessing energy equal to u_i . Let $g_1, g_2, g_3, \dots, g_k$ be the number of cells in the compartments number 1, 2, 3, ..., k respectively. So the number of cells in the i th compartment is g_i .

The system operates under the following two constraints :

(i) Total number of particles is constant and is equal to n

$$\text{i.e. } n_1 + n_2 + n_3 + \dots + n_k = n$$

$$\text{or } \sum_{i=1}^{i=k} n_i = n = \text{a constant}$$

$$\therefore \sum_{i=1}^{i=k} dn_i = 0 \quad \dots(i)$$

(ii) Total energy of the system is constant.

$$\text{i.e. } n_1 u_1 + n_2 u_2 + \dots + n_k u_k = \text{a constant}$$

$$\text{or } \sum_{i=1}^{i=k} n_i u_i = \text{a constant}$$

$$\therefore \sum_{i=1}^{i=k} u_i dn_i = 0 \quad \dots(ii)$$

Since fermions obey Pauli's exclusion principle, that is, one cell can contain either one or zero particle, therefore, the number of cells g_i should be equal to or more than the particles n_i in the i th compartment. We assume $g_i > n_i$. Out of g_i cell n_i cells are filled up and $(g_i - n_i)$ are vacant.

Now g_i cells can be arranged among themselves in $(g_i)!$ ways. Also, $(n_i)!$ permutations of the filled up cells among themselves and $(g_i - n_i)!$ permutations of vacant cells among themselves are meaningless because the cells are identical and the particles are also identical or indistinguishable, i.e. they do not give any different arrangement.

The total number of meaningless arrangements is $(n_i)!(g_i - n_i)!$ Also :

$$\left[\frac{\text{Number of meaningful arrangements}}{\text{Number of meaningless arrangements}} \right] = \frac{\text{Total number of arrangements}}{\text{Number of meaningless arrangements}}$$

If the number of meaningful arrangements of n_i particles in g_i cells be denoted by W_i , then

$$W_i = \frac{(g_i)!}{(n_i)!(g_i - n_i)!} \quad \dots(4.11.1)$$

Similar arrangements can be obtained for other compartments.

So, the thermodynamic probability of the macrostate $(n_1, n_2, n_3, \dots, n_k)$ is :

$$W = \prod_{i=1}^{i=k} \frac{(g_i)!}{(n_i)!(g_i - n_i)!} \quad \dots(4.11.2)$$

Taking natural logarithms, we find :

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

Using Stirling formula, we get :

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

$$\text{or } \ln W = \sum_{i=1}^{i=k} [g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i)]$$

Differentiating and noting that g_i is a constant, we get :

$$d(\ln W) = \sum_{i=1}^{i=k} \left[0 - \left\{ (dn_i) \ln n_i + n_i \times \frac{1}{n_i} dn_i \right\} - \left\{ (-dn_i) \ln (g_i - n_i) + (g_i - n_i) \frac{1}{(g_i - n_i)} (-dn_i) \right\} \right]$$

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

$$\text{or } d(\ln W) = \sum_{i=1}^{i=k} [\ln (g_i - n_i) - \ln n_i] dn_i$$

Since for the most probable state W and hence $\ln W$ is constant, therefore $d(\ln W) = 0$

$$\text{i.e. } \sum_{i=1}^{i=k} [\ln (g_i - n_i) - \ln n_i] dn_i = 0 \quad \dots(iii)$$

For making use of the Lagrangian method of undetermined multipliers, we multiply the equation (i) by α and equation (ii) by β and subtracting these products from equation (iii), we get :

$$\sum_{i=1}^{i=k} [\ln (g_i - n_i) - \ln n_i - \alpha - \beta u_i] dn_i = 0$$

Since dn_i 's are independent of one another, so

$$\ln (g_i - n_i) - \ln n_i - \alpha - \beta u_i = 0$$

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

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

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

$$n_i = \frac{g_i}{e^{\alpha} e^{\beta u_i} + 1} \quad \dots (iv)$$

or
If n_u be the number of particles per unit energy interval corresponding to the mean energy magnitude u , then

$$n_u du = \frac{g_u}{e^{\alpha} e^{\beta u} + 1} du$$

where g_u is the number of levels corresponding to the energy state u .

It has already been found that $\beta = 1/kT$, where k is Boltzmann constant and T is the temperature in kelvin. The value of α is evaluated from the conditions under which the system is operating.

$$\therefore n_u du = \frac{g_u}{(e^{\alpha} e^{u/kT} + 1)} du \quad \dots (4.11.3)$$

This is called Fermi-Dirac distribution law for energy. It gives the number of fermions within the energy range u and $u + du$ when the system of particles is in equilibrium state.

Example 4.5. Find the number of ways in which 3 fermions may be distributed in 5 cells.

Solution. The number of meaningful ways of distributing n_i fermions in g_i cells is given by

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

Here

$$n_i = 3 \text{ and } g_i = 5$$

$$\therefore W = \frac{5!}{3!2!} = \frac{5 \times 4 \times 3!}{3! \times 2 \times 1} = 10.$$

4.12. DISTRIBUTION OF ENERGY AMONG THE FREE ELECTRONS IN A METAL

The free electrons in the metals move about at random in the same way as gas molecules do. So, this collection of free electrons is called electron gas. The energy distribution among the electrons in a metal obeys the FD distribution law.

The FD distribution law is :

$$n_u du = \frac{g_u}{e^{\alpha} e^{u/kT} + 1} du, \quad \dots (i)$$

where the value of α is obtained from the actual constraints on the system.

Fermi and Dirac in the year 1926, applied the statistical method to the electron gas assuming that the distribution of their energy is quantised and obtained an expression as explained below.

It is a known fact that as T decreases, the energy of the electrons decreases, and hence the energy of the system as a whole decreases. At absolute zero ($T = 0$ K) the energy of the electrons and hence that of the system is minimum. That is, at 0 K only the lower energy levels should be occupied by the electrons. Electrons obey Pauli's exclusion principle. That is, each energy level is occupied by one electron only. So, at absolute zero, filling up of the energy levels starts from the lowest energy level and it continues till all the electrons are accommodated. There comes an energy level above which no electron exists. It is termed as the **fermi energy level**. Above this level all energy levels are vacant.

The energy of the fermi level is called fermi energy (u_f). Thus, the energy of a level below which all levels are filled up and above which all the energy levels are vacant is called fermi energy.

In the language of statistics we can say that at $T = 0$ K :

$$n_u = 0 \text{ for } u > u_f$$

In other words, the occupation index :

$$(i) \quad \frac{n_u}{g_u} = 0 \text{ for } u > u_f$$

and (ii)

$$\frac{n_u}{g_u} = 1 \text{ for } u \leq u_f.$$

If we plot the occupation index against the energy u , the graph obtained is as shown in Fig. 4.12.1.

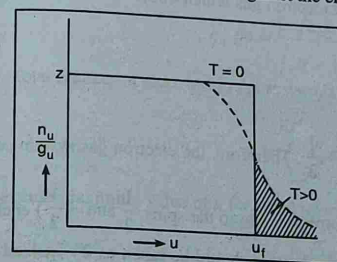


Fig. 4.12.1

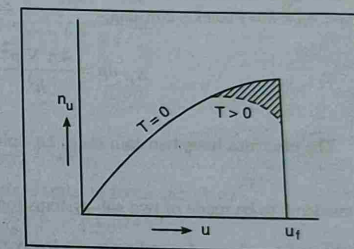


Fig. 4.12.2

The graph between n_u and u is as shown in Fig. 4.12.1. At temperature above 0 K there is no sudden cut off as evident from the figure. These facts are used in obtaining the value of α as follows :

Value of α

From Eq. (i), we have

$$\frac{n_u}{g_u} = \frac{1}{e^{\alpha} e^{u/kT} + 1} \quad \dots (ii)$$

From (ii), we find that the dimensions of α should be the same as that of u/kT .

Also, for $u \leq u_f$ the occupation index $\left(\frac{n_u}{g_u}\right)$ is 1, that is :

Putting $u = u_f$ we get :

$$\frac{1}{e^{\alpha} e^{u_f/kT} + 1} = 1$$

or

$$e^{\alpha} e^{u_f/kT} + 1 = 1$$

or

$$e^{\alpha} e^{u_f/kT} = 0$$

or

$$e^{\alpha + u_f/kT} = 0$$

or

$$\alpha + u_f/kT = 0$$

i.e. $\alpha = -\frac{u_f}{kT}$

Substituting the value of α in (i), we get

$$n_u du = \frac{g_u}{e^{(u-u_f)/kT} + 1} du \quad \dots(iii)$$

Determination of g_u

The number of phase space cells corresponding to the momentum interval p and $p + dp$ is :

$$g_p dp = \frac{4\pi V p^2}{h_0^3} dp$$

where h_0 is the size of the phase space cell. In case of electron gas which obeys the FD statistics, we have $h_0 = h = \text{Planck's constant}$.

$$\therefore g_p dp = \frac{4\pi V p^2}{h^3} dp \quad \dots(iv)$$

The electrons have two spin states i.e. spin $\frac{1}{2}$ and $-\frac{1}{2}$. Therefore, the electron gas system can be

considered to be made of two sub-systems (one each corresponding to the spins $\frac{1}{2}$ and $-\frac{1}{2}$) enclosed in the same volume. Accordingly, the total volume of the system should be taken as $2V$ instead of V and the expression (iv) becomes :

$$g_p dp = \frac{8\pi V p^2}{h^3} dp. \quad \dots(v)$$

Also, if m be the mass of electron, v be the velocity, then KE of electron is given by :

$$u = \frac{p^2}{2m} \text{ or } p^2 = 2mu$$

It is assumed that whole of the energy of the electron is kinetic. Differentiating we get :

$$2p dp = 2m du$$

or $dp = \frac{m}{p} du$

or $dp = \frac{m}{\sqrt{2mu}} du = \sqrt{\frac{m}{2u}} du$

Substituting the values of p^2 and dp in the right hand side of equation (v), we get the number of cells in the interval u and $u + du$ as :

$$g_u du = \frac{8\pi V}{h^3} (2mu) \sqrt{\frac{m}{2u}} du$$

or $g_u du = \frac{8\sqrt{2}\pi V m^{3/2} u^{1/2}}{h^3} du \quad \dots(vi)$

Substituting the value in equation (ii), we get

$$n_u du = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \times \frac{u^{1/2}}{e^{(u-u_f)/kT} + 1} du \quad \dots(4.12.1)$$

This is the Fermi-Dirac distribution law for the electron gas.

4.13. FERMI ENERGY

The **fermi energy** is the energy of the level at 0 K, above which all the energy levels are vacant and below which all the energy levels are completely filled.

The number of electrons in the energy interval u and $u + du$ according to Fermi-Dirac distribution law is given by

$$n_u du = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \times \frac{u^{1/2}}{e^{(u-u_f)/kT} + 1} du \quad \dots(i)$$

$\therefore$ Total number of electrons in the system is given by :

$$n = \int_0^{u_f} n_u du$$

Because maximum value of u for filled up energy levels is equal to fermi energy u_f

$$\therefore n = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^{u_f} \frac{u^{1/2}}{e^{(u-u_f)/kT} + 1} du$$

At $T = 0$ for $u \leq u_f$, we get $e^{(u-u_f)/kT} = e^{-\infty} = 0$, Therefore

$$n = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^{u_f} u^{1/2} du$$

$$n = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \left[\frac{u^{3/2}}{\frac{3}{2}} \right]_0^{u_f} \quad \dots(ii)$$

or

$$n = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \left[\frac{2}{3} u_f^{3/2} \right],$$

or

which gives :

$$u_f = \left[\frac{3n}{2} \times \frac{h^3}{8\sqrt{2}\pi V m^{3/2}} \right]^{2/3}$$

or

$$u_f = \frac{h^2}{2m} \left(\frac{3n}{8\pi V} \right)^{2/3}$$

From the above expression we find that n_u depends upon $\frac{n}{V}$, the number of free electrons per unit volume, and is independent of the volume of the system.

FD distribution law in terms of fermi energy

From equation (ii), we find :

$$\frac{8\sqrt{2}\pi V m^{3/2}}{h^3} = \frac{3}{2} \times u_f^{-3/2} n.$$

Substituting in equation (i), we get

$$n_u du = \frac{3}{2} n u_f^{-3/2} \frac{u^{1/2}}{e^{(u-u_f)/kT} + 1} du \quad \dots(4.13.1)$$

This gives the Fermi-Dirac distribution law in terms of fermi energy.

4.14. MEAN (OR AVERAGE) ENERGY OF ELECTRONS AT 0 K

Mean Energy

The number of electrons possessing energy between u and $u + du$ is :

$$n_u du = \frac{3}{2} n u_f^{-3/2} \frac{u^{1/2}}{e^{(u-u_f)/kT} + 1} du$$

At absolute zero, $T = 0$, $u \leq u_f$

$$\therefore e^{(u-u_f)/kT} = e^{-\infty} = 0.$$

Hence

$$n_u du = \frac{3}{2} n u_f^{-3/2} u^{1/2} du$$

Now

u = Total energy of the system

$$= \int_0^{u_f} [n_u du] u$$

or

$$= \int_0^{u_f} \left[\frac{3}{2} n u_f^{-3/2} \right] u^{3/2} du$$

or

$$u = \left[\frac{3}{2} n u_f^{-3/2} \right] \left[\frac{u^{5/2}}{\frac{5}{2}} \right]_0^{u_f}$$

or

$$u = \left[\frac{3}{2} n u_f^{-3/2} \right] \left[\frac{2}{5} u_f^{5/2} \right]$$

or

$$u = \frac{3}{5} n u_f$$

$$\text{Mean energy} = \frac{\text{Total energy of the system}}{\text{Total number of particles}} = \frac{u}{n}$$

$\therefore$ Mean energy,

$$u_m = \frac{u}{n} = \frac{\frac{3}{5} n u_f}{n} = \frac{3}{5} u_f$$

4.15. AVERAGE SPEED OF ELECTRONS AT 0 K

Average speed

The number of electrons possessing energy between u and $u + du$ is :

$$n_u du = \frac{3}{2} n u_f^{-3/2} \frac{u^{1/2}}{e^{(u-u_f)/kT} + 1}$$

At absolute zero $T = 0$ and $u \leq u_f$

$$\therefore e^{(u-u_f)/kT} = e^{-\infty} = 0$$

Hence

$$n_u du = \frac{3}{2} n u_f^{-3/2} u^{1/2} du \quad \dots(i)$$

Now $u = \frac{1}{2} m v^2$, where m is mass of electron and v is its velocity.

$$\therefore du = \frac{1}{2} m \times 2v dv = mv dv.$$

Also, $u_f = \frac{1}{2} m v_f^2$, where v_f is the velocity of electron at fermi energy level.

Substituting in equation (i), we get the number of particles having velocity between v and $v + dv$ as :

$$n_v dv = \frac{3}{2} n \left(\frac{1}{2} m v_f^2 \right)^{-3/2} \left(\frac{1}{2} m v^2 \right)^{1/2} (mv dv)$$

or

$$n_v dv = 3n v_f^{-3} v^2 dv.$$

If v_a be the average velocity of the electrons at 0 K, then

$$\begin{aligned} v_a &= \frac{\int_0^{u_f} v n_v dv}{n} \\ &= \frac{\int_0^{u_f} v (3n v_f^{-3} v^2) dv}{n} \\ &= 3v_f^{-3} \int_0^{v_f} v^3 dv \\ &= 3v_f^{-3} \times \left[\frac{v^4}{4} \right]_0^{v_f} = 3v_f^{-3} \times \frac{v_f^4}{4} \end{aligned}$$

or

$$v_a = \frac{3}{4} v_f.$$

4.16. MB STATISTICS AS A SPECIAL CASE OF BE AND FD STATISTICS

In classical statistics, the particles are considered distinguishable, because the size of the phase space cell can be as small as we like. So, the space can be divided into very large number of cells such that each cell contains one particle or none. In this way, the particles can be numbered in terms of the number of the cells and they can be distinguished from each other. In quantum statistics, the size of the cell cannot be less than Planck's constant. So, the number of the space cells is limited and each cell may contain more than one particle. Therefore, they cannot be distinguished from one another in terms of the identity of the cell, any particle occupies.

From the above, we find that in classical statistics, the number of phase space cells is more than the number of particles. However, if the number of particles is not very large, then even in quantum statistics the number of the cells can be large than that of the particles. In that case particles can be distinguished in the same way as in classical statistics. So, the results of quantum statistics should be similar to the classical or MB statistics. This can be shown as follows :

FD distribution formula is :

$$n_u du = \frac{n_u}{e^\alpha e^{u/kT} + 1} du \quad \dots(i)$$

BE distribution formula is :

$$n_u du = \frac{g_u}{e^\alpha e^{u/kT} - 1} du \quad \dots(ii)$$

MB distribution formula is :

$$n_u du = \frac{g_u}{e^\alpha e^{u/kT}} du \quad \dots(iii)$$

For low occupation index :

$$\frac{n_u}{g_u} < 1.$$

For the above expression to be true, in FD statistics :

$$(e^\alpha e^{u/kT} + 1) \gg 1$$

For the same reason, in BE statistics :

$$(e^\alpha e^{u/kT} - 1) \gg 1$$

Neglecting +1 or -1 in the L.H.S. of above expressions, we find that the denominators of both (i) and (ii) reduce to :

$$n_u du = e^\alpha e^{u/kT}$$

which is also the denominator of (iii).

Thus, we find that for low occupation index, FD and BE statistics reduce to MB statistics, or the quantum statistics reduce to classical statistics.

Example 4.6. Show that for energy $u > kT$, the quantum as well as classical statistics yield same results, but they are different from each other to a great extent for $u < kT$.

Solution. The distribution laws for energy are as follows :
For classical (MB) statistics :

$$n_u du = \frac{g_u}{e^\alpha e^{u/kT}} du \quad \dots(i)$$

For quantum statistics :

$$n_u du = \frac{g_u}{e^\alpha e^{u/kT} \pm 1} du \quad \dots(ii)$$

(+ 1 for FD statistics and - 1 for BE statistics)

When $u \gg kT$, we find that $e^{u/kT}$ is very large. Therefore, $e^\alpha e^{u/kT} \gg 1$. Hence equation (ii) reduces to

$$n_u du = \frac{g_u}{e^\alpha e^{u/kT}} du$$

which is the same as that for classical statistics.

For $u < 0$ we find that $e^{u/kT}$ is very small.

Therefore $e^\alpha e^{u/kT} < 1$.

And $(e^\alpha e^{u/kT} - 1)$ is smaller than $(e^{u/kT} + 1)$. Therefore, occupation index n_u is higher for BE statistics than that for FD statistics. Because of different values of occupation index, the three statistics give different results.

4.17. COMPARISON BETWEEN MB, BE AND FD STATISTICS

The three types of statistics can be compared in terms of different characteristics as follows :

1. Nature of particles.

The particles obeying MB statistics may be identical yet they are considered as distinguishable. However, the particles obeying BE or FD statistics are considered indistinguishable.

2. Size of the phase space cell.

In MB statistics, the available volume of the phase space cell can have any value and can even approach to zero.

In BE and FD statistics, the available volume of the phase space cell cannot be less than h^3 , where h is Planck's constant.

3. Number of phase space cells.

In MB statistics, the phase can be divided into as large number of cells as we desire.

In BE and FD statistics, the number of cells into which the phase space can be divided is limited, as the available volume of each cell cannot be less than h^3 .

4. Number of particles in a cell.

In MB and BE statistics, any number of particles can occupy a phase space cell. But in FD statistics, no phase space cell can contain more than one particle.

5. Macro and microstates of the system

For the systems obeying MB statistics, a macrostate can have more than one microstates.

For the system obeying BE and FD statistics, each macrostate has one microstate. The total number of macrostates in BE statistics is generally more than that in FD statistics.

6. Radiation laws.

MB statistics can lead to Rayleigh Jean's law. It gives the Weins law as well with the help of quantum theory but does not lead to the Planck's law.

BE statistics leads to Planck's law. The Rayleigh Jean's law and Wein's law are the special cases of the Planck's law.

FD statistics fails to give the Planck's law and hence cannot be used to obtain the Rayleigh Jean's law or the Wein's law.

7. Energy distribution.

The energy distribution laws for the three types of statistics are as follows :

$$\text{MB statistics : } n_u du = \frac{g_u}{e^\alpha e^{u/kT}} du$$

$$\text{BE statistics : } n_u du = \frac{g_u}{e^\alpha e^{u/kT} - 1} du$$

$$\text{FD statistics : } n_u du = \frac{g_u}{e^\alpha e^{u/kT} + 1} du$$

8. Quantisation of energy.

MB statistics does not assume the quantisation of energy whereas BE and FD statistics are based on the assumption of quantisation of energy.

9. Occupation index

The occupation index (n_i/g_i) depends upon the value of the mean energy (u_i) of the state.

For values of energy much larger than kT , $e^\alpha e^{u_i/kT} < 1$.

Hence for $\frac{n_i}{g_i} = \frac{1}{e^\alpha e^{u_i/kT}}$ all the three statistics.

For values of energy much smaller than kT , $e^\alpha e^{u_i/kT}$ cannot be neglected as compared to 1. So, the occupation index for the three statistics differs from one another.

In general.

For $u_i > kT$, the occupation index $n_i/g_i < 1$ for all the three statistics gives the same results.

For $u_i < kT$, we have :

$$\left[\frac{n_i}{g_i} \right]_{\text{BE}} > \left[\frac{n_i}{g_i} \right]_{\text{MB}} > \left[\frac{n_i}{g_i} \right]_{\text{FD}}$$

So, the results of the three statistics differ from one another.

4.18. RELATIVE OCCUPANCY OF THE ENERGY LEVELS

Let the occupation index of the i th energy level be denoted by f_i . Then,

$$f_i = \frac{n_i}{g_i}$$

Now for $u_i > kT$, we have seen in section 4.11, that the $f_i = n_i/g_i < 1$ for all three statistics. Also, the distribution law for all the three statistics reduces to that for the MB statistics. That is,

$$f_i = \frac{n_i}{g_i} = \frac{1}{e^\alpha e^{u_i/kT}}$$

$$\therefore \frac{f_i}{f_j} = e^{(u_j - u_i)/kT}$$

This gives the relative occupancy of the i th energy levels.

4.19. FERMI-DIRAC GAS

An assembly of indistinguishable elementary particles having half integral spin (i.e. fermions) is regulated as *Fermi-Dirac gas*. Let us consider a perfect Fermi-Dirac gas consisting of n fermions distributed among quantum states such that there are $n_1, n_2, \dots, n_i, \dots$ number of particles in quantum states whose approximate constant energies are $u_1, u_2, \dots, u_i, \dots$ respectively.

For a perfect Fermi-Dirac gas, the most probable distribution is given by

$$n_i = \frac{g_i}{e^\alpha e^{\beta u_i} + 1} \quad \dots(4.19.1)$$

where g_i is the number of phase space cell in the i th compartment and is a measure of degeneracy.

For convenience, let $e^{-\alpha} = A$

So eq. (4.19.1) becomes

$$n_i = \frac{g_i}{\frac{1}{A} e^{\beta u_i} + 1}$$

Since

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

$$\therefore n_i = \frac{g_i}{A^{-1} e^{u_i/kT} + 1} \quad \dots(4.19.2)$$

Since in the denominator of Eq. (4.19.2), we have factor +1, so α can have positive or negative value.

Since phase space cells according to the momentum interval p and $p + dp$ is given by

$$g_p dp = \frac{4\pi V p^2}{h_0^3} dp$$

where h_0 is the size of the phase space cell. In case of Fermi-Dirac gas $h_0 = h$ (Planck's constant)

$$\therefore g_p dp = g_s \frac{4\pi V p^2}{h^3} dp, \quad \dots(4.19.3)$$

where $g_s (= 2s + 1)$ is the spin degeneracy factor (arising due to spin s of the fermions).

From Eq. (4.19.3) for most probable distribution, the number of particles in the momentum range p and $p + dp$ is given by

$$n_p dp = \frac{g_p dp}{A^{-1} e^{u/kT} + 1} \quad \dots (4.19.4)$$

Since momentum and energy are related by

$$u = \frac{p^2}{2m}$$

$$\therefore p^2 = 2mu$$

$$\text{or } 2p dp = 2m du$$

$$\text{or } dp = \frac{m du}{p} = \frac{m}{\sqrt{2mu}} du = \left(\frac{m}{2u}\right)^{1/2} du$$

So Eq. (4.19.4) becomes

$$n_u du = g_s \frac{4\pi V}{h^3} \frac{(2mu) \left(\frac{m}{2u}\right)^{1/2} du}{A^{-1} e^{u/kT} + 1}$$

$$\text{or } n_u du = g_s \frac{4\pi m V}{h^3} \frac{(2m)^{1/2} u^{1/2} du}{A^{-1} e^{u/kT} + 1} \quad \dots (4.19.5)$$

$$\text{Let } x = \frac{u}{kT} \quad \dots (4.19.6)$$

$$\therefore dx = \frac{du}{kT}$$

$$\therefore n_u du = g_s \frac{4\pi m V}{h^3} \frac{(2m)^{1/2} (kT)^{1/2} kT}{(A^{-1} e^x + 1)}$$

$$\text{or } n_u du = g_s \frac{V}{h^3} (2\pi m kT)^{3/2} \frac{2}{\sqrt{\pi}} \frac{x^{1/2} dx}{(A^{-1} e^x + 1)} \quad \dots (4.19.7)$$

$\therefore$ Total number of particles is given by

$$n = \int n_u du = g_s \frac{V}{h^3} (2\pi m kT)^{3/2} \left[\frac{2}{\sqrt{\pi}} \frac{x^{1/2} dx}{(A^{-1} e^x + 1)} \right]$$

$$n = g_s \frac{V}{h^3} (2\pi m kT)^{3/2} F_1(\alpha) \quad \dots (4.19.8)$$

where

$$F_1(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{A^{-1} e^x + 1} \quad \dots (4.19.9)$$

And total energy of the system is given by

$$E = \int u(n_u du)$$

Using Eq. (4.19.6), we get

$$E = \int kTx \, dn(u)$$

Using Eq. (4.19.5)

$$E = g_s \frac{V}{h^3} (2\pi m kT)^{3/2} kT \cdot x \cdot \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{A^{-1} e^x + 1}$$

$$= g_s \frac{3V}{2h^3} (2\pi m kT)^{3/2} kT \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2} dx}{A^{-1} e^x + 1}$$

$$\text{or } E = g_s \frac{3V}{2h^3} (2\pi m kT)^{3/2} kT F_2(\alpha), \quad \dots (4.19.10)$$

where

$$F_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2} dx}{A^{-1} e^x + 1} \quad \dots (4.19.11)$$

Now we shall evaluate the integrals $F_1(\alpha)$ and $F_2(\alpha)$ for both positive and negative value of α . When α is positive, $A < 1$ and the condition so obtained is called *slight or weak degeneracy*. When α is negative, $A > 1$ and the condition is called *strong degeneracy*.

(i) Case of weak degeneracy

At intermediate temperature when α is positive (i.e. at $T < T_F$) and $A < 1$, and the integral $F_1(\alpha)$ is given by

$$\begin{aligned} F_1(\alpha) &= \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{A^{-1} e^x + 1} = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{A^{-1} e^x (1 + A e^{-x})} \\ &= \frac{2}{\sqrt{\pi}} \int_0^\infty A x^{1/2} e^{-x} (1 + A e^{-x})^{-1} dx \\ &= \frac{2}{\sqrt{\pi}} \left[A \int_0^\infty x^{1/2} e^{-x} (1 - A e^{-x} + A^2 e^{-2x} - \dots) dx \right] \\ &= \frac{2}{\sqrt{\pi}} \left[A \int_0^\infty x^{1/2} e^{-x} dx - A^2 \int_0^\infty x^{1/2} e^{-2x} dx + \dots \right] \\ &= \frac{2}{\sqrt{\pi}} \left[\frac{\sqrt{\pi}}{2} \left(A - \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} - \dots \right) \right] \end{aligned}$$

or

$$F_1(\alpha) = A - \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} - \dots$$

Similarly

$$F_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2} dx}{A^{-1}e^x + 1} = \frac{4}{3\sqrt{\pi}} \left[\frac{3\sqrt{\pi}}{4} \left(A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} - \dots \right) \right]$$

or $F_2(\alpha) = A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} - \dots$

Putting the value of $F_1(\alpha)$ in equation (4.19.8) and $F_2(\alpha)$ in equation (4.19.10), we get

$$n = g_s \frac{V}{h^3} (2\pi mkT)^{3/2} \left[A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} - \dots \right] \quad \dots(4.19.12)$$

and $E = g_s \frac{3V}{2h^3} (2\pi mkT)^{3/2} \cdot kT \left[A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} - \dots \right] \quad \dots(4.19.13)$

$$\therefore \frac{E}{n} = \frac{3}{2} kT \left[A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} - \dots \right] \left[A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} - \dots \right]^{-1}$$

or $E = \frac{3nkT}{2} A \left[1 - \frac{A^2}{2^{5/2}} + \frac{A^2}{3^{5/2}} - \dots \right] A^{-1} \left[1 - \frac{A}{2^{3/2}} + \frac{A^2}{3^{3/2}} - \dots \right]^{-1}$

or $E = \frac{3nkT}{2} \left[1 - \frac{A}{2^{5/2}} + \frac{A^2}{3^{5/2}} - \dots \right] \left[1 + \frac{A}{2^{3/2}} - \frac{A^2}{3^{3/2}} + \dots \right]$

$$= \frac{3nkT}{2} \left[1 - \frac{A}{2^{5/2}} + \frac{A^2}{3^{5/2}} + \frac{A}{2^{3/2}} - \frac{A^2}{3^{3/2}} + \dots \right]$$

$$E = \frac{3nkT}{2} \left[1 + \frac{A}{2^{5/2}} - \frac{A^2}{3^{5/2}} + \dots \right] \quad \dots(4.19.14)$$

If $A \ll 1$, then $E = \frac{3}{2} nkT \quad \dots(4.19.15)$

From Eq. (4.19.14) and (4.19.15), we find that ideal Fermi gas deviates from perfect gas behaviour and this is called *degeneracy*. Since degeneracy is a function of A or $e^{-\alpha}$, so larger the value of A , more marked will be the degeneracy. Thus for $A < 1$ or $T > T_p$ the Fermi gas is slightly degenerate.

(ii) Case of strong degeneracy

When the value of α is large and negative, $e^{-\alpha} \gg 1$ or $A \gg 1$. This increases the value of A and hence the degeneracy will become more prominent. So Eq. (4.19.12) can be written as

$$n \approx g_s \frac{V}{h^3} (2\pi mkT)^{3/2} A$$

or

$$A = \frac{1}{g_s} \frac{h^3}{(2\pi mkT)^{3/2}} \cdot \frac{n}{V}$$

Thus at low temperature and at high densities $\left(\frac{n}{V}\right)$, the gas will be highly degenerate. Let us discuss this case of strong degeneracy at absolute zero i.e. at $T = 0$ K.

Since number of fermions in Fermi-Dirac gas having energy u and $u + du$ is given by

$$n_u du = g_s \frac{4\pi mV}{h^3} \frac{(2m)^{1/2} u^{1/2} du}{A^{-1} e^{u/kT} + 1} \quad \text{(See Eq. 4.19.5)}$$

or

$$n_u du = g_s \frac{4\pi mV}{h^3} \frac{(2m)^{1/2} u^{1/2} du}{e^{\alpha} \cdot e^{u/kT} + 1}$$

Since

$$\alpha = \frac{-u_f}{kT} \quad \text{(See Eq. 4.19.2)}$$

$\therefore$

$$n_u du = g_s \frac{4\pi mV}{h^3} \frac{(2m)^{1/2} u^{1/2} du}{e^{(u-u_f)/kT} + 1}$$

At $T = 0$, for $u \leq u_f$, we get $e^{(u-u_f)/kT} + 1 = e^{-\infty} + 1 = 1$

So

$$n_u du = g_s \frac{4\pi mV}{h^3} \cdot (2m)^{1/2} u^{1/2} du \quad \dots(4.19.16)$$

$\therefore$ Total number of particles in the system are given by

$$n = \int_0^{u_f} n_u du = g_s \frac{4\pi mV}{h^3} (2m)^{1/2} \int_0^{u_f} u^{1/2} du$$

$$= g_s \frac{4\pi mV}{h^3} (2m)^{1/2} \left[\frac{u^{3/2}}{3/2} \right]_0^{u_f}$$

or

$$n = g_s \frac{4\pi mV}{h^3} (2m)^{1/2} \frac{u_f^{3/2}}{3/2}$$

or

$$g_s \frac{4\pi mV}{h^3} (2m)^{1/2} = \frac{3}{2} n u_f^{-3/2} \quad \dots(4.19.17)$$

Putting Eq. (4.19.17) in Eq. (4.19.16), we get

$$n_u du = \frac{3}{2} n u_f^{-3/2} u^{1/2} du$$

$\therefore$ Total energy of the system,

$$E = \int_0^{u_f} u n_u du = \frac{3}{2} n u_f^{-3/2} \int_0^{u_f} u^{3/2} du$$

$$= \frac{3}{2} n u_f^{-3/2} \left| \frac{u^{5/2}}{5/2} \right|_0^{u_f}$$

$$E = \frac{3}{2} n u_f^{-3/2} \cdot \frac{2}{5} u_f^{5/2} = \frac{3}{5} n u_f \quad \dots(4.19.18)$$

Thus we find that a strongly degenerate Fermi-Dirac gas possesses energy even at 0 K in contrast to Bose-Einstein and Classical gases where the energy is zero.

4.20. ELECTRON GAS IN METALS

It was suggested by P. Drude in 1900, that the metal crystals consist of positive ion cores with their valence electrons (also known as conduction electrons since these are responsible for the conduction of electricity in metals) free to move among these positive metal ions (cores). The coulomb's force of attraction between these positive ions and negatively charged electrons do not allow these free electrons to leave the metal surface. The potential field due to these ion cores is supposed to be uniform and hence potential energy of electrons may be taken as constant, which is taken to be zero for convenience. Hence we have to deal only with the kinetic energy of the electrons. The mutual repulsion between the electrons is neglected.

It has been suggested that the free electrons in the metal behave like those of atoms or molecules in a perfect gas. Hence, these electrons are sometimes known as *free electron gas* or *fermi gas* or *free electron cloud*.

However this fermi gas differs from ordinary gas in the following ways :

- Fermi gas is constituted by electrons which are charged particles while the atoms or molecules which constitute ordinary gas are neutral.
- The concentration of electrons in fermi gas is large 10^{29} per m^3 as compared with concentration of atoms or molecules of ordinary gas (10^{25} per m^3).

Classical theory explains certain properties of metals like electrical and thermal conductivity, thermionic emission, thermoelectricity, Photoelectric effect etc; but could not explain the specific heat of metals.

Sommerfield in 1928, suggested that electron gas should be treated quantum mechanically in the light of Pauli's exclusion principle which states that no two particles can have all the quantum numbers identical. According to him, the electrons in the metal are not bound but can not leave the metal and work has to be done to extract an electron from the metal. He used Fermi-Dirac statistics rather than Maxwell-Boltzmann statistics and succeeded in explaining many experimental facts.

The upper most filled energy level at absolute zero is known as *Fermi level and energy value* corresponding to this level is known as *fermi energy* u_f .

From Eq. (4.13.3), we have

$$u_f = \frac{h^2}{2m} \left(\frac{3n}{8\pi V} \right)^{2/3}$$

And mean energy of the electrons at 0 K is given by

$$u_n = \frac{3}{5} u_f$$

Let us define a temperature T_F called *Fermi-temperature* by

$$T_F = \frac{u_f}{k} = \frac{h^2}{2mk} \left[\frac{3n}{8\pi V} \right]^{2/3}$$

$$= \frac{h^2}{2m^{5/3} k} \left[\frac{3\rho}{8\pi} \right]^{2/3}, \quad \dots(4.20.1)$$

where $\rho = \left(\frac{mn}{V} \right) \text{ kgm}^{-3}$ is the density of the gas. For conduction electrons in metals $\rho = 0.1 \text{ kgm}^{-3}$

For electron, $m = 9.1 \times 10^{-31} \text{ kg}$, $k = 1.38 \times 10^{-23} \text{ J/deg}$

$h = 6.6 \times 10^{-34} \text{ Js}$, we get

$$T_F \approx 10^5 \text{ K}$$

Thus electron gas below 10^5 K temperature is degenerate.

Since total number of particles is given by

$$n = g_s \frac{V}{h^3} (2\pi mkT)^{3/2} \cdot \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{A^{-1} e^x + 1} \quad \dots(4.20.2)$$

At $T \rightarrow 0$, $A \rightarrow \infty$

$$\text{So } \frac{1}{A^{-1} e^x + 1} \rightarrow 1$$

So Eq. (4.20.2) becomes ($g_s = 2$)

$$n = \frac{4V}{\sqrt{\pi}} \frac{(2\pi mkT)^{3/2}}{h^3} \int_0^\infty x^{1/2} dx$$

Since at $T = 0$, $A = \infty$. So, let us replace upper limit of above integration by A .

$$\therefore n = \frac{uV}{\sqrt{\pi}} \frac{(2\pi mkT)^{3/2}}{h^3} \int_0^A x^{1/2} dx$$

or

$$n = \frac{4V}{\sqrt{\pi}} \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{2}{3} A^{3/2}$$

or

$$A = \frac{h^2}{2mkT} \left(\frac{3n}{8\pi V} \right)^{2/3} \\ = \frac{h^2}{2m^{5/3} kT} \left(\frac{3\rho}{8\pi} \right)^{2/3}$$

$$= \frac{(6.6 \times 10^{-34})^2}{2 \times (9.1 \times 10^{-31})^{5/3} \times 1.32 \times 10^{-23} \times T} \left(\frac{3 \times 0.1}{8 \times 3.142} \right)^{2/3} \\ A = \frac{4.56 \times 10^5}{T} \quad \dots(4.20.3)$$

Thus at low temperature the electron gas is strongly degenerate.

4.21. SPECIFIC HEAT OF METALS

Specific heat is really a measure of the number of degrees of freedom. Since degrees of freedom imply freedom to absorb potential or kinetic energy, the problem is to know how many modes are there for the system to absorb the energy.

Joule expressed the equivalence between mechanical work and heat energy. This is true only if the whole of work done is used in producing heat or vice-versa. But in actual practice when a certain amount of heat is given to a system, it is used in parts, in increasing the internal energy of the system by raising its temperature and the remaining heat energy is used in doing external work depending upon the conditions under which the heating takes place. Once the conditions on heating process are specified, the amount of work done is fixed and the quantity of heat required for a desired change in temperature can be well defined.

The specific heat of a substance is defined as the heat energy absorbed by one unit mass of the substance to raise its temperature by one degree. While measuring the specific heat either volume or pressure is kept constant. But in case of solids we usually speak of the specific heat at constant volume and it is given as

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v \quad \dots(4.21.1)$$

Partial derivative is taken since E may be function of other quantities, subscript V shows that volume is kept constant.

Whenever energy is added to a solid, the increase in its energy occurs in two ways, firstly the energy is used to vibrate the atoms and secondly the free electrons in metals may be excited to higher energy levels.

$$\therefore C_v (\text{metals}) = C_v (\text{atomic}) + C_v (\text{electronic})$$

On increasing the temperature, the atoms of the metal start vibrating about their mean position and the restoring force is proportional to displacement as long as the amplitude of vibration is small. Thus the vibrations of the atoms are simple harmonic in nature. The total vibrational energy of N independent harmonic oscillators in three dimensional for a gram molecule of a substance will be

$$E_{\text{atomic}} = 3NkT$$

(From law of equipartition of energy, the average energy associated with the motion of atom along one coordinate is $2 \times \frac{1}{2} kT = kT$ and in three coordinate axes, the total average energy of each atom is $3kT$.)

$\therefore$ Molar specific heat at constant volume due to atomic contribution will be given by

$$C_v (\text{atomic}) = \left[\frac{\partial E_{\text{atomic}}}{\partial T} \right] = \left[\frac{\partial}{\partial T} (3NkT) \right] = 3Nk = 3R \quad \dots(4.21.2)$$

i.e.

$$C_v (\text{atomic}) = 3R$$

Since the electrons inside the metals are assumed to be free, so they possess no potential energy and only kinetic energy, so the average energy due to the motion of electrons is given by

$$E = 3 \cdot \frac{1}{2} kT = \frac{3}{2} kT$$

If there is one free electron per atom in the metal, then

$$E_{\text{electronic}} = \frac{3}{2} NkT$$

$$\therefore C_v (\text{electronic}) = \left[\frac{\partial E_{\text{electronic}}}{\partial T} \right] = \frac{3}{2} Nk$$

$$\text{or } C_v (\text{electronic}) = \frac{3}{2} R \quad \dots(4.21.3)$$

$\therefore$ specific heat of metals at constant volume will be

$$C_v = 3R + \frac{3}{2} R = \frac{9}{2} R \quad \dots(4.21.4)$$

But experimentally it is found that

(i) At room temperature heat capacity is independent of temperature and is approximately equal to $3R = 24.9 \text{ J mol}^{-1}\text{K}^{-1} = 5.96 \text{ cal deg}^{-1} \text{ mol}^{-1}$, upto melting point of solids where R is universal gas constant. This is the well known law of Dulong and Petit. This is shown in Fig (4.21.1).

(ii) At low temperature C_v begins to fall and tends to zero as $T \rightarrow 0$.

(iii) Heat capacity follows T^3 law near $T = 0$ i.e. $C_v = (\text{constant})T^3$ in case of insulators and $C_v = (\text{constant})T$ in case of metals.

This anomaly of specific heat of solids was solved by Fermi-Dirac statistics to a large extent.

At low temperature, according to Fermi-Dirac statistics, the specific heat at constant volume due to electronic contribution is given by

$$C_v (\text{electronic}) = \frac{1}{2} \frac{Nk^2 \pi^2 T}{u_f} = \lambda T \quad \dots(4.21.5)$$

$$\left(\text{where } \lambda = \frac{1}{2} \frac{Nk^2 \pi^2}{u_f} \right)$$

$$\text{or } C_v (\text{electronic}) \propto T.$$

Thus we find that the electronic contribution to specific heat of metal at low temperature is directly proportional to absolute temperature and reduces to zero at $T = 0$, which is in agreement with the experimental observation. The electronic contribution to specific heat is about 1% of specific heat of atoms at room temperature, hence we consider the specific heat contributed by atoms only.

In 1912, Peter Debye calculated the specific heat of solids and its expression for metals at low temperature is given by

$$C_v = \beta T^3 + \lambda T, \quad \dots(4.21.6)$$

where first term is due to atomic consideration and second term is due to electronic consideration. At low temperature, the atomic specific heat becomes small and electronic specific heat becomes relatively high. At very low temperature (from 1.5 K to 3 K), the specific heat varies according to Eq. 4.21.5 and above 3 K, the T^3 term predominates. Thus Fermi-Dirac statistics solved the problem of specific heat of metals.

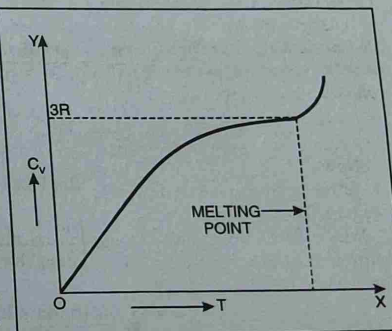


Fig. 4.21.1

Example 4.7. Calculate the fermi energy of the electrons in a metal of atomic weight 'w', density ρ and each atom of which gives out 'p' free electrons. Given that $h = 6.63 \times 10^{-34}$ Js; mass of electron = 9.1×10^{-31} kg. Avogadro's number is 6.02×10^{23} .

Solution.
 Number of atoms per mole = 6.02×10^{23}
 Each atoms gives out free electrons = p
 $\therefore$ Number of free electrons per mole = $n = p \times 6.02 \times 10^{23}$
 Mass of one mole of metal = w
 Volume of one mole of metal = $V = \frac{w}{\rho}$

$$\therefore \frac{n}{V} = \frac{\rho \times 6.02 \times 10^{23}}{\frac{w}{\rho}} = \frac{\rho p \times 6.02 \times 10^{23}}{w}$$

Now

$$\begin{aligned} u_f &= \frac{h^2}{2m} \left(\frac{3}{8\pi} \right)^{\frac{2}{3}} \left(\frac{n}{V} \right)^{\frac{2}{3}} \\ &= \left(\frac{h^2}{2m} \right) \left(\frac{3}{8\pi} \right)^{\frac{2}{3}} \left(\frac{\rho p \times 6.02 \times 10^{23}}{w} \right)^{\frac{2}{3}} \\ u_f &= \frac{(6.63 \times 10^{-34} \text{ Js})^2}{2 \times 9.1 \times 10^{-31} \text{ kg}} \times \left(\frac{3}{8\pi} \right)^{\frac{2}{3}} \times \left(\frac{6.02 \times 10^{23}}{1} \right)^{\frac{2}{3}} \left(\frac{\rho p}{w} \right)^{\frac{2}{3}} \\ &= (2.415 \times 10^{-37}) (0.2424) (7.1296 \times 10^{15}) \left(\frac{\rho p}{w} \right)^{\frac{2}{3}} \\ u_f &= 4.1736 \times 10^{-22} \left(\frac{\rho p}{w} \right)^{\frac{2}{3}} \text{ J}^2 \text{ s}^2 \text{ kg}^{-1} \end{aligned}$$

Remarks : Here ρ is to be substituted in kg m^{-3} and w in kg. So, u_f will come out in :

$$\begin{aligned} &\text{J}^2 \text{ s}^2 \text{ kg}^{-1} \left(\frac{\text{kg m}^{-3}}{\text{kg}} \right)^{\frac{2}{3}} \\ &= \text{J} [\text{kg m}^2 \text{ s}^{-2} \text{ kg}^{-1}] (\text{m}^{-3})^{\frac{2}{3}} \\ &= \text{J} [\text{m}^2] (\text{m}^{-2}) = \text{J}. \end{aligned}$$

Example 4.8. Show that for energy $u > kT$, the quantum as well as classical statistics yield same results, but they are different from each other to a great extent for $u < kT$.

Solution.

The distribution laws for energy are as follows :

For classical (MB) statistics :

$$n_u du = \frac{g_u}{e^{\alpha} e^{u/kT}} du \quad \dots(I)$$

For quantum statistics :

$$n_u du = \frac{g_u}{e^{\alpha} e^{u/kT} \pm 1} du \quad \dots(II)$$

+ 1 for FD statistics and -1 for BE statistics.

When $u \gg kT$ we find that $e^{u/kT}$ is very large. Therefore $e^{\alpha} e^{u/kT} \gg 1$. Hence equation (II) reduces to

$$n_u du = \frac{g_u}{e^{\alpha} e^{u/kT}} du.$$

which is the same as that for classical statistics.

For $u < 0$ we find that $e^{u/kT}$ is very small.

Therefore $e^{\alpha} e^{u/kT} < 1$.

And $(e^{\alpha} e^{u/kT} - 1)$ is smaller than $(e^{u/kT} + 1)$. Therefore, occupation index n_u is higher for BE statistics than that for FD statistics. Because of different values of occupation index, the three statistics give different results.

MULTIPLE CHOICE QUESTIONS

Q. 4.01. What do the various distribution laws of speeds represent ?

- Distribution of most probable speeds
- Distribution of speeds in the most probable state
- Distribution of the average speeds
- None of the above.

Q. 4.02. The velocity distribution among which of the following particles can be explained by the Bose Einstein statistics ?

- Photons
- Electrons
- Protons
- None of the above.

Q. 4.03. The minimum volume of an arbitrary cell in quantum mechanics is :

- h_0^3
- h^3
- less than h^3
- more than h^3 .

Q. 4.04. In which statistics, the occupation index can tend to zero ?

- Maxwell Boltzmann statistics
- Fermi Dirac statistics
- Bose Einstein statistics
- None of the statistics.

Q. 4.05. Which of the following is the most appropriate requirement for considering the identical particles as distinguishable ?

- The occupation index should be about 1.
- The number of cells in any compartment should be very much larger than the number of particles in it.
- The available volume of the cell should be comparable with h^3 .
- The system should be in the state of equilibrium.

Q. 4.06. In which of the following, no phase space cell can contain more than one particle :

- MB statistics
- BE statistics
- FD statistics
- None of these.

- Q. 4.07. The occupation index should be less than 1 both in the :
 (a) MB and FD statistics (b) MB and BE statistics
 (c) BE and FD statistics.
- Q. 4.08. Which of the following is not the characteristic of a system of fermions at absolute zero ?
 (a) The occupation index upto fermi energy level is 1.
 (b) All the energy levels below the fermi energy level are completely filled.
 (c) All the fermions are in the fermi energy level.
 (d) Maximum number of fermions are in the fermi energy level.
- Q. 4.09. What limits the size of the phase space cell ? Select the most appropriate answer out of following :
 (a) Planck's constant (b) Principle of uncertainty
 (c) Number of particles (d) Spin of the particles.
- Q. 4.10. What restricts the number of the particles that can occupy a phase space cell ?
 (a) Planck's constant (b) Principle of uncertainty
 (c) Pauli's exclusion principle (d) None of the above.
- Q. 4.11. The number of the meaningful ways in which 4 fermions can be distributed in 5 compartments is :
 (a) 1 (b) 4
 (c) 5 (d) 9.
- Q. 4.12. The number of the meaningful ways in which 5 bosons can be distributed in 4 cells is :
 (a) 1 (b) 9
 (c) 20 (d) None of the above.
- Q. 4.13. In which one of the following cases MB, BE and FD statistics lead to similar results ?
 (a) $n_i \gg g_i$ (b) $n_i = g_i$
 (c) $n_i \ll g_i$ (d) None of the above.
- Q. 4.14. The average energy of an electron in Fermi gas at 0 K is :
 (a) $0.3 E_f$ (b) $0.4 E_f$
 (c) $0.5 E_f$ (d) $0.6 E_f$
- Q. 4.15. Which of the following is a Boson ?
 (a) electrons (b) protons
 (c) neutrons (d) alpha particles.
- Q. 4.16. Black body radiation consists of :
 (a) protons (b) photons
 (c) electrons (d) alpha particles.

ANSWERS

- 4.01. (b) 4.02. (a) 4.03. (b) 4.04. (a) 4.05. (b) 4.06. (c)
 4.07. (a) 4.08. (c) 4.09. (b) 4.10. (c) 4.11. (c) 4.12. (d)
 4.13. (c) 4.14. (d) 4.15. (d) 4.16. (b)

SHORT ANSWER QUESTIONS

Q. 1. Distinguish between classical and quantum statistics.

Or

What is the difference between classical and quantum statistics ?

Or

How does classical statistics differ from a quantum statistics ?

Ans. The main points of differences between the classical and quantum statistics are the following :

Classical statistics	Quantum statistics
1. Volume of the elementary cell in phase space can be as small as we please.	1. Volume of the elementary cells in phase space cannot be less than h^3 , where h is Planck's constant.
2. Number of cells in phase space can be as large as we please.	2. The number of cells in phase space is limited by the minimum volume possible for the cell.
3. The size or volume of phase space cell can approach zero.	3. The size or volume of phase space cell cannot approach zero.
4. The particles of the system are considered distinguishable.	4. The particles of the system are considered indistinguishable.
5. Any number of particles can occupy the phase space cell.	5. In one type of quantum statistics (BE) any number of particles can occupy the phase space cell but in the other type (FD) there cannot be more than one particle in a cell.
6. It is also known as Maxwell Boltzmann statistics.	6. It is of two kinds depending upon the nature of particles. The two kinds are termed as Bose Einstein statistics and Fermi Dirac statistics.

Q. 2. Distinguish between BE statistics and FD statistics.

Or

What are the main points of difference between BE statistics and FD statistics ?

Ans. Distinction between FD statistics and BE statistics. The main points of difference between BE statistics and the FD statistics are the following :

BE statistics	FD statistics
1. Any number of particles can occupy a phase space cell.	1. The number of particles in one phase space cell cannot be more than 1.
2. The particles are termed as bosons.	2. The particles are termed as fermions.
3. It applies to particles with integral spins.	3. It applies to particles with half integral spin.
4. Particles like photons, mesons, ${}^1\text{H}^1$ and ${}^2\text{He}^4$ atoms can be studied with it.	4. Particles like electrons, protons, neutrons and ${}^2\text{He}^3$ can be studied with it.
5. It applies to particles other than those which obey Pauli's exclusion principle.	5. It applies to those particles which obey Pauli's exclusion principle.

Q. 3. Can quantum statistics be used to explain the behaviour of all types of particles, including the gas molecules ?

Ans. Yes, classical statistics is a special case of quantum statistics for very small values of occupation index. Thus, assuming the occupation index as small, quantum statistics can be used to explain the behaviour of gas molecules.

Q. 4. Which of the three statistics can have occupation index more than 1 and why ?

Ans. The occupation index can be more than 1, only in the case of the Bose Einstein statistics. It is not so in case of the Maxwell Boltzmann statistics, because to be able to distinguish the particles, the number of cells must be very, very large as compared to the number of particles. In fact, in case of MB statistics the occupation index should tend to zero.

In case of the FD statistics, the particles obey the Pauli's exclusion principle, and no cell can be occupied by more than one particle. So, the number of cells must be atleast equal to the number of particles or more. That is, the occupation index should be either equal to or less than 1.

Q. 5. Show that the occupation index can be more than 1 only for the BE statistics and not for the FD statistics.

Ans. For BE statistics, the occupation index is given by

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

Apparently, from the right hand side we find that no anomalous situation is created if $n_i > g_i$

So, n_i/g_i can be equal to or more than 1.

For FD statistics, we find

$$\frac{n_i}{g_i} = \frac{g_i}{n_i! (g_i - 1)!}$$

Here if $n_i > g_i$, then occupation index becomes negative, which is meaningless.

However, n_i can be equal to g_i . Hence, n_i/g_i cannot be more than 1.

Q. 6. Name three types of statistics.

Ans. Three statistics :

- Maxwell-Boltzmann statistics or M-B statistics
- Bose-Einstein statistics or B-E statistics
- Fermi-Dirac statistics or F-D statistics.

Q. 7. What do you understand by Fermi energy level of a metal ?

Or

What is Fermi energy ? Give its value.

Ans. Fermi Energy.

Fermi energy is the energy of the level below which all the states are completely filled and above which all the states are empty at 0 K. i.e. Fermi-energy is the energy of the uppermost filled level at 0K.

Fermi energy is given by

$$u_f = \frac{h^2}{2m} \left(\frac{3n}{8\pi V} \right)^{2/3}$$

Q. 8. What is the value of occupation index of fermions at 0 K for $u > u_f$ and $u < u_f$ where u_f denotes the fermi energy ?

Ans. For $u > u_f$ the occupation index is 0 and for $u < u_f$ its value is 1.

Q. 9. What is the energy of the electrons in metals at 0 K ?

Ans. At 0 K, the electron inside the metal have energy equal to or less than the fermi energy (u_f).

Q. 10. Do electrons come to rest inside the metals at 0 K ? Explain.

Or

Do electrons have zero energy at 0 K ? If not, explain why ?

Ans. No. At 0 K, the energy of electrons is not zero. Hence they are not at rest. At 0 K, the average speed of electrons is about 75% of the speed corresponding to the fermi energy level. Because

$$E = \frac{3}{5} n E_f$$

Q. 11. What is the energy of a particle at 0 K ? What happens in case of fermions ?

Ans. According to the MB statistics, the energy of a particle at 0 K is zero. However, in case of fermions, which obey FD statistics, the particles possess energy upto the fermi level.

Q. 12. What are fermions and bosons ?

Or

What are fermions ? Give examples.

Ans. Fermions

Fermions have following characteristics :

- The energy spectrum of fermions can be explained on the basis of FD statistics.
- They obey Pauli's exclusion principle.
- They have half integral spin.
- Electrons, positrons, neutrons, protons, atoms like ${}^2\text{He}^3$ are the examples of fermions.

Bosons

Characteristics of bosons :

- The energy spectrum of bosons can be explained on the basis of BE statistics.
- They do not obey Pauli's exclusion principle.
- They have integral spin or zero spin.
- Photons (spin 1), K and π mesons (spin 0), atom like ${}^2\text{He}^4$ (total spin of e, p & n is integral), phonons (spin 1) are the examples of bosons.

Q. 13. Discuss the limitations of MB statistics.

Or

What is the need for quantum statistics ?

Ans. MB statistics provides a satisfactory explanation of distribution of energy (and velocity) of ideal gas molecules. There are other systems like photons in a constant temperature enclosure and conduction electrons in a metal. They also have continuous random movements and mutual interaction between them can be disregarded as is the case with gas molecules. That is why, they are often termed as "photon gas" and "electron gas." However, their energy spectrum cannot be explained by the MB statistics. It is found that electron gas and photon gas systems were dominated by some other constraints like indistinguishability of particles, uncertainty principle and Pauli's exclusion principle. To take them into account, Bose, Einstein, Fermi and Dirac developed statistics, commonly known as quantum statistics. As the name implies, the energy states in the photon gas and electron gas systems are assumed to be discrete or quantised.

Q. 14. Explain why under low concentration of particles the quantum statistics should give the same result as the classical statistics ?

Or

Explain why for systems consisting of small number of particles the result of quantum statistics should be identical with classical statistics ?

Ans. In classical statistics, the particles are considered distinguishable, because the size of the phase space cell can be as small as we like. So, the space can be divided into very large number of cells such that each cell contains one particle or none. In this way, the particles can be numbered in terms of the number of the cells and they can be distinguished from each other. In quantum statistics, the size of the cell cannot be less than Planck's constant. So, the number of the space cells is limited and each cell may contain more than one particles. Therefore, they cannot be distinguished from each other in terms of the number of the cells.

From the above discussion we find that in classical statistics, the number of phase space cells is more than the number of particles. However, if the number of particles is not very large, then even in quantum statistics the number of the cells can be large than that of the particles. In that case particles can be distinguished in the same way as in classical statistics. So, the results of quantum statistics should be similar to that of classical statistics.

Q. 15. Give the basic assumptions or postulates of Bose Einstein statistics.

Ans. The basic assumptions of BE statistics are given below :

- The particles of the system are indistinguishable.
- Available volume of the phase space cell cannot be less than h^3 , where h is Planck's constant.
- Any number of particles can occupy a phase space cell.

Q. 16. Does the Fermi energy depend upon the size or volume of conductor ? Explain.

Ans. No, because the Fermi energy is function of electron density i.e. number of electrons per unit volume of the conductor and is independent of size or volume of conductor.

Q. 17. Explain the role of Pauli exclusion principle in deciding the behaviour of fermions when $n_i \ll g_i$?

Ans. When $n_i \ll g_i$, the Pauli's exclusion principle does not play any significant role in deciding the behaviour of the fermions, because the chances of two or more particles occupying the same cell simultaneously are almost negligible.

Q. 18. How does free electron gas differ from an ordinary gas ?

Ans. The main point of differences between electron gas and an ordinary gas.

S. No.	Electron gas	Ordinary gas
1.	Electron gas is charged.	1. Molecules of an ordinary gas are neutral.
2.	It obeys F-D statistics.	2. It obeys M-B statistics.
3.	Free electrons are indistinguishable.	3. Molecules of a gas are distinguishable.
4.	Number density of free electrons in a free gas is $\approx 10^{29}$ electrons m^{-3} .	4. Number density of ordinary gas is $\approx 10^{25}$ molecules m^{-3} .

Q. 19. Under what conditions do M-B, B-E and F-D statistics yield classical, statistics ?

Ans. The values of occupation index given by three statistics are as follows :

For M-B statistics

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + u_i/kT}} \quad \dots (i)$$

For B-E statistics

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + u_i/kT} - 1} \quad \dots (ii)$$

For F-D statistics

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + u_i/kT} + 1} \quad \dots (iii)$$

If $\frac{n_i}{g_i} \ll 1$, then $e^{\alpha + u_i/kT} \gg 1$ and the above three equations are equal and

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + u_i/kT}} \text{ for all statistics.}$$

Thus we find that for $\frac{n_i}{g_i} \ll 1$, all statistics give same result. Hence we can say that classical statistics is limiting case of quantum statistics.

QUESTIONS

- What is the need for quantum mechanics ?
- State and explain clearly the basic difference between classical and quantum statistics.
- Describe the salient differences in M-B, B-E and F-D statistics.
- Explain the need for quantum statistics and compare Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics.
- State the basis assumption of Bose-Einstein (B-E) statistics and derive the B-E distribution law.
- Write basic assumption of Bose-Einstein quantum statistics and then derive the expression

$$u_i = \frac{g_i !}{e^{\alpha} e^{u_i/kT} - 1}$$

- Discuss the basic assumptions of M-B, B-E and F-D statistics. Explain with the help of suitable example, the effect of assumptions on the distribution of particles among phase space cells.
- What is Bose-Einstein statistics ? What are its assumptions ? Derive the Bose-Einstein Distribution law.
- What are different kinds of statistics ? Discuss them.
- Compare M-B, B-E and F-D statistics on the basis of their assumptions and distribution law.
- Using F-D statistics, derive the expression :

$$n_i = \frac{g_i !}{e^{\alpha} e^{u_i/kT} + 1}$$

for the most probable distribution of Fermi particles.

- Apply F-D statistics to free electrons inside a conductor and deduce the expression

$$n(u) du = \frac{8\pi \sqrt{2} \pi V}{h^3} \frac{m^{3/2} u^{1/2} du}{e^{\alpha} e^{u/kT} + 1}$$

13. Apply F-D distribution law to derive the energy distribution of free electron inside a conductor.
14. What is Fermi energy? Derive an expression for it.
15. Explain that Planck's law is a correct and complete law of radiation.
16. What are Fermions? Write down the postulates in FD statistics. Derive an expression for the probability distribution of particles governed by FD statistics.
17. (a) Using F-D distribution law, in predicting the behaviour of free electrons in conductors.
(b) What do you mean by Fermi energy of conductor electrons?
18. Using the energy distribution for free electrons in a conductor, discuss the behaviour of these electrons at higher temperature.
19. Derive an expression for the probability distribution of fermions.
20. From B-E statistical thermodynamics, show that

$$E(\lambda) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

21. Show that the Fermi-Dirac distribution law for continuous energies is

$$N(E) dE = \frac{2(E) dE}{e^{\alpha} e^{E/kT} + 1}$$

Use this law to show that $\alpha = \frac{-E_f}{kT}$, where the symbols have their usual meanings.

22. Apply F-D distribution law and show that

$$u_f = \frac{h^2}{2m} \left[\frac{3n}{8\pi V} \right]^{2/3}$$

23. Do electrons have zero energy at 0 K? Why?
24. What are the constraints which are obeyed by a photon gas at a given temperature?
25. Using the expression $\left[n(u) \cdot du = \frac{3}{2} n \cdot u_f^{-3/2} u^{1/2} du \right]$ for electron gas. Prove that at absolute

zero, the average energy of electron is $\bar{u} = \frac{3}{5} u_f$, where u_f is the Fermi energy.

26. Show that the average energy of electron at 0 K is given by $\frac{3}{5} u_f$, where u_f is fermi energy.
27. Discuss the conditions under which quantum statistics merges with classical statistics.
28. What is electron gas? Starting from F - D distribution law, derive the expression for energy distribution of free electrons in metal.

NUMERICAL PROBLEMS

1. Copper gives out one free electron per atom. The density of copper is 8.94 g cm^{-3} and mass of one mole of copper is 0.0635 kg . Calculate the fermi energy of copper in electron volt.
Hint. $\rho = 8.94 \text{ g cm}^{-3} = 8940 \text{ kg m}^{-3}$, $p = 1$, $A = 0.0635 \text{ kg mol}^{-1}$, $e V = 1.6 \times 10^{-19} \text{ J}$.
[Ans. 7.05 eV]
2. A metal gives out free electrons per atom. The density of the metal 19.3 g cm^{-3} and atomic weight of the metal is 197. Calculate the fermi energy.
Hint. $A = 197 \text{ g mol}^{-1}$, $p = 2$
[Ans. $1.41 \times 10^{-18} \text{ J}$]

UNIVERSITY QUESTION PAPER 2022

B.Sc. (G.J.U.)

FOURTH SEMESTER

PHYSICS

(Statistical Mechanics)

Time Allowed : 3 Hours

Maximum Marks : 80

Note : Q. No. 1 is compulsory. Out of remaining eight questions (divided in 4 Units), attempt four questions by selecting either one question from each Unit or by selecting two questions from any one Unit and remaining two questions from two different Units out of remaining three Units.

(Compulsory Question)

1. (a) What do you mean by Canonical ensemble? 2
(b) What is the difference between macrostate and a microstate? 2
(c) What do you understand by Brownian motion? Explain. 2
(d) What do you mean by transport phenomenon? Explain it with example. 2
(e) What do you mean by negative temperature? Explain. 2
(f) What do you mean by Position space? 2
(g) What are fermions and bosons? Give examples. 2
(h) What are the differences between electron gas and ordinary gas? 2

UNIT-I

2. (a) What is meant by thermodynamic probability of a macrostate? What is the relation between thermodynamic probability and probability of a macrostate? 6
(b) What is the thermodynamical probability for distributing and distinguishable particles in two compartments? Find the probability of macrostate and most probable macrostate. 10
3. Define Partition Function. Derive its relation with various thermodynamic quantities. 16

UNIT-II

4. (a) Derive Maxwell's speed distribution law. Find the expressions for most probable speed, average speed and root mean square speed. 12
(b) Calculate root mean square speed and most probable speed of Hydrogen at 30°C . Given $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$ and mass of hydrogen molecule $= 3.34 \times 10^{-27} \text{ kg}$. 4
5. (a) What do you mean by mean free path? Derive an expression for it. 8
(b) Explain viscosity of a gas as transport phenomenon. How does viscosity of a gas vary with temperature? 8

UNIT-III

6. (a) Define phase space and momentum space. Determine the number of phase space cells in the momentum interval p and $p + dp$. 10
 (b) Find the number of phase space cells in the energy interval E and $E + dE$. 6
7. What is Maxwell Boltzmann Statistics ? Derive an expression for Maxwell Boltzmann law of distribution of molecular speeds. 16

UNIT-IV

8. What is Bose Einstein Statistics ? What are its assumptions ? Derive the Bose Einstein distribution law. 16
9. (a) What is Fermi energy ? Derive an expression for it. 7
 (b) What are the differences between Bose Einstein and Fermi Dirac statistics ? 5
 (c) Do electrons have zero energy at 0 K ? Explain. 4

NOTES