# STATISTICAL MECHANICS

(FOR THREE YEAR'S DEGREE & POST-GRADUATE
STUDENTS OF ALL INDIAN UNIVERSITIES)

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# CONCEPTS OF THERMODYNAMICS

## 1.1 Introduction

Thermodynamics and statistical mechanics are two of the most important tools of Physics. Incidently, there is a close connection between them and one can be transformed into another through simple conversion relations. For example, the thermodynamic entropy of a closed system has its maximum when the system is in the equilibrium condition. On the other hand, the statistical probability is also maximum in the equilibrium condition of the system. Thus there should be a close relationship between entropy and probability as per Boltzmann's suggestion. This relation between thermodynamic entropy and statistical probability forms the core of the **statistical mechanics**.

Thermodynamics is the exact mathematical science that describes the relationships of heat and mechanical energy. With the passage of time the scope of thermodynamics has increased and at present it covers all the branches of physics as well as chemistry whenever we have to deal with heat and its relationship to energy in any of its diverse forms-electrical, mechanical, chemical magnetic~~, nuclear~~ etc.

Thermodynamics constitutes a very subtle study in physics, chemistry and engineering and has innumerable applications. It is based ~~upon~~ three general laws, namely (i) The first law of the law of conservation of energy which represents the connection between heat and mechanical work; (ii) the second law which deals with the entropy changes in the system and manner in which energy changes takes places, and (iii) the third law which deals with the absolute value of entropy.

Thermodynamics makes no hypothesis about the structure of matter. Here we only deal with macroscopic (large scale) properties and do not go into detailed structure. Thermodynamics is an experimental or empirical science and the laws of thermodynamics have been developed by means of observations and experiments over a long period of years. Thermodynamic formulae have necessarily the same general validity as the three laws from which they are derived.

## 1.2 Some Definitions

**1. System and Surroundings :** A **thermodynamic system** is that part of the universe which is being subjected to thermodynamic scrutiny; everything else in the universe constitutes the **surroundings.**

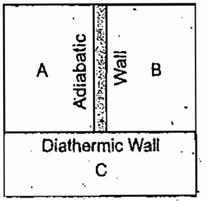
**2. Open and Closed Systems :** An **open system** one which can exchange matter and energy with the surroundings while a closed system is one which can not exchange matter but can exchange energy with the surroundings.

If a system can not exchange matter or energy of any kind with its surroundings, it is called an **isolated system**. As there is no barrier to gravitation, a perfectly isolated system is impossible, but the influence of gravity is often negligible. The boundary of the closed system must be impenetrable by matter while the boundary of an isolated system must not be crossed by matter, heat, radiation or other forms of energy and must not be displaced against a force. These definitions require that accrding to this non-relativistic view of the universe, mass and energy are not interconvertible , they (mass and energy) must be conserved separately in any change.

The properties of a system are classed as *intensive* or *extensive*, according to whether the given property is idependent of or dependent on mass of the substance. **A homogeneous system** is one whose intensive properties like density and pressure are continuous functions of position. If the intensive properties of a system are discontionuous, the system is said to be **inhomogeneous** or **heterogeneous.** *A heterogeneous system* may be considered to be composed of a number of homogeneous ones separated from one another by surfaces of discontinuity, each separate portion being called a **phase** *e.g.* a solution of water and oil, water contained in a closed vessel with vapour above the water. Water and oil ordinarily form two phases *i.e.*, there is a region rich in water where the intensive properties like density and elemental composition correspond closely to the values for water, and there is another region where the intensive properties correspond closely to those for oil. At the interface between the two liquid phases, various intensive properties appear discontinuous to the eye. The **state of a system** is determined by ascribing values to a sufficient number of variables callled **thermodynamic coordinates** or its **state variables** *e.g.* pressure, density, temperature, volume etc.

When there is no unbalanced force between the system and its sorroundings and none exists between different parts of the system itself, the system is said to be in a state of **mechanical equilibrium.** If the temperatue in all parts of the system is uniform and is the same as that of the sorroundings, the system is said to be in **thermal equilibrium.** If the chemical composition of the system is the same throughout, the system is said to be in **chemical equilibrium.** *A system which is in thermal, mechanical and chemical equilibrium is said to be in* **thermodynamic equilibrium.** The *state of a system in thermodynamic equilibrium* can be represented by specifying its pressure, volume and temperature. The subject of thermodynamics deals chiefly with systems which are in thermodynamic equilibrium.

## 1.3 Zeroth Law of Thermodynamic and Concept of Temperature



(Fig. 1.1)

According to the zeroth law of thermodynamics, *if two systems are in thermal equilibrium with a third system, then they must be in thermal equilibrium with one another.*

This statement forms the basis of **concept of temperature** and may be demonstrated by following experiment.

Consider two systems $A$ and $B$ separated from each other by an adiabatic wall (one that conducts no heat), but each being in contact of a third system $C$ through a diathermic wall which permits heat to pass (Fig. 1.1). Then the system $A$ will be in thermal equilibrium with system $C$ and similarly system $B$ will also be in thermal equilibrium with system $C$. Now if the adiabatic wall between systems $A$ and $B$ is replaced by a diathermic wall, experiments show that no further change occurs in systems $A$ and $B$, indicating thereby that system $A$ was also in thermal equilibrium with system $B$.

***If two systems A and B are in thermal equilibrium with a third system C separately, then they will be in thermal equilibrium with each other.***

All these three systems can be said be to possess that ensures their being in thermal equilibrium with one another. This property is known as *temperature.* We may, therefore, define the *temperature of a system as the property that determines whether or not the system is in thermal equilibrium with the neighbouring systems.* It is obvious that if two systems are not in thermal equilibrium, they will be at different temperatures.

## 1.4 Equation of state of an ideal gas

An ideal gas is one which has following two characteristics.

(i) The volume of molecules of gas is negligible as compared to volume of containing vessel.

(ii) The intermolecular forces are negligible.

It is found experimentally that all the gases behave essentially in the same way provided their densities are not too high, *i.e.*, if the temperatures are not too low and the pressures are not too high, all real gases show the same simple behaviour.

Suppose that one has measured the pressure $P$, volume $V$ and temperature $T$ and mass $m$ of a certain gas over wide ranges of these variables. It is observed under a wide range of conditions that at a constant temperature, the pressure of a gas is inversely proportional to its specific volume $\frac{V}{m}$ (Boyle's law) and that the product of the pressure and the specific volume is directly proportional to the absolute temperature (Charle's law). These experimental results can be summarised by the relation.

$$P \cdot \frac{V}{m} = rT, \qquad \ldots(1)$$

where $r$ is a constant of proportionality whose value depends upon the specific gas being investigated.

When we compare the values of $r$ for various gases experimentally, it is observed that $r$ is inversely proportional to the molecular weight $M$ of the gas, *i.e.* $r = \frac{R}{M}$ where $R$ is a constant of proportionality and is same for all gases. Constant $R$ is termed as *universal gas constant* and its numerical value is found to be

$$R = 8{\cdot}314 \text{ joule/(mole (K)} = 1{\cdot}96 \text{ cal/(mole) (K)}.$$

$$P \cdot \frac{V}{m} = \frac{R}{M} \cdot T$$

or

$$PV = \frac{m}{M} RT. \qquad \ldots(2)$$

Hence, it is convenient to define a new unit of mass called *'mole'* or *'one gram molecule'*. It is defined as the mass of that number of grams to which the molecular weight is numerically equal, *i.e. 'mole'* or *'one gram molecule'* is equal to $M$ grams. The mass in *mole* is commonly expressed as $n$, so that if $m$ is the mass of a gas in grams, then $n$ *moles* $= \frac{m}{M}$ grams.

Hence eqn. (2) takes the familiar form

$$PV = nRT. \qquad \ldots(3)$$

For 1 mole ($n = 1$), the equation (3) takes the

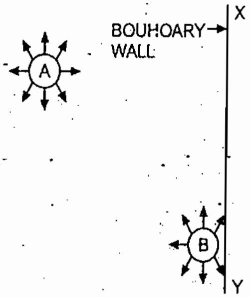
$$PV = RT. \qquad \ldots(4)$$

From equation (4) it is obvious that the *molar specific volume, i.e., the volume per mole of a gas* $\left(V = \frac{RT}{P}\right)$ depends only on the temperature and pressure and not on the nature of the gas. Under standard conditions ($P = 1$ atmosphere and $T = 273$ K) the volume occupied by one mole of any gas is 22·4 litres. An ideal gas is one which behaves according to equation (4) under all conditions. Equation (4) is called the *equation of state of an ideal gas for one gram molecule.*

The real gases behave closely to equation (4) under a wide range of conditions and begin to deviate from it only as densities become higher.

### 1.5 Vanderwaal's Equation of State

While deriving the equation of state of ideal gas it is assumed that the volume occupied by the molecules themselves is negligible compared with the total volume of the gas, and that the molecules exert no appreciable forces on one another. It is evident that both these assumptions can not be exactly true for actual gases particularly at high pressures. In deriving Vander Walls equation of state the effect of both these factors is taken into account.



(Fig. 1.2)

Due to the finite size of the molecules, the free space available for their movement is less than the actual measured volume of the gas. Also the number of collisions with the walls of containing vessel, and hence the pressure, will be greater than the calculated by the simple theory. The actual volume can be brought about by subtracting a correction term $b$ from the measured volume and using $(V-b)$ in place of $V$ in ideal gas equation.

The effect of the forces of cohesion can be seen by considering fig. 1.2. $XY$ is a portion of the boundary wall. Consider a molecule $A$ in the interior far from the boundary, wall. It is surrounded by other molecules equally distributed in all directions. These molecules exert attractive forces on molecule $A$. When averaged out over a sufficient interval of time, they cancel out and the net cohesion force on the average will be zero. On the other hand the molecule $B$ is as near the boundary as it can go. In this case the molecular distribution is only along one side. The adhesive force between the gas ~~moleeules~~ and the boundary walls are always much smaller than the cohesive forces between the gas molecules themselves. The force on $B$ due to each adjecent molecule can be resolved into components parallel and perpendicular to the boundary wall. The parallel components cancel out on the average but the perpendicular components will result a field of force acting inwards on the molecules near the boundary wall. Thus whenever a molecule will strike the walls of the containing vessel as at $B$ to contribute its share towards the total gas pressure, the other molecules will pull it away from the wall. The measured pressure $P$ is thus less than the ideal pressure calculated on the assumption that the cohesive forces are absent. If we represent the effect per unit area of cohesive forces by $p_1$, we should add a correction therm $p_1$ to the measured pressure $P$ and use $(P+p_1)$ in place of $P$ in the ideal gas equation.

On using both corrections in the ideal gas equation, we get for *a gram* molecule of a gas,

$$(P+p_1)(V-b)=RT. \qquad \ldots(1)$$

The value of $p_1$ is proportional to the number of molecules striking unit area of the wall in unit time and to the intensity of the field of force. Both of these factors are proportional to the density $\rho$ of the gas and therefore we may write

$$p_1=c\rho^2,$$

where $c$ is a constant, and density $\rho=\dfrac{m}{V}$:

Hence
$$p_1=c\frac{m^2}{V^2}$$

$$\Rightarrow \qquad p_1=\frac{a}{V^2}$$

where $a\ (=cm^2)$ is a constant.

Substituting this value of $p_1$ in equation (1), we get

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT. \qquad \ldots(2)$$

This is *Vander Waal's equation of state. This is the simplest and the most well-known equation of state for real gases.*

Another useful form of the equation of state of a real gas is

$$PV=A+\frac{B}{V}+\frac{C}{V^2}+\ldots \qquad \ldots(3)$$

where $A, B, C, \ldots,$ etc. are functions of the temperature and are called the *Virial coefficients*.

For an ideal gas it is evident that $A=RT$ and all other Virial coefficients are zero.

Vander Waals equation can be put in Virial form as follows :

Equation (2) can rewritten as

$$1=\frac{RT}{\left(P+\dfrac{a}{V^2}\right)(V-b)}$$

or
$$PV=RT\left(1+\frac{a}{PV^2}\right)^{-2}\left(1-\frac{b}{V}\right)^{-1} \qquad \ldots(4)$$

The correction terms $\dfrac{a}{PV^2}$ and $\dfrac{b}{V}$ are both small compared with unity provided the gas is not too much compressed. Therefore we may use $PV=RT$ (approximately) in the terms of binomial expansion of equation (4). Using binomical theorem and neglecting the terms containing higher powers of $1/V$, equation (4) becomes

$$PV=RT\left(1-\frac{a}{PV^2}\right)\left(1+\frac{b}{V}+\frac{b^2}{V^2}\right)$$

$$=RT+RT\cdot\frac{b}{V}-\frac{RT}{PV}\cdot\frac{a}{V}+\frac{RTb^2}{V^2}$$

Since $PV=RT$ approximately, we have

$$\therefore\ PV=RT+\frac{(RTb-a)}{V}+\frac{RTb^2}{V^2} \qquad \ldots(5)$$

This is Vander Waal's equation in Virial form having only three Virial coefficients, $A$, $B$, and $C$ given by

$$A=RT,\ B=RTb-a,\ C=RTb^2$$

**Note** : Vander Waal's equation of state for $n$ gram moles is

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT.$$

## 1.6 Concepts of Work, Internal Energy and Heat

**Work** : The term *work* refers to an interchange of energy between its system and its surroundings. If a force **F** produces an infinitesimal displacement $dS$, then the work done by the force

$$dW = \mathbf{F}\,.\,d\mathbf{S}.$$

If a force is exerted by the system as a whole on its surroundings and a displacement takes place, the work done either by the system or on the system is called *external work*. For example a gas contained in a cylinder at a uniform pressure while expanding pushes the piston out and does external work on its surroundings. On the other hand the work done by one part of the system on another part of the same system is called the *internal work*. For example, in an actual gas there exist intermolecular attractions and when such a gas expands, the work is done against these mutual attractions between the molecules, which is the internal work. Thus interactions of the molecules of a system on one another constitute internal work.

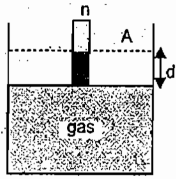
Suppose we now try to compute $W$ for a specific thermodynamic process. Consider a constant mass of a gas in a cylindrical container with a movable piston. We may consider the gas as a system and the piston and cylinder as the surroundings. Let initially the system be in equilibrium with its surroundings and has a pressure $P_1$ and volume $V_1$. Heat can flow into the system or out of it through the walls and work can be done on the system by having the piston compressed or work can be done by the system by expanding against the piston. Consider some process whereby the system interacts with its surroundings and reaches a final equilibrium state characterised by a pressure $P_2$ and a volume $V_2$.

Suppose the gas is expanding against the piston. The work done by the gas in displacing the piston through an infinitesimal displacement $ds$ is given by

$$dW = F\,ds$$

where $F$ is the force exerted by the gas on the piston.

If $A$ is the area of the piston and $P$ the pressure at the instant when displacement $ds$ is taking place, then



(Fig. 1.3)

$$dW = PA\;ds = P\,dV$$

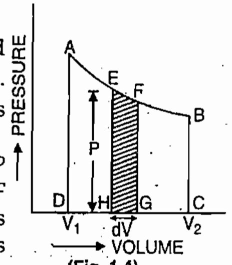
where $dV$ (= $A\,ds$) is the differential increase in the volume of the gas.

In general the pressure varies during a displacement and we must know how $P$ varies with the displacement. The total work $W$ done by the gas on the piston is found by the integration,

$$W = \int dW = \int_{V_1}^{V_2} P\,dV.$$

Let now represent the initial state ($P_1$, $V_1$) of the gas by the point $A$ and its final state ($P_2$, $V_2$) by the point $B$ on a pressure volume diagram (Fig. 1.4). The intermediate changes of the process are represented by different points on the line $AB$ which therefore represents the whole operation.

At any point such as $E$ during this change, let the pressure of the gas be $P$ and let its volume increase by an infinitesimal amount $dV$ to reach point $F$ which is infinitesimally close to $E$. The shaded strip $EFGH$ may be regarded as a rectangle of area $P\,dV$. But $P\,dV$ is the amount of work done by the gas during the small expansion $dV$. Thus the work done by the gas $P.\,dV$ is represented by the area of the shaded strip.



(Fig. 1.4)

The total work done by the gas in moving from $A$ to $B$ is clearly equal to the sum of areas of all such strips *i.e.*, equal to the area $ABCD$ bounded between the curve $AB$ and the volume axis from $V_1$ to $V_2$.

Hence $$W = \int_{V_2}^{V_2} P.\,dV = \text{Area of } ABCD$$

Thus on an indicator diagram *the area between the P-V curve, the volume axis and the two ordinates at the extermities of the P-V diagram gives directly the work done during the operation.*

**Internal Energy of a System**

Every thermodynamic system has within itself a definite quantity of energy. For instance (a) a liquid freezes into a solid yielding heat energy, (b) zinc and copper sulphate in a Daniell cell react producing electrical energy, (c) a mixture of hydrogen and oxygen gas explodes providing mechanical energy. This store of energy which is not apparently shown by a system but is still capable of doing work, is called *the internal energy* or *intrinsic energy*.

Thermodynamics has nothing to do with the source of this energy, it is sufficient for its purpose that such an energy exists. However, according to kinetic theory of matter, matter is made up of large number of tiny particles called molecules which are in a state of constant rapid motion and hence possess kinetic energy. The total kinetic energy of the molecules is called the *internal kinetic energy* while the potential energy arising due to the intermolecular attraction is called the internal *potential energy*. The energy of the system may be increased by causing its molecules to move faster (a gain in kinetic energy) or by causing the molecules to move against intermolecular forces into a configuration of greater potential energy, or both. The sum of the kinetic and potential energies ~~of the molecules of a~~ body, apart from ~~any~~ kinetic or potential energy of the body as a whole, is called its **internal energy** and is denoted by the letter $U$. ***Thus internal energy may be defined as the energy possessed by a body or by a system by virtue of its molecular motion and the constitution of these molecules.***

Let us now consider an isolated thermodynamic system subjected to external forces. Let an amount of work $W_{i \to f}$ be done on the system in going from a state $i$ to a state $f$ adiabatically (*i.e.* without sharing energy from outside) and the internal energies in the initial and final states be represented by $U_i$ and $U_f$ respectively, then assuming the law of conservation of energy,

$$U_f - U_i = -\,W_{i \to f}$$

where the minus sign is introduced becasue the work is done on the system.

The physical interpretation of the difference $U_f - U_i$ is the increase in the energy of the system. Thus there exists an energy function the difference in the two values of which is just equal to the work done in going from $i$ to $f$. Thus internal energy function is a function of the state (thermodynamical coordinates) *i.e.* ***the internal energy function is independent of the path.*** If a system returns to its initial state after passing through various states, the change in its internal energy will be zero.

**Concept of Heat**

Heat may be defined as the *energy in transit*. It flows from one point to another. If the flow of heat stops, we can not use the word heat *i.e.* the word heat may be used only when there is transfer of energy between two or more thermodynamic systems. When two bodies of different temperatures are placed in contact with each other, the two temperatures approach each other and after some time become aqual. This phenomenon is described by saying that energy has flown from one body to another. *Thermodynamically this flow of energy from one body to another on account of difference of temperature between them is called heat.* Thus the flow of heat is a non-mechanical energy transfer brought about by a temperature difference between two bodies.

For example, if a system loses energy by conduction or radiation, we may say that it is giving up heat as the process of conduction or radiation depends upon the temperature difference between the system and its surroundings.

## 1.7 The First Law of Thermodynamics

The first law of thermodynamics is a particular form of the general law of conservation of energy. Let us suppose that a quantity $Q$ of heat is supplied to a system. It is, in general spent in two ways.

(i) Partially, it is spent in increasing internal energy of system.

(ii) The remaining part of it is spent in expanding the body against the external pressure, *i.e.* **in doing external work $W$.**

If $\Delta U$ the change in internal energy since "energy can neither be created nor destroyed but only converted from one form to another", we have then

$$Q = \Delta U + W \qquad ...(1)$$

If $dQ$, $dU$ and $dW$ are infinitesimal changes in heat, internal energy and work respectively, then equation (1) becomes

$$dQ = dU + dW \qquad ...(2)$$

This equation represents the *differential form of first law of thermodynamics*, which may therefore be stated. "*In all transformations, the energy due to heat units supplied must be balanced by the external work done plus the increase in internal energy*".

Internal energy are of two forms.

**(i) Internal kinetic energy** : The energy possessed by system due to molecular motion is called internal kinetic energy. It increases when temperature of system increases.

**(ii) Internal Potential Energy** : The energy possessed by system due to molecular configuration is called internal potential energy. It increases when separation between molecules increases.

If $dU_k$ and $dU_p$ represent the changes in internal kinetic energy and internal potential energy we have

$$dU = dU_k + dU_p$$

While using eq. (1), two things should be kept in mind :

(i) $Q$, $\Delta U$ and $W$ are all to be measured in the same units *i.e.* all the three either in joules or in calories or kilo calories.

(ii) If the heat is taken by the system, then $Q$ is positive and if it is given by the system, then $Q$ is negative. Similarly if the work is done by system, then $W$ is positive and if the work is done by some external agency on the system, then $W$ is negative.

(iii) For $n$ moles of a perfect gas, $\Delta U = nC_v \Delta T$, where $C_v$ is molar heat at constant volume.

If change occurs at constant pressure, then

$$\Delta Q = nC_p \Delta T$$

$C_p$ = molar heat at constant pressure with condition $C_p - C_v = R$ (Mayer's formula)

### Supplement of the First Law

If $Q$ is given in cal. or kilo cal. and $U$ and $\Delta W$ is joule, then $Q$ can be converted into joule by the help of relation

$$W = JQ$$

where $W$ is work and $Q$ is heat and $J = 4{\cdot}2$ joule/cal. $= 4{\cdot}2 \times 10^3$ joule/kilo cal. is a universal constant, called the mechanical equivalent of heat. This states "*When mechanical work is spent in producing heat, a definite quantity of heat is produced for every unit of work spent; and conversely, when heat is employed to do work, the same define quantity of heat disappears for every unit of work obtained*". This statement is called supplement of I law.

The first law of thermodynamics, thus establishes an exact relationship between heat and work. According to it a definite quantity of heat will produce a definite amount of work and vice versa. It denies that work or energy can be created out of nothing. It means that it is impossible to construct a thermal machine which may operate without any expenditure of fuel and may thus create energy out of nothing. A machine that would do this could run itself and is generally called a perpetual motion machine of the first kind. The first law rules out such machine and is therfore sometimes defined in the form. "*Perpetual motion of the first kind is impossible*". The fact that no exception to the first law has been found yet and no one has succeeded in building such a machine, forms an experimental basis for the first law.

## 1.8 Thermodynamic Processes

Any change in thermodynamic coordinates of a system is called a process.

If work is done by the thermodynamic system or by external energy, a process is said to be occuring. The following are familiar processes in thermodynamics.

**Isothermal Process :** If a thermodynamic system is perfectly conducting to the surroundings, and undergoes a physical process in such a way that ***its temperature remains constant throughout, the process is said to be isothermal process.*** In such a process, the heat developed or heat lost is given out to or taken from the surroundings in such a way that the temperature of the system remains constant. If a gas contained in a metallic cylinder fitted with a piston is compressed slowly the heat generated by the external work done upon the gas, conducts away to the surroundings through the walls of the cylinder. Similarly, if the gas is allowed to expand slowly, a slight cooling will be produced as the gas does work against the piston but an equivalent amount of heat will enter the system from the surroundings and equalize the temperature. Thus in both cases the temperature remains constant and hence the processes are isothermal. The melting of ice at its melting point and vaporization of water at its boiling point are the examples of isothermal processes.

The curves showing the variation in the volume of a substance when the pressure acting on it changes under isothermal conditions are called isothermals.

The equation connecting the pressure $P$ and volume $V$ of one mole of a gas for an isothemal process is

$$PV = RT = \text{constant}$$

For $n$ moles of a gas

$$PV = n\,RT \left( n = \frac{m}{M} = \frac{\text{mass in grams}}{\text{molecular weight}} \right)$$

where $R = 8{\cdot}3$ *joule/g mole* $= 8{\cdot}3 \times 10^3$ *joule/kg mol K* is the universal gas constant and $T$ is the absolute temperature.

In isothermal changes, there is no change in temperature, hence no change in internal energy *i.e.* $dU = 0$

$$\therefore \qquad dQ = 0 + dW$$

or $$dQ = dW$$

Thus during an isothermal process.

Heat added (or subtracted) = work done by (or on) the gas.

**(ii) Adiabatic Process.**

If a thermodynamic system is perfectly insulated from the surroundings and undergoes a process in such a way *that no exchange of heat takes place between it and the surroundings, the process is said to be adiabatic process.* In such a process no heat is allowed either to enter the system or to leave it, but all along the process, there is a change in temperature. If a gas is suddenly compressed, the external work done upon it increases its internal energy and consequently its temperature rises. Similarly, if the gas suddenly expands, it does work against the surroundings at the cost of its internal energy and therefore, its temperature falls. Thus there is no exchange of heat between the gas and surroundings, being perfectly insulated from each other, and hence these processes are adiabatic. The compressions and rarefactions produced in air during the propagation of sound waves is also an example of adiabatic process. The sudden expansion of the enclosed air into the atmosphere when a motor tyre bursts, is approximately adiabatic and hence the tyre is cooled.

Thus all processes that take place quickly or suddenly are adiabatic processes.

The curves showing the variation in the volume of a substance when the pressure acting on it change under adiabatic conditions are called *adiabatics.*

During an adiabatic process, no heat enters or leaves the system, but temperature changes, because work is done at the cost of internal energy.

For adiabatic change in a perfect gas, $dQ = 0$ and hence

$$0 = dU + dW$$

$$dU = -dW$$

*i.e.,* change internal energy = mechanical work done on the system.

**(iii) Isobaric Process.**

***If the working susbtance is taken in an expanding chamber in which the pressure is kept constant, the process is called isobaric process.*** In these processes the gas either expands or contracts to maintain a constant pressure and hence a net amount of work is done by the system or on the system. The amount of heat $dQ$ given to the working substance is partly used in increasing the temperature $dT$ of the working substance and partly used in doing external work. Considering one mole of the working substance

$$dQ = C_P\, dT = C_V\, dT + P.\, dV$$

**(iv) Isochoric Process.**

***If a substance undergoes a process in which the volume remains unchanged, the process is called an isochoric process.*** The increase of pressure and temperature produced by the heat supplied to a working substance contained in a non-expanding chamber is an example of isochoric process. Since there is no change in volume, the work done in such a process is zero ($dW = P.\, dV = 0$) and, therefore, from first law

$$dQ = dU$$

Thus whole of the heat supplied increases the internal energy of the system. The heat supplied in such a process for one mole of working substance

$$dQ = C_V\, dT$$

Hence $$dU = C_V\, dT$$

### (b) Quasi-static Process

A quasi static process is defined as the process in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through which the system passes during a quasistatic process may be treated as equilibrium states. Thus it may be defined a succession of equilibrium states. For example, consider a system, a gas contained in a cylinder fitted with a movable piston. If the piston is pushed in very rapidly, the gas immediately behind the piston acquires kinetic energy and is set into turbulent motion which is a non-equilibrium state. In such a case the work done on the system is not governed by the equation $dW = P.\, dV$. If, however, the piston is pushed in at a infinitely slow rate, the system is at all times in a quiescent equilibrium state and then the process can be considered quasistatic. Thus during a quasi-static process, the system is at every moment infinitesimally near a state of thermodynamic equilibrium and all the states through which the system passes can be described by means of thermodynamic variables referring to the system as a whole. The vanishingly slowness of the process is an essential features of a quasi-statis process.

A quasi-static process is an idealized concept and the conditions for it can never be rigorously satisfied in practice. It is quite distinct from a real physical process because a real process always involves non-equilibrium intermediate states. A quasi-static process in contrast to a real process, does not involve considerations of rates, velocities or times. A real process is a temporal succession of equilibrium and non-equilibrium states whereas a quasi-static process is an ordered succession of equilibrium states.

## 1.9 Adiabatic Equation of a Perfect Gas

The process in which heat can neither enter or leave the system is called *adiabatic process.* A sudden and rapid process is the adiabatic, *i.e.* for an adiabatic process $Q$ = constant or $\Delta Q = 0$.

Let us consider one gram. molecule of a perfect gas thermally insulated from its surroundings. Let it suffer a very small adiabatic expansion doing external work at the cost of its own internal energy. The temperature of the gas therefore falls.

If the volume of the gas increases by an infinitesimal amount $dV$ against an external pressure $P$, the external work done by the gas in its expansion will be

$$dW = P.\, dV \qquad \text{...(1)}$$

Since in a perfect gas, the molecules do not attract one another, the internal energy depends only on its temperature. Hence the decrease in internal energy of the gas, suffering a fall $dT$ in its temperature is equal to the heat drawn from it *i.e.,*

$$dU = 1 \times C_V \times dT \qquad \text{...(2)}$$

where $C_V$ is the specific heat for one gm. mole of the gas at constant volume. Applying now the first law of thermodynamics

$$dQ = dU + dW$$

or $$dQ = C_V\, dT + P.\, dV$$

where $dQ$, $C_V\, dT$ and $P.\, dV$ are all measured in the same units *i.e.,* either in joules or in calories.

Since in an adiabatic change, no heat is supplied from outside.

Hence $$dQ = 0$$

Therefore, we have

$$C_V\, dT + P.\, dV = 0 \qquad \text{...(3)}$$

Also for one gram molecule of a perfect gas we have the relation $PV=RT$ ($R$ being gas constant) which on differentiation yields

$$P\,dV+V\,dP=R\,dT$$

or

$$dT=\frac{P\,dV+V\,dP}{R}$$

Putting this value in equation (3)

$$C_V\left(\frac{P\,.\,dV+V\,.\,dP}{R}\right)+P\,.\,dV=0$$

or

$$C_V(P\,.\,dV+V\,.\,dP)+R\,(P\,.\,dV)=0$$

But from Mayer's relation

$$C_P-C_V=R$$

$$\therefore \qquad C_V(P.\,dV+V.\,dP)+(C_P-C_V)\,P.\,dV=0$$

$$C_V\,.\,V.\,dP+C_P\,.\,P.\,dV=0$$

Dividing by $C_V\,PV$,

$$\frac{dP}{P}+\frac{C_P}{C_V}\frac{dV}{V}=0.$$

But $\frac{C_P}{C_V}=\gamma$, the ratio of the principal specific heats of the gas.

Hence

$$\frac{dP}{P}+\gamma\frac{dV}{V}=0$$

Integrating, $\log_e P+\gamma\log_e V=Constant$ or $\log_e P+\log_e V^{\gamma}=Constant$

or

$$\log_e PV^{\gamma}=Constant$$

or

$$PV^{\gamma}=Constant \qquad \ldots(4)$$

This is the equation connecting pressure and volume during adiabatic proccess and is knwon as *Poisson's law*.

There are two other forms of the above relation.

**Relation between temperature and volume.** Putting $P=\frac{RT}{V}$ in eq. (4), we get

$$\frac{RT}{V}V^{\gamma}=\text{constant}$$

or

$$TV^{\gamma-1}=\text{constant} \qquad \ldots(5)$$

**Relation between temperature and volume.** Putting $P=\frac{RT}{V}$ in eq. (4), we get

$$P\left(\frac{RT}{P}\right)^{\gamma}=\text{constant}$$

or

$$\frac{T^{\gamma}}{P^{\gamma-1}}=\text{constant}$$

or

$$T\,P^{(1-\gamma)/\gamma}=\text{constant} \qquad \ldots(6)$$

## 1.10 Molar Specific Heats $C_p$ and $C_v$

**(i) The specific heat at constant volume $C_V$:** It is defined as the amount of heat required to raise the temperature of a 1 mole of a gas through 1°C when its volume is kept constant. It is denoted by $C_V$ and given by

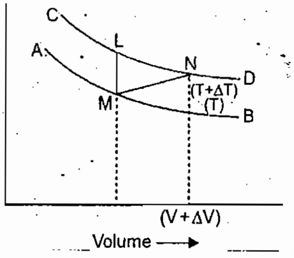
$$C_V=\left(\frac{\Delta Q}{\Delta T}\right)_V$$

**(ii) The specific heat at constant pressure $C_p$:** It is defined as the amount of heat required to raise the temperature of 1 mole of the gas through 1°C when its pressure is kept constant. It is denoted by $C_P$ and given by

$$C_P=\left(\frac{\Delta Q}{\Delta T}\right)_P$$

**Derivation of Mayer's Formula $C_p-C_V=R$.** Cconsider two isothermals $AB$ and $CD$ drawn for 1 mole of an ideal gas at close temperatures $T$ and $(T+\Delta T)$. Let the initial state of the gas be represented by point $M$ on lower isothermal at $T$. Let it now be heated at constant volume until its temperature rises to $T+\Delta T$ and its new pressure correspond to point $L$ on the upper isothermal $CD$. As the volume of the gas is kept constnat no external work has been done by the gas and hence the change in internal energy in the process $M\rightarrow L$ is given by first law to be

$$U_L-U_M=\Delta Q-\Delta W=C_V\,\Delta T \qquad (\because\ \Delta W=0) \quad \ldots(1)$$



(Fig. 1.5)

Again starting from the same initial condition of the gas represented by $M$, let it now be heated at constant pressure until its temperature rises to $(T+\Delta T)$ and its new volume $(V+\Delta V)$ corresponds to point $N$ on upper isothemal $CD$. Hence the change in internal energy in the process $M\rightarrow N$ is

$$U_N-U_M=\Delta Q-\Delta W=C_P\,\Delta T-P\,\Delta V \qquad \ldots(2)$$

because in this case $\Delta Q=C_P\,\Delta T$ and work performed by the gas $\Delta W=P\,.\,\Delta V$

Since the gas is supposed to be a perfect one, the perfect gas equation $(PV=RT)$ holds good. In the initial position at $M$, the pressure, volume and temperature of the gas were respectively $P$, $V$ and $T$ while at $N$ volume becomes $(V+\Delta V)$ and temperature $(T+\Delta T)$. Hence according to gas equation at $M$ and $N$ respectively we have

$$PV=RT \qquad \ldots(3)$$

and

$$P\,(V+\Delta V)=R\,(T+\Delta V) \qquad \ldots(4)$$

Subtracting eq. (3) from (4), we have

$$P\,\Delta V=R.\,\Delta T$$

Putting this value of $P\,.\,\Delta V$ in eqn. (2), we get

$$U_N-U_M=C_P\,.\,\Delta T-R\,.\,\Delta T \qquad \ldots(5)$$

As the *internal energy of a perfect gas depends only upon its temperature*, the same change in internal energy will take place in both the processes $M\rightarrow L$ and $M\rightarrow N$ because temperature changes from $T$ to $T+\Delta T$ in both the processes. Thus

$$U_L-U_M=U_N-U_M$$

or

$$C_V\,\Delta T=C_P\,\Delta T-R\,.\,\Delta T \qquad \text{[using eqn. (1) and (5)]}$$

or : Dividing throughout by $\Delta T$, we have

$$C_V = C_P - R$$

or $$C_P - C_V = R \qquad \text{...(6)}$$

This formula is known as *Mayer's* formula. All the three quantities $C_P$, $C_V$ and $R$ in this equation should be expressed in the same units either in Joule/mole°C or in cal./mole°C.

## 1.11. External Work Done By an Ideal Gas in Isothermal Expansion

Any process in which the temperature remains constant is called an 'isothermal process'. When an ideal gas expands isothermally, work is done *by* the gas against the external surroundings* and an equivalent amount of heat flows from outside into the gas. Similarly, when the gas is compressed isothermally, work is done *on* the gas and an equivalent amount of heat flow out from the gas.

Let us consider 1 mole of an ideal gas at a temperature $T$ (kelvin). If it expands from an initial volume $V_i$ to a final volume $V_f$ at constant temperature, the external work done by it can be represented as

$$W = \int_{V_i}^{V_f} p\, dV,$$

where $p$ is the instantaneous pressure of the gas while suffering an infinitesimal expansion $dV$.

Since the expansion is isothermal (at a constant temperature $T$), it will be governed by the Boyle's law. Thus

$pV = K$, where $K$ is a constant.

$$\therefore \quad W = \int_{V_i}^{V_f} p\, dV = \int_{V_i}^{V_f} (K/V)\, dV$$

$$= K\Big[\log_e V\Big]_{V_i}^{V_f} = K \log_e (V_f/V_i).$$

But $p_iV_i = p_fV_f = K$.

$$\therefore \quad W = p_iV_i \log_e (V_f/V_i) = p_f V_f \log_e (V_f/V_i).$$

For 1 mole the equation of state of the gas is

$$p_iV_i = p_fV_f = RT.$$

$$\therefore \quad W = RT \log_e (V_f/V_i) = 2{\cdot}3026\, RT \log_{10} (V_f/V_i).$$

For $n$ moles of an ideal gas, the work done is

$$\mathbf{W = n\, RT \log_e (V_f/V_i).} \qquad \text{...(i)}$$

As the gas expands, $V_f > V_i$ *i.e.* $V_f/V_i > 1$ (whose logarithm is positive) and work done is positive. This means that work is done *by* the gas. If, however, the gas is compressed, $V_f/V_i < 1$ (whose logarithm is negative), the work done is negative, *i.e.* work is done *on* the gas.

## 1.12 External Work Done By An Ideal Gas In Adiabatic Expansion

Let us consider one mole of an ideal gas. If it expands adiabatically from an initial volume $V_i$ to a final volume $V_f$, the external work done by it can be represented as

$$W = \int_{V_i}^{V_f} p\, dV,$$

---

*Since the gas is *ideal*, its molecules do *not* attract each other, hence no *internal* work is done during expansion.

where $p$ is the instantaneous pressure of the gas while suffering an infinitesimal expansion $dV$.

Since the expansion is adiabatic, it will be governed by the Poisson's law. Thus

$$pV^{\gamma} = K \text{ (a constant).}$$

$$\therefore \quad W = \int_{V_i}^{V_f} p\, dV = \int_{V_i}^{V_f} KV^{-\gamma} dV = \frac{K}{1-\gamma}\Big[V^{1-\gamma}\Big]_{V_i}^{V_f}$$

$$= \frac{K}{1-\gamma}\Big[V_f^{1-\gamma} - V_i^{1-\gamma}\Big] = \frac{1}{\gamma-1}\left[\frac{K}{V_i^{\gamma-1}} - \frac{K}{V_f^{\gamma-1}}\right].$$

But $p_iV_i^{\gamma} = p_f V_f^{\gamma} = K$.

$$\therefore \quad W = \frac{1}{\gamma-1}\left[\frac{p_i V_i^{\gamma}}{V_i^{\gamma-1}} - \frac{p_f V_f^{\gamma}}{V_f^{\gamma-1}}\right]$$

or $$W = \frac{1}{\gamma-1}(p_iV_i - p_fV_f).$$

For $n$ moles of the gas, the work is

or $$\boxed{\mathbf{W = \frac{n}{\gamma-1}(p_iV_i - p_fV_f).}} \qquad \text{...(ii)}$$

Let $T_i$ and $T_f$ be the temperatures of the gas before and after the expansion respectively. Then for $n$ moles of gas

$$p_iV_i = nRT_i \quad \text{and} \quad p_fV_f = nRT_f.$$

$$\therefore \quad \boxed{\mathbf{W = \frac{nR}{\gamma-1}(T_i - T_f).}} \qquad \text{...(iii)}$$

This equation shows that the work done depends only upon the initial and final temperatures $T_i$ and $T_f$. That is, ***the work done along an adiabatic between two given isothermals is independent of the particular adiabatic.***

If work is done *by* the gas (adiabatic expansion) *i.e.* $W$ is positive then $T_f < T_i$ *i.e.* the gas is cooled. If work is done *on* the gas, the gas is heated up.

Since $R = C_p - C_V$ and $\gamma = C_p/C_V$, the above expression may alternatively be written as

$$W = \frac{n\,(C_p - C_V)}{(C_p/C_V) - 1}(T_i - T_f)$$

or $$\boxed{\mathbf{W = n\, C_V (T_i - T_f).}} \qquad \text{...(iv)}$$

Again, for adiabatic expansion, we have

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

or $$T_f = T_i (V_i/V_f)^{\gamma-1}.$$

Substituting this value of $T_f$ in eq. (iii), we have

$$\boxed{\mathbf{W = \frac{n R T_i}{\gamma-1}\left[1 - \left(\frac{V_i}{V_f}\right)^{\gamma-1}\right].}} \qquad \text{...(v)}$$

## SOLVED EXAMPLES

**Ex. 1.** *One mole of an ideal gas is heated from 273 K to 546 K at a constant pressure of* $1{\cdot}013 \times 10^5$ *newton/*$\text{metre}^2$*. Calculate the work done by the gas. One mole of gas at N.T.P. has a volume of* $22{\cdot}4 \times 10^{-3}\ \text{metre}^3$.

**Solution.** The gas is heated at 'constant' pressure. Initial volume of the gas is $V_i = 22{\cdot}4 \times 10^{-3}\ \text{metre}^3$, initial temp. $T_i = 273$ K, final temp $T_f = 546$ K, $V_f = ?$ By Charle's law, $V/T =$ constant, so that

$$\frac{V_f}{V_i} = \frac{T_f}{T_i}$$

or $\quad V_f = V_i \times (T_f/T_i) = 22{\cdot}4 \times 10^{-3} \times (546/273) = 44{\cdot}8 \times 10^{-3}\ \text{metre}^3.$

The work done is

$$\begin{aligned} W &= p\,(V_f - V_i) \\ &= (1{\cdot}013 \times 10^5\ \text{N/m}^2)(44{\cdot}8 - 22{\cdot}4) \times 10^{-3}\ \text{m}^3 \\ &= 1{\cdot}013 \times 22{\cdot}4 \times 10^2\ \text{N-m} \\ &= \mathbf{2{\cdot}27 \times 10^3\ joule.} \end{aligned}$$

The balance (219–62) = 157 cal is used to increase the temperature *i.e.* internal energy of the gas.

**Ex. 2.** *A quantity of an ideal gas at 17°C is adiabatically (suddenly) compressed to one-tenth its initial volume. Calculate the final temperature if the gas is (i) monatomic, (ii) diatomic.*

**Solution.** (i) For a monatomic gas, $\gamma = 5/3 = 1{\cdot}67$ (It must be remembered).

The relation between the temperature (kelvin) and volume of an ideal gas undergoing an adiabatic change is—

$T\,V^{\gamma-1} =$ constant.

Therefore, if $T_i$, $V_i$ be the initial and $T_f$, $V_f$ the final temperature and volume respectively, we have

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

or
$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{\gamma-1}.$$

Here, $T_i = (17 + 273) = 290\ \text{K}, \dfrac{V_i}{V_f} = 10, \gamma = 1{\cdot}67, T_f = ?$

$$\therefore \quad \frac{T_f}{290} = (10)^{1{\cdot}67-1} = (10)^{0{\cdot}67}$$

or
$$\begin{aligned} \log T_f &= \log 290 + 0{\cdot}67 \log 10 \\ &= 2{\cdot}4624 + 0{\cdot}67 = 3{\cdot}1324. \end{aligned}$$

$$\therefore \mathbf{T_f = 1356\ K = 1083°C.}$$

(ii) For a diatomic gas, $\gamma = 1{\cdot}40$.

$$\therefore \quad \frac{T_f}{290} = (10)^{1{\cdot}40-1} = (10)^{0{\cdot}40}$$

or
$$\log T_f = \log 290 + 0{\cdot}40 \log 10 = 2{\cdot}4624 + 0{\cdot}40 = 2{\cdot}8624.$$

$$\therefore \mathbf{T_f = 728{\cdot}5\ K = 455{\cdot}5°C.}$$

### 1.13 Heat Engine and Efficiency

*Any device which converts heat continuously into mechanical work is called a heat engine.* This idea of conversion of heat into work has come from very early times when it was observed that bodies when heated develop power. Thus for instance, when water is boiled in a vessel closed by a lid, the steam generated inside throws off the lid, showing thereby that high pressure steam can be made to do work. Similarly the gun powder and other explosives do work in breaking rocks etc. Likewise, the high velocity winds, caused by the heating of parts of earth's surface by the sun, do work in driving wind mills and in propelling ships with the aid of sail etc.

All these simple and elementary facts indicate that transference of heat to a body results in mechanical work and have developed in due course of time to provide us respectively several types of modern heat engines—*the steam engine, internal combustion engines and gas turbines.* We shall now discuss their essential thermodynamics.

For any heat engine there are three essential requirements :

(i) *SOURCE :* A hot body, at a fixed high temperature $T_1$ from which the heat can be drawn heat, is called source or hot reservoir.

(ii) *SINK :* A cold body at a fixed lower temperature $T_2$, to which any amount of heat can be rejected, is called sink or cold reservoir.

(iii) *WORKING SUBSTANCE :* The material, which on being supplied with heat, performs mechanical work is called the working substance.

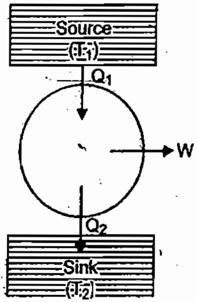
Thus in a heat engine, the working substance takes in heat from the source, converts a part of it into external work, gives out the rest to the sink and returns to its initial state. This series of operations constitute *a cycle.* This has been shown in fig. (1·6). The work can be continuously obtained by performing the same cycle over and over again.

Let $Q_1$ be the amount of heat absorbed by the working substance, $Q_2$ that rejected by it to the sink and $W$ the net amount of work done by it. The net amount of heat absorbed by the substance is then $Q_1 - Q_2$. Remembering that the working substance returns to its initial condition, the change in internal energy $dU$ is zero, we have by the application of first law of thermodynamics.

$$Q_1 - Q_2 = W. \qquad \text{...(1)}$$

*The thermal efficiency* of the engine $\eta$ is defined as the ratio of the net work obtained in the cycle (output) to the heat absorbed by the working substance from the source (input), *i.e.*

$$\begin{aligned} \eta &= \frac{\text{Work output in any energy unit}}{\text{Heat input in the same energy unit}} \\ &= \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} \qquad \text{[using eq. (1)]} \\ \eta &= 1 - \frac{Q_2}{Q_1}. \qquad \text{...(2)} \end{aligned}$$



(Fig. 1.6)

It is clear from this equation that $\eta$ will be unity (efficiency 100%) if $Q_2$ is zero i.e. heat rejected to sink in a cycle is zero.

## 1.14 Reversible and Irreversible Processes

A reversible process is one which can be retraced in opposite order by slightly changing the external conditions. the working substance in the reverse process passes through all the stages as in the direct process in such a way that all changes occuring in the direct process are exactly repeated in the opposite order and inverse sense and no changes are left in any of the bodies participating in the process or in the surroundings. If heat is absorbed by the substance in the direct process, the same quantity will be given out by it in the reverse process, and if work is done by the substance in the direct porocess, an equal amount of work will be done on the substance in the reverse process. Thus there is no wastage of energy at all in the reversible process.

As an *example of a reversible process* consider a gas enclosed in a cylinder, made of a perfectly conducting material and immersed in a large tank of water at a constant temperature. Let the gas be compressed very slowly such that its temperatue remains unchanged throughout. Obviously to do so small pauses will have to be given in between various small compressions to enable the heat generated by compression to pass out into the surrounding water. If now after reducing considerably the volume of the gas, it is allowed to expand isothermally and the expansion be just as infinitely small as compressions with similar pauses in between, heat will flow in from the enclosing water to compensate for the loss during expansion and will keep the temperature of the gas unchanged. Exaclty the same amount of heat will be reveived during the expansion as will be given up during compression. Thus all stages of the process are retraced in the opposite direction and inverse order and hence the slow isothermal expansion and compression of a gas is reversible process. Infact ***all isothermal and adiabatic operations are reversible when carried out very slowly.*** Similarly an extremely slow contraction or extension of a spring is also reversible if the work done by the spring in each step of infinitesimal contraction is exactly equal to that done on the spring in each corresponding step during extension.

Those processes which can not be retraced in the opposite order by reversing the controlling factors are known as *irreversible processes.*

An *example of irreversible process* is the conduction of heat from a hot body to colder one. Production of heat by friction or by the passage of current through an electrical resistance are also irreversible processes, because heat will again be produced (and not absorbed) if the direction of motion or the direction of flow of current are reversed. Rapid isothermal and adiabatic changes are irreversible.

### Conditions of reversibility

(i) The substance undergoing a reversible change must not lose heat be conduction, convection or radiation or in overcoming friction. No heat must at all be converted into magnetic or electrical energy. Hence for reversibility complete absence of dissipative effects such as friction, electrical resistance, magnetic hysteresis etc. is a must.

(ii) The change in the pressure and volume of the working substance must take place at an infinitely slow rate ; so that when the substance is receiving heat its temperature differs from the hotter body only an infinitesimal amount and when it is losing heat the temperature again differs by an infinitesimal amount from the colder body. Thus all reversible processes must take place infinitely slowly.

These conditions are never strictly realized in practice because no mechanical process is frictionless and no insulator or conductor is perfect. ***Thus rigorous reversibility is an ideal conception while irreversibility is the rule.*** However, the conditions necessary for reversibility can be fulfilled approximately and such processes may be regarded as reversible within the limits of experimental errors.

## 1.15 Carnot's Engine and Carnot's Cycle

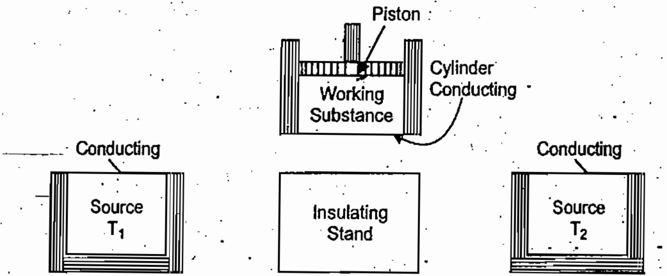
A heat engine is a practical arrangement to convert heat into mechanical work. Sadi Carnot conceived an ideal theoretical engine free from all the imperfectness of actual engines and hence never realized in actual practice. His imaginary engine is, however, taken as a standard agaisnt which the performance of actual engines is judged.

The plan of Carnot's ideal engine is shown in fig. (1.7). It consists of :

(i) **Source :** A hot body of infinitely large heat capacity maintained at a constant high temperature $T_1$ absolute serving as the 'source' of heat.

(ii) **Sink :** A cold body of infinitely large heat capacity maintained at a constant low temperature $T_2$ absolute serving as the 'sink'.

(iii) **Working Substance :** A perfect gas (or air), enclosed in a cylinder with perfectly non-conducting walls but perfectly conducting base, as the 'working substance' and fitted with a perfectly insulating and frictionless piston upon which weights can be placed.

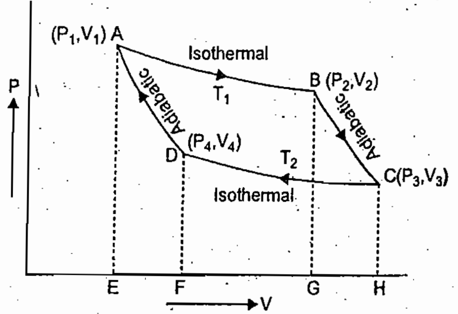


(Fig. 1.7)

(iv) A perfectly insulating platform serving as a 'stand' for the cylinder.

The cylinder may be placed on any of the three bodies (i), (ii) and (iv) and may be moved from one to the other without friction, *i.e.*, without doing any work.

The working substance is subjected to a cycle of four operations, consisting of two isothermal operations and two adiabatic operations. Such a cycle is known as Carnot's cycle and is represented on the $P—V$ indicator diagram of fig. 1.8.



(Fig. 1.7)

Let us now consider the four operations of the Carnot's cycle. Let the cylinder contain one gm. mol. of the working substance and the original condition of the substance be represented by point $A$ on the indicator diagram, where it has temperture $T_1$, pressure $P_1$ and volume $V_1$.

**Operations 1.** The cylinder is placed on the source and the load (pressure) on the piston is slowly decreased. The working substance thus expands doing external work in raising the piston. This would make the substance fall in temperature, but as it is in contact with the source, it takes in necessary heat by conduction through the base to expand isothermally at the constant temperature $T_1$ of the source. This operation is represented by the isothermal curve $AB$ on the indicator diagram. Let the quantity of heat absorbed in this process be $Q_1$. Then, in accordance with the first law of thermodynamics, $Q_1$ must be equal to the external work done by the gas in expanding isothermally from $A$ to $B$ at temperature $T_1$ (as internal energy remains unchanged). Hence

$$Q_1 = W_1 = RT_1 \log_e \frac{V_2}{V_1} \qquad \ldots(1)$$

**Operation 2.** The cylinder is removed from the source, put on the perfectly non-conducting stand and by further decreasing the load on the piston, the substance is allowed to expand. This expansion is completely adiabatic because no heat can enter or leave the substance through the insulating cylinder. The substance performs external work in raising the piston at the expense of its internal energy and its temperature therefore falls. The gas is thus allowed to expand adiabatically until its temperature falls to $T_2$ the temperature of the sink. It has been represented by the adiabatic curve $BC$ on the indicator diagram. If $P_3$, $V_3$ be the pressure and volume of the substance at $C$, then work done by substance from $B$ to $C$ (adiabatic process).

$$W_2 = \frac{R\,(T_1 - T_2)}{\gamma - 1} \qquad \ldots(2)$$

**Operation 3.** The cylinder is removed from the non-conducting stand and placed on the sink at temperature $T_2$. The load on the piston is slowly increased so that the gas compressed until its pressure and volume become $P_4$, $V_4$ represented by the point $D$. The heat developed due to compression immediately passes into the sink through the conducting base and the temperature of the working substance remains constant at $T_2$, the temperature of the sink which remains unchanged due to its infinite heat capacity. This compression is represented by the isothermal $CD$ on the indicator diagram. The quantity of heat $Q_2$ rejected to the sink during this process is equal the work done $W_3$ on the working substance is compressing it isothermally from $C$ to $D$. Hence,

$$Q_2 = W_3 = RT_2 \log_e \frac{V_4}{V_3} = -RT_2 \log_e \frac{V_3}{V_4} \qquad \ldots(3)$$

**Operation 4.** The cylinder is again transferred to the insulating stand and the load on the piston is again slightly increased so that the substance undergoes a slow adiabatic compression and its temperature rises. This compression is continued until the temperature rises to $T_1$ and the substance comes back to its original pressure $P_1$ and volume $V_1$. Thus the internal energy of the substance is the same as at the beginning of the process. This compression is represented by the adiabatic $DA$ on the indicator diagram. The work done on the substance during this adiabatic compression from $D$ to $A$ is

$$W_4 = -\frac{R\,(T_1 - T_2)}{\gamma - 1} \qquad \ldots(4)$$

**Expression for efficiency :**

*Work Done by the Engine per Cycle* : During the above cycle of operations, the working substance takes in an amount of heat $Q_1$ from the source and rejects $Q_2$ to the sink.

At the same time, the net work done by the engine in one complete cycle

$$W = W_1 + W_2 + W_3 + W_4$$

$$= RT_1 \log_e \frac{V_2}{V_1} + \frac{R\,(T_1 - T_2)}{\gamma - 1} - RT_2 \log_e \frac{V_3}{V_4} - \frac{R\,(T_1 - T_2)}{\gamma - 1}$$

or

$$W = RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_3}{V_4} \qquad \ldots(5)$$

Now, since points $A$ and $D$ lie on the same adiabatic $DA$

$$T_1 V_1^{\gamma - 1} = T_2 V_4^{\gamma - 1}$$

or

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma - 1} \qquad \ldots(6)$$

Similarly the points $B$ and $C$ also lie on the same adiabatic $BC$.

Hence

$$T_1 V_2^{\gamma - 1} = T_2 V_3^{\gamma - 1}$$

or

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma - 1} \qquad \ldots(7)$$

Comparing equations (6) and (7)

$$\left(\frac{V_1}{V_4}\right)^{\gamma - 1} = \left(\frac{V_2}{V_3}\right)^{\gamma - 1}$$

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}, \quad i.e. \quad \frac{V_2}{V_1} = \frac{V_3}{V_4} \qquad \ldots(8)$$

Subsituting it in equation (5)

$$W = RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_2}{V_1}$$

$$= R\,[T_1 - T_2] \log_e \left(\frac{V_2}{V_1}\right) \qquad \ldots(9)$$

The efficiency of the engine is given by

$$\eta = \frac{\text{Heat converted into work}}{\text{Heat taken in from the source}} = \frac{W}{Q_1}$$

$$= \frac{R\,[T_1 - T_2] \log_e \left(\frac{V_2}{V_1}\right)}{RT_1 \log_e \left(\frac{V_2}{V_1}\right)} \qquad \text{[using (9) and (1)]}$$

or

$$= \frac{T_1 - T_2}{T_1} \quad i.e. \quad \eta = 1 - \frac{T_2}{T_1} \qquad \ldots(10)$$

The expression shows that efficiency of the engine depends upon the temperature $T_1$ and $T_2$ of the source and sink respectively and greater the difference between $T_1$ and $T_2$, the greater is the efficiency. Since however, $T_2 < T_1$ the *efficiency is always less than* 1 *or* 100%.

The efficiency may also be expressed in terms of adiabatic expansion ratio ρ. From equation (8)

$$\frac{V_3}{V_2}=\frac{V_4}{V_1}$$

Each one of these ratio is the adiabatic expansion ratio ρ and hence

$$\frac{V_2}{V_3}=\frac{V_1}{V_4}=\frac{1}{\rho}$$

Substituting it in equation (6) or (7)

$$\frac{T_2}{T_1}=\left(\frac{1}{\rho}\right)^{\gamma-1}$$

And, therefore, *efficiency*

$$\eta=1-\left(\frac{1}{\rho}\right)^{\gamma-1} \qquad ...(11)$$

### Practical impossiblility of Carnot reversible cycle

Remembering the conditions of reversibility we can say that a reversible engine can be realized if (i) the various parts of the engine are free from friction, (ii) pressure and temperature of the working substance never differ sensibly from its surroundings, and (iii) all the processes involved in the cycle are described infinitely slowly.

Applying the conditions of reversibility to Carnot's ideal engine, it is seen that it is reversible in the truest sense of the term. This is so because :

(i) The disssipative effects like friction or conduction of heat etc. are all made completely absent by using a perfactly insulting frictionless piston and a cylinder with perfectly insulating walls.

(ii) The working substance differs in temperature with the hot or cold body only by an infinitesimal amount owing to the perfectly conducting base of the cylidner and hence remains in almost thermal equilibrium with it throughout the cycle.

(iii) The changes of pressure at which the working substance is subjected are infinitely small and therefore all the operations performed on its are extremely slow and hence the processes are reversible.

With such an arrangement, the Carnot's cycle is perfectly reversible and can be exactly traversed in the reverse order, (*i.e., ADCBA*). In this case, the working substance will extract heat $Q_2$ from the sink at $T_2$, some amount of work will be done on it by an external agency and give out $Q_1$ heat to the source at $T_1$. The engine thus acts as a refrigerator, *i.e.* by doing work on it; it is made to transfer heat from a body at a lower temperature to a body at a high temperature.

(iv) In a carnot engine all the heat is absorbed at a constant temperature (of the source) and whatever heat is to be rejected is rejected at another constant lower temperature (of the sink) and thus it utilizes the full temperature difference where the heat continues to be absorbed throughout the rise of temperature.

*The features of Carnot's engines cannot be realized in actual practice* and hence the Carnot's reversible engine is not only an ideal but is of extremely immense theoretical importance and can serve as a standard to judge the performance of actual heat engines.

## 1.16 Two Carnot Engines Operating in Series

Let us consider two Carnot engines operating is series. Let the first engine absorb an amount of heat $Q_1$ at a temperature $T_1$ and after peforming work $W_1$ reject the remaining heat $Q_2$ at a lower temperature $T_2$. If the second engine absorbs the heat $Q_2$ rejected by the first and after performing work $W_2$, rejects the remaining heat $Q_3$ at a still lower temperature $T_3$, then the total work done by the combination in one cycle is $W_1 + W_2 = (Q_1 - Q_2)$

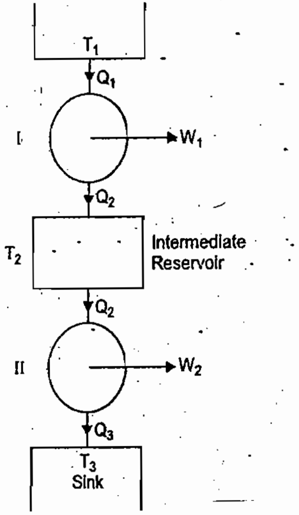
$$= (Q_2 - Q_3) = Q_1 - Q_3.$$

Since the heat absorbed by the combination is $Q_1$, therefore, the efficiency of the combination

$$\eta=\frac{\text{Total work done}}{\text{Heat taken in}}=\frac{Q_1-Q_3}{Q_1}$$

$$=1-\frac{Q_3}{Q_1}=1-\frac{T_3}{T_1} \qquad \left(\because \frac{Q_3}{Q_1}=\frac{T_3}{T_1}\right)$$

This expression is the same as the efficiency of a single engine operating between the temperatures $T_1$ and $T_3$.



(Fig. 1.9) Carnot engines in series

## 1.17 Second Law of Thermodynamics

The first law of thermodynamics states the equivalence of heat and energy. It simply tells that whenever work is obtained, an equivalent amount of heat is used up or vice versa. It does not say anything either about the limitation in the conversion of heat into work or about the condition necessary for such a conversion. Thus for example, the first law does not tell us, whether water can flow against gravity of itself. It has no answer to the query, can a metallic rod at one uniform temperature become warmer at one end and cooler at the other of itself. In its reply it can only say that if this process occurred the heat energy lost by one end will be exactly equal to that gained by the other end. The first law can account for the stopping of a revolving wheel as being due to conversion of its kinetic energy into heat produced in overcoming the friction at the bearing; the heat produced cannot be converted into kinetic energy of wheel making it to revolve once again.

It was the quest for replies of several such questions which led to the formulation of second law of thermodynamics. This law is a generalization of certain experiences and observations and is concerned with the direction in which energy transfers take place. The law has been stated in a number of ways, but all the statements, though differently worded, are logically equivalent to one another. Two of them are :

**Kelvin-Planck statement of the second law :** This may be stated as :

*"It is impossible to construct a device which operating in a cycle, has the sole effect of extracting heat from a reservoir and performing an equivalent amount of work".*

According to this statement, a single reservoir at a single temperature can not continuously transfer heat into work. It is a negative statement and may be treated as the denial of what is known as a perpetual motion machine (working forever) of the second kind. As an example, it is impossible to drive a steamship across the ocean by extracting heat from the oceal or to run a power plant by extracting heat from the surrounding air. Both the ocean and the surrounding air contain an enormous store of internal energy which, in principle, may be extracted in the form of a flow of heat. In doing so we will not violate the first law, because we do not plan to get work out of nothing, we are only planning to get motion from a single reservoir. The operation of a machine that utilizes the internal energy of a single heat reservoir, is called perpetual motion of the second kind. The impossibility of such a device is an essence of the second law of thermodynamics. **Ostwald** put the second law, in the form. ***"Perpetual motion machine of the second kind is impossible."***

**Clausius statement of the second law** : This statement is based upon the performance of refrigerator—a heat engine working in the backward direction. In a refrigerator the working substance takes in heat from a cold body, a certain amount of work is done on it by some outside agency and rejects a larger amount of heat to a hotter body. Thus a refrigerator transfers heat from a cold body to a hot body with the aid of an outside agency. No refrigerator has every been constructed which can do this work without the supply of energy from an external agency. Considerations such as this led Clausius to state the second law in the form :

*"It is impossible for a self-acting machine working in a cyclic process, unaided by any external agency to transfer heat from a body at a lower temperature to a body at a higher temperature."*

In other words it may be stated as *"Heat cannot flow itself from a colder to a hotter body."*

These both are the enunciations of the second law of thermodynamics and apply to reversible cyclic processes only. At first sight, these statements appear to be quite unconnected but we shall see that they are in all respects equivalent. To show this, suppose a refrigerator transfers an amount of heat $Q_2$ from a colder to a warmer body without having any work done on it by some outside agency, thus violating the Clausius statement of the second law. Let us now suppose another heat engine also working between the same, hot and cold bodies, extracting heat $Q_1$ from hot body and giving back heat $Q_2$ to the cold body. This engine alone does not violate any law, but if the refrigerator and engine are coupled together, the net result is that the cold body is giving out amount of heat $Q_2$ and receiving back the same amount and thus there is no change in its heat contents. On the other hand, the hot body receives a heat $Q_2$ while gives out heat $Q_1$ and thus in each cycle it loses an amount of heat $Q_1 - Q_2$ which is completely converted into work without delivering any to the cold body. This system thus violates the Kelvin-Planck's statement of the second law.

In a similar way we can show that a violation of the Kelvin Planck's statement leads to a violation of Clausius statement. Let us think of an engine which extracts an amount of heat $Q_1$ from a hot body and converts all into work without rejecting any to the cold body thus violating the Kelvin Planck statement. Now suppose that a refrigerator also works between the same hot and cold bodies while it extracts an amount of heat $Q_2$ from the cold body and let an amount of work $W = Q_1$ be done upon it so that finally it delivers an amount $(Q_1 + Q_2)$ of heat to the hot body. If the engine and refrigerator are coupled together to work simultaneously, they will consitute a self acting machine, drawing a heat $Q_2$ from the cold body and transferring it to the hot body. Such a system violates the Clausius statement of second law.

Thus, we see that the violation of the conditions imposed by the Kelvin-Planck's statement also means a violation of the Clausius statement and vice versa. Hence *both the enumerations of the law are completely equivalent to each other.* No direct proof of the law can, however, be given; but the main evidence for its truth is that it has never been possible to construct a machine working against this law.

## 1.18 Carnot's Theorem

*It states no engine working between two given temperatures can be more efficient than a reversible (Carnot) engine working between the same limits of temperatures (i.e., between same source and sink).*

In order to prove the theorem, let us consider two engines $I$ and $R$ working between the same source and sink. Let $I$ be irreversible and $R$ reversible. Let the quantities of working substance in the two engines be so adjusted that the work performed by them per cycle is the same. Let the irreversible engine $I$ absorb an amount of heat $Q_1$ from the source at a temperature $T_1$, perform an external work $W$ and rejects heat $(Q_1 - W)$ to the sink at temperature $T_2$. Its efficiency $\eta_I$ is then equal to $W/Q_1$. Similarly if the reversible engine $R$ absorbs heat $Q_1'$ from the source does an external work $W$ and rejects heat $(Q_1' - W)$ to the sink, then its efficiency $\eta_R$ is equal to $W/Q_1'$.

Suppose that irreversible engine $I$ is more efficient than reversible engine $R$, *i.e.*,

$$\eta_I > \eta_R$$

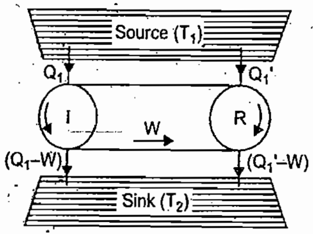
or

$$\frac{W}{Q_1} > \frac{W}{Q_1'}$$

$$Q_1' > Q_1.$$

Thus $(Q_1' - Q_1)$ is a positive quantity.

Now suppose that the two engines $I$ and $R$ are coupled together by a belt in such a way that as engine $I$ works directly *i.e.*, forward, it drives engine $R$ backward, as shown in fig. 1.10 Engine $R$ now works as a refrigerator driven by $I$, extracts heat $(Q_1')$ from the sink at temperature $T_2$ requires work $W$ to be done upon it and gives out heat $Q_1$ to the source at temperature $T_1$. The work required to be done on $R$ is directly supplied by $I$, working directly and in this way the engine $I$ and refrigerator $R$ coupled together form a self-acting device.



(Fig. 1.10)

The source now loses $Q_1$ heat to $I$ and gains $Q_1'$ from $R$

$\therefore$ Heat gained by the source $= Q_1' - Q_1$.

The sink gains $(Q_1 - W)$ heat from $I$ and loses $(Q_1' - W)$ to $R$

$\therefore$ Heat lost by the sink $= (Q_1' - W) - (Q_1 - W)$

$= Q_1' - Q_1$

Which is a positive quantity (*since* $Q_1' > Q_1$).

Thus the coupled device is transferring in each cycle an amount of heat $Q_1' - Q_1$ from the sink at a temperature $T_2$ (lower temperature) to a source at temperature $T_1$ (higher temperature) without the aid of any external energy. This transference of heat from a lower to a higher temperature without any expenditure of work is contrary to the second law of thermodynamics and hence impossible. It follows therefore, that our original assumption that the irreversible engine is more efficient than the reversible one is wrong. Hence *no engine working between a given source and sink can be more efficient than a reversible engine working between the same source and sink; or in other words a reversible (Carnot) engine operating between a given source and sink has maximum efficiency.*

## SOLVED EXAMPLES

**Ex. 3.** *Defend or refute the following statement :*

*From a theoritical viewpoint it is claimed that with temperature of surroundings 300K, 12000 k. cal heat available from a reservoir at 900K, is more useful than 15000 k. cal. of heat available at 600K.*

**Solution.** For the first case $\eta_1 = 1 - \frac{300}{900} = \frac{2}{3}$

Similarly, for second case $\eta_2 = 1 - \frac{300}{600} = \frac{1}{2}$.

Now, efficiency $\eta_1 = \frac{\text{Work output}}{\text{Heat input}}$

∴ $\eta_1 = \frac{2}{3} = \frac{W_1}{12000}$

or $W_1 = 8000$ k. cals.

Similarly $\eta_2 = \frac{1}{2} = \frac{W}{15000}$

or $W_2 = 7500$ k. cals.

It is clear that $W_1 > W_2$.

Hence 12000 k. cal. of heat available at 900 K is more useful than 15000 k. cal. of heat available at 600 K. Thus the **statement is to be defended.**

**Ex. 4.** *A Carnot engine whose low temperature reservoir is at 7°C has an efficiency 50%. It is desired to increase the efficiency to 70%. By how many degrees should the temperature of the high temperature reservoir be increased ?*

**Solution.** For this we shall first calculate the temperature of high temperature reservoir

$$\eta = 50\% = 0.5, \quad T_2 = 7°\text{C} = 280\text{ K}, \; T_1 = ?$$

$$\eta = 1 - \frac{T_2}{T_1}$$

∴ $$0.5 = 1 - \frac{280}{T_1}$$

or $$\mathbf{T_1 = 560\text{ K}}$$

$$\eta = 70\% = 0.7, \; T_2 = 280\text{ K}, \; T_1' = ?$$

∴ $$0.7 = 1 - \frac{280}{T_1'}$$

or $$\mathbf{T_1' = 933.3\text{ K}}$$

Hence required increase in temperature of high temperature reservoir

$$= 933.3 - 560 = \mathbf{373.3\text{ K}}.$$

**Ex. 5.** *Two Carnot engines A and B are operated in series. The first one A, receives heat 900 K and rejects to a reservoir at temperature TK. The second engine B receives the heat rejected by the first engine and in turn rejects to a heat reservoir at 400 K. Calculate the temperature T for the situation when :*

*(i) the work outputs of the two engines are equal.*

*(ii) the efficiencies of the two engines are equal.*

**Solution.** The effieicny of a Carnot's engine is given by

---

$$\eta = \frac{\text{Work output}}{\text{Heat Input}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

or, On the Kelvin's temperature scale,

$$\eta = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}$$

Now, for engine $A$ ; $\eta_1 = \frac{W}{Q_1} = \frac{900 - T}{900}$.

And for engine $B$, $\eta_2 = \frac{W'}{Q_1'} = \frac{T - 400}{T}$.

(i) When work outputs of the two engines are equal *i.e.*,

$$W = W'$$

$$\frac{900 - T}{900} Q_1 = \frac{T - 400}{T} Q_1'$$

or $$\frac{900 - T}{900} = \frac{T - 400}{T} \frac{Q_1'}{Q_1}$$

But $$\frac{Q_1'}{Q_1} = \frac{T}{900} \quad \text{(from property of Carnot's cycle)}$$

or ∴ $$900 - T = T - 400$$

or $$2T = 1300$$

or $$\mathbf{T = 650\text{ K}.}$$

(ii) When efficiencies of the two engines are equal *i.e.*,

$$\eta_1 = \eta_2$$

or $$\frac{900 - T}{900} = \frac{T - 400}{T}$$

or $$900\,T - T^2 = 900\,T - 360000$$

or $$T^2 = 360000$$

or $$\mathbf{T = 600\text{ K}.}$$

**Ex. 6.** *Two Carnot engines A and B are operated in series. First engine A absorbs heat at 1100K and rejects it to the sink at TK. Second engine B absorbs half amount of heat rejected by first engine and rejects heat to the sink at 200 K. if the work performed by both the engines are equal, calculate the temperature T.*

**Solution.** Let the two engines be operating as shown in diagram 1.11 Let the temperatures and heat absorbed and rejected be as indicated therein. Then the efficiencies of two engines are

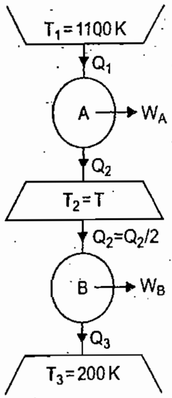
$$\eta_A = 1 - \frac{T}{T_1} = 1 - \frac{Q_2}{Q_1} \qquad \text{...(1)}$$

$$\eta_B = 1 - \frac{T_3}{T} = 1 - \frac{Q_3}{Q_2/2} \qquad \text{...(2)}$$

Since the works performed by two engines are equal *i.e.*,

$$W_A = W_B$$

Hence $$Q_1 - Q_2 = \frac{Q_2}{2} - Q_3$$



**(Fig. 1.11)**

or $$Q_1 - \frac{3}{2} Q_2 + Q_3 = 0$$

or $$1 - \frac{3}{2}\frac{Q_2}{Q_1} + \frac{Q_3}{Q_1} = 0$$

or $$1 - \frac{3}{2}\frac{Q_2}{Q_1} + \frac{Q_3}{Q_2}\cdot\frac{Q_2}{Q_1} = 0$$

or $$1 - \frac{3}{2}\frac{T}{T_1} + \frac{T_3}{2T}\cdot\frac{T}{T_1} = 0. \qquad \text{[Using equs. (1) and (2)]}$$

or $$1 - \frac{3}{2}\cdot\frac{T}{1100} + \frac{200}{2 \times 1100} = 0$$

or $$3T = 2400$$

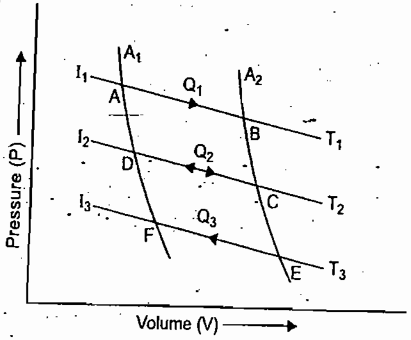
or $$T = 800 \text{ K}$$

## 1.19 Entropy

The concept of entropy (literal meaning 'transformation') was first introduced by Clausius in 1854 while working on the formulation and application of the second law of thermodynamics.

***Physically entropy of a system is a measure of disorder of its molecular motion. Greater is disorder of molecular motion of the system greater is the entropy.*** If heat is supplied to the system, the disorder of molecular motion increases therefore entropy increases and if heat is extracted from a system, the disorder or molecular motion decreases and hence entropy decreases.

Consider a number of isothermals $I_1, I_2, I_3$ ....etc. at temperatures $T_1, T_2, T_3$ .... etc. on an indicator diagram (Fig. 1.12). Let $A_1$ and $A_2$ be two adiabatics which intersects these isothermals in points $A$ and $B$, $C$ and $D$, $E$ and $F$ etc. Then all along the adiabatics $A_1$ and $A_2$ there is a change in volume and temperature with change in pressure. Let $ABCD$ and $DCEF$ represent the Carnot's reversible cycle. Considering the cycle $ABCD$, let $Q_1$ be the heat absorbed from $A$ to $B$ at temperature $T_1$ and let $Q_2$ be the heat rejected from $C$ to $D$ at temperature $T_2$, then from the theory of a Carnot engine.



(Fig. 1.12)

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Similarly considering the cycle $DCEF$, if $Q_2$ be heat drawn as $T_2$ and $Q_3$ heat liberated at $T_3$.

$$\frac{Q_2}{T_2} = \frac{Q_3}{T_3}$$

$$\therefore \qquad \frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = \ldots = \text{constant}$$

In going from one adiabatic to the other, heat energy is either absorbed or liberated. The amount of heat absorbed or liberated is not constant but depends upon the temepratrue. Higher the temperature, the more is the heat absorbed or liberated and vice versa. In general, if $Q$ is the amount of heat absorbed or rejected at a temperature $T$ is going from one adiabatic to the other, then

$$\frac{Q}{T} = \text{constant}$$

This constant ratio is called the *change in entropy* between the states represented by the two adiabatics.

Let $S_1$ and $S_2$ (arbitrary quantities) be respectively the entropy for the adiabatics $A_1$ and $A_2$ then

$$S_2 - S_1 = \frac{Q}{T} = \text{constant} \qquad \ldots(1)$$

If the adiabatic lie very close to each other and $dQ$ is the quantity of heat absorbed or rejected at a temperature $T$ in going from one adiabatic to the other, then change in entropy,

$$dS = \frac{dQ}{T} \qquad \ldots(2)$$

Hence, in general, the change in entropy in passing from one adiabatic to another

$$\Delta S = S_2 - S_1 = \int_{S_1}^{S_2} dS = \int_{A_1}^{A_2} \frac{dQ}{T} \qquad \ldots(3)$$

The expression $\Delta S = \int_{A_1}^{A_2} \frac{dQ}{T}$ is a function of the thermo-dynamic coordinates of a system and refers to the value of the functions at the final state minus the value at the initial state. This function is represented by the symbol $S$ and is called *entropy*. Hence *entropy of a system is a function of the thermodynamical coordinates defining the state of the system viz., the pressure, temperature, volume or internal energy, and its change between two states is equal to the integral of the quantity dQ/T between the states along any reversible path joining them. dS is an exact differential as it is differential of an actual function.*

Further it can be easily seen that since during an adiabatic change no heat energy is given to or removed from the system $dQ = O$, so that the change in entropy $\frac{dQ}{T} = O$. It means there is no change of entropy during an adiabatic process, or *the entropy remains constant during an adiabatic reversible process.* That is why the adiabatic curves on the $P$—$V$ diagram are called *as isentropics* curves of constant entropy. Therefore ***the entropy of substance is that physical quantity which remains constant when the substance undergoes a reversible adiabatic process.***

It is, however, difficult to form **physical conception of entropy** as there is nothing physical to represent it and it can not be felt like temperature or pressure. But since

$$\text{Change in entropy} = \frac{\text{Heat added or subtracted}}{\text{Absolute temperature}}$$

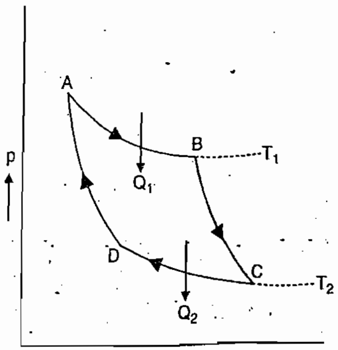
We may say that heat energy has the same dimensions as the product of entropy and absolute temperature. Since the gravitational potential energy of a body is proportioanl to the product of its mass and height above some zero level hence if we take temperature (measured from absolute zero) equivalent to height we may regard entropy as analogous to mass or inertia. In this way, *we may think of entropy as thermal inertia which bears to heat motion a relation similar to that which mass bears to linear motion or moment of inertia bears to rotational motion.*

The **unit of entropy** depends on the unit of heat employed and the absolute temperature. It is measured in kilocal/K or joule/K.

## 1.20 Change in Entropy in Reversible and Irreversible Processes

**Change of Entropy in a Reversible Process.**

Let us consider a complete reversible process—A Carnot's cycle *ABCD* shown in fig. 1.13. In the isothermal expansion from A to B, the working substance absorbs an amount of heat $Q_1$ at a constant temperature $T_1$ of the source. When heat is absorbed by the system, $Q_1$ is positive, and hence entropy change is positive because $T_1$ is positive. Hence gain is entropy of working substance from *A* to $B = \frac{Q_1}{T_1}$ (Source loses this heat $Q_1$ at temeprature $T_1$ so its entropy decreases by $Q_1/T_1$.) During the adiabatic expansion from B to C, there is no change in entropy (since heat is neither taken in nor given out). During the isothermal compression from C to D, the working substance gives out a quantity of heat $Q_2$ at a constant temperature $T_2$, to sink so the loss in its entropy from C to $D = \frac{Q_2}{T_2}$. (The sink gains this heat $Q_2$ at temperature $T_2$, so its entropy increases by $Q_2/T_2$). Again during the adiabatic compression from *D* to *B*, there is no change in entropy. Thus the net gain in the entropy of working substance in the whole cycle *ABCDA*



(Fig. 1.13)

$$= \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

But since in a complete reversible Carnot's cycle

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Therefore $\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$

It means that the total change in entropy of the working substance in a complete cycle of reversible process is zero. Similarly, the change in entropy of the combined system of source and sink is also zero. *Thus in a cycle of reversible process, the entropy of the system remains unchanged or the change in entropy of the system is zero, i.e.,*

$$\int dS = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = \Sigma \frac{Q}{T} = 0$$

Where the integral sign refers to a complete cycle. This equation is also referred as *Clausius theorem.*

### Change of Entropy in an Irreversible Process.

Suppose, the working substance in an engine performs an irreversible cycle of changes, absorbing an amount of heat $Q_1$ at a temperature $T_1$ from the source and rejecting the quantity of heat $Q_2$ at a temperature $T_2$ of the sink, then the efficiency of this cycle is given by

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}.$$

According to Carnot's theorem, this efficiency is less than that of a reversible engine working between the same two temperatures $T_1$ and $T_2$ for which

$$\eta = 1 - \frac{T_2}{T_1}.$$

Thus $$1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1}$$

or $$\frac{Q_2}{Q_1} > \frac{T_2}{T_1} \text{ or } \frac{Q_2}{T_2} > \frac{Q_1}{T_1}$$

or $$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} > 0.$$

Considering the whole system, source loses entropy by an amount $Q_1/T_1$ and the sink gains an entropy $Q_2/T_2$. Therefore, the net change in entropy for thw whole system is

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

which is clearly greater than zero or positive. Thus *there is an increase in entropy of the system during an irreversible process.*

We may make this point still more clear by taking another concrete example for an irreversible process like conduction or radiation of heat. Let a system consist of two bodies at temperatures $T_1$ and $T_2$ respectively, where $T_1 > T_2$. Since heat always flows from a higher to a lower temperature, both by conduction and radiation, let $Q$ be the quantity of heat thus transmitted.

Decrease in entropy of hotter body $= \frac{Q}{T_1}$

Increase in entropy of colder body $= \frac{Q}{T_2}$

Therefore, the net increase in entropy of the system

$$= \frac{Q}{T_2} - \frac{Q}{T_1}$$

Which is a positive quantity since $T_1 > T_2$ We may, therefore generalise the result and say that *the entropy of a system increases in all irreversible processes.* This is known as the principle of increase of entropy.

## 1.21 Principle of Increase of Entropy or Degradation of Energy

The entropy of a system remains constant in reversible cyclic processes but increases inevitably in all irreversible processes. Since a reversible process represents a limiting ideal case, all actual processes are inherently irreversible. It means that as cycle after cycle of operation is performed, the entropy of the system increases and tends to a maximum value. This is the *principle of increase of entropy* and may be stated as "*The entropy of an isolated system either increases or remains constant according as the processes it undergoes.are irreversible or reversible.* Analytically it may be expressed as $dS \geq 0$, where the equality sign refers to reversible process and the inequality sign to irreversible process. Therefore, the necessary and sufficient condition of equilibrium of an isolated system is that its entropy should be maximum, for for then entropy '$S$' can not increase and $dS$ cannot be greater than zero.

Now since all physical operations in the universe are irreversible, for every such operation performed a certain quantity of energy of the universe becomes unavailable for useful work and is added to the unvierse in the form of heat through friction, conduction or radiation. In this way, in a distant furture on account of irreversibility, all energies existing in different forms will be converted into heat energy and will not be available for conversion into mechanical work, *i.e., the available energy of the universe will tend towards zero.* It will correspond to a state of a maximum entropy and all temperature differences between various bodies of the unvierse will be equalized due to convection etc. No heat engine will then will able to work in this state, because no heat flow would be possible due to the uniformity of temperature throughout the universe. This is spoken as *the principle of degradation of energy* and implies though the total amount of energy is conserved, it is transformed into a form which is unavailable for a work. Thus the energy is 'running downhill' and the universe is marching towards a stage of stagnancy to a die a 'heat death'.

With an increase in entropy, the thermal agitation and hence disorder of the molecules of substance increases, *i.e.*, growth of entropy implies a transition from order to disorder. Thus the *principle of increase of entropy is intimately connected with the less ordered state of affairs.* According to it, a high entropy system should be great in disorder of chaos. Thus the entropy of a substance in gaseous state is more than in the liquid state because the molecules are more free to move about in great disorder in a gas than in a liquid. Moreover the entropy is more in the liquid state than in the solid state, as the molecules are more free to move in a liquid than in a solid. Hence when ice is converted into water and then into steam, the entropy and disorder of molecules increases. On the other hand, when the steam is converted into water and then into ice, the entropy and disorder of molecules continually decrease. Thus when temperature of a system is lowered, the amount of an entropy and disorder in it decrease. ***Entropy of a substance is therefore, said to be a measure of the degree of disorder prevailing among its molecules,*** just as temperature is a measure of the degree of hotness of a substance. At the absolute zero of temperature the thermal motion completely disappears so that the disorder and hence entropy tend to zero and the molecules of a substance are in perfect order *i.e.*, well arranged (*third law of thermodynamics*).

We may now summarize the above arguments and say that the *entropy of any isolated system increases and approaches, more or less rapidly, to the innert state of maximum entropy.* We may recognise this fundamental law of physics to be an inherent tendency of nature to proceed from a more ordered state to a less ordered or from a less disordered to a more disordered state, or we may state in other words that *the ultimate destiny of universe is not order but chaos.*

## 1.22 Formulation of the Second Law in Terms of Entropy

The first law of thermodynamics implies, according to Clausius, that *the energy of the universe remains constant* (the law of conservation of energy); the second law was summed up by him by saying that *the entropy of the universe tends to a maximum* (law of increase of entropy). We may, therefore, attempt to enunciate the general statement of second law in terms of entropy in the following words; *Every physical or chemical process in nature takes place in such a way so as to increase the entropy of the system.*

In order to formulate the second law mathematically, let $S_A$ and $S_B$ be the entropies of a substance in initial and final states $A$ and $B$ respectively, measured from some arbitrary zero. The entropy change is then given by

$$S_B - S_A = \int_A^B \frac{dQ}{T}$$

If any how the two states $A$ and $B$ are infinitesimally close, the above equation may be put as

$$dS = \frac{dQ}{T}$$

or
$$dQ = T \,.\, dS$$

This is the required mathematical formulation of second law of thermodynamics.

## 1.23 Clausius Inequality

The inequality $\Delta S = \int \frac{dQ}{T} \geq 0$ is called Clausius inequality. It embodies both the Kelvin-Planck and Clausius statements of the second law of thermodynamics.

According to Kelvin-Planck statement of law, there can not be a perfect heat engine which may convert all the heat $Q$ taken from the source at temperature $T$ into work. If it were so, the entropy of the source would decrease by $\frac{Q}{T}$ where that of the working substance would remain unaltered, because it returns to initial state after completing the cycle. Thus the entropy of the system plus surrounding would decrease which is against the principle of increase of entropy.

In the same way, according to Clausius statement of the second law, there cannot be a perfect refrigerator which, unaided by an external agency, may transfer heat $Q$ from a cold body at temperature $T_2$ to a hot body at temperature $T_1$. If it were so, the entropy of cold body would decrease by $\frac{Q}{T_2}$, that of hot-body would increase by $\frac{Q}{T_1}$ and ~~that of working~~ substance would remain unchanged. Since $T_2 > T_1$, the total entropy of the system plus surroundings would decrease by $\left(\frac{Q}{T_2} - \frac{Q}{T_1}\right)$ which is against the entropy principle because the entropy of a thermodynamic system plue surroundings either remains constant or increases but can never decrease.

Thus the principle of increase of entropy is consistent with both the Kelvin-Planck and Clausius statements of the second law of thermodynamics.

## 1.24 Change in Entropy of a Solid or Liquid

Change in entropy $\Delta S$ is given by

$$\Delta S = \frac{\Delta Q}{T}$$

(i) When m kg of substance changes state from solid to liquid = $Q = mL_1$
where $L_1$ is latent heat of fusion

$$\therefore \quad \Delta S = \frac{mL_1}{T}$$

When m kg of substance changes state from liquid to solid, heat is extracted from substance

$$\therefore \quad \Delta S = -\frac{mL_1}{T}$$

(ii) When m kg of substance changes state from liquid to vapour, $\Delta Q = mL_2$.
where $L_2$ is latent heat of sublimation.

When m kg of substance changes state from vapour to liquid,

$$\Delta Q = -mL_2$$

$$\therefore \quad \Delta S = -\frac{mL_2}{T}$$

(iii) When temperature of $m$ $kg$ of substance is raised from $T_1$ to $T_2$, the change in entropy is given by

$$\Delta S = \frac{\Delta Q}{T} = \int_{T_1}^{T_2} \frac{dQ}{T}$$

where $dQ$ is heat given to substance for infinitesimal temperature rise $dT$, *i.e.* $dQ = mcdT$, $c$ being specific heat

$$\therefore \quad \Delta S = \int_{T_1}^{T_2} \frac{mc\, dT}{T} = mc\left[\log_e T\right]_{T_1}^{T_2} = mc \log_e \frac{T_2}{T_1}$$

### 1.25 Entropy of Steam

Let us consider $m$ kg. of ice at absolute temperature $T_1$. We shall find an expression for the total gain in entropy when this ice is converted into steam at 100°C.

If a small amount of heat $dQ$ is given to a substance at temperature $T$, the change in entropy is given by

$$dS = \frac{dQ}{T}.$$

To convert m kg. of ice at $T_1$ $K$ into water at the same temperature, an amount of heat $mL_i$ is added to it where $L_i$ is the latent heat of ice. Hence

The change in entropy during this process $= \dfrac{mL_i}{T_1}$ ...(1)

Again, when $m$ kg. water at $T_1$ $K$ is heated to $T_2$ $K$.

$$\text{The change in entropy} \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{mc\, dT}{T}$$

$$= mc \log_e \frac{T_2}{T_1} \qquad ...(2)$$

where $c$ is the specific heat of water, supposed to remain constant.

Now when $m$ kg. of water at $T_2$ $K$ is converted into steam at the same temperature, it absorbs $mL_s$ kilo calories of heat, where $L_s$ is the latent heat of steam. Thererfore,

Change of entropy in this process $= \dfrac{mL_s}{T_2}$. ...(3)

Therefore the total gain in entropy, adding (1), (2) and (3)

$$= \frac{mL_i}{T_1} + mc \log_e \frac{T_2}{T_1} + \frac{mL_s}{T_2} \qquad ...(4)$$

### 1.26 Entropy of a Perfect Gas

Let us consider 1 g-mole of a perfect gas occupying a volume $V$ at a pressure $P$ and temperature $T$. Let a quantity of heat $dQ$ be given to the gas, then by the first law of thermodynamics, we have

$$dQ = dU + dW$$

Now if $C_V$ is the specific heat of the gas at constant volume, $dT$ the rise in temperature, $dV$ the change in volume, then

$$dU = C_V\, dT \text{ and } dW = P\, dV$$

Hence $\qquad dQ = C_V\, dT + P\, dV.$

If $S$ is the entropy per g-mol of the gas, then change in entropy when its thermodynamic coordinates change from $(P_1, V_1, T_1)$ to $(P_2, V_2, T_2)$ is given by

$$\Delta S = \int \frac{dQ}{T} = \int_{P_1 V_1 T_1}^{P_2 V_2 T_2} \frac{(C_V\, dT + P\, dV)}{T}$$

$$= \int C_V \frac{dT}{T} + \int \frac{P\, dV}{T}. \qquad ...(i)$$

(A) *Value of S in terms of temperature and volume* : From the

Relation $PV = RT$ we get $\dfrac{P}{T} = \dfrac{R}{V}$, Substituting in (i), we have

$$\Delta S = \int C_V \frac{dT}{T} + \int R \frac{dV}{V}$$

∴ Change in entropy when the thermodynamic co-ordinates vary from $(V_1, T_1)$ to $(V_2, T_2)$, we get

$$\Delta S = C_V\left[\log_e T\right]_{T_1}^{T_2} + R\left[\log_e V\right]_{V_1}^{V_2}$$

or $$\Delta S = C_V \log_e \frac{T_2}{T_1} + R \log \frac{V_2}{V_1} \qquad ...(ii)$$

(B) *Value of S in terms of temperature and pressure* : Since

$$PV = RT,\ V = \frac{RT}{P}$$

and $\qquad P\, dV + P\, dV = R\, dT$

so that $\qquad P\, dV = R\, dT - V\, dP.$

Substituting this value in (i), we get

$$\Delta S = \int_{(T_1, P_1)}^{(T_2, P_2)} \left[C_V \frac{dT}{T} + \frac{R\, dT - V\, dP}{T}\right]$$

$$= \int_{(T_1, P_1)}^{(T_2, P_2)} \left[C_V \frac{dT}{T} + \left(R \frac{dT}{T} - \frac{dP}{P}\right)\right] \qquad \left[\because \frac{V}{T} = \frac{R}{P} \text{ from } PV = RT\right]$$

$$= \int_{(T_1, P_1)}^{(T_2, P_2)} \left[C_V \frac{dT}{T} + \left(R \frac{dT}{T} - R \frac{dP}{P}\right)\right]$$

$$\Delta S = \int_{(T_1, P_1)}^{(T_2, P_2)} \left[C_P \frac{dT}{T} - R \frac{dP}{P}\right] \qquad (\because C_P - C_V = R)$$

$$= C_P\left[\log_e T\right]_{T_1}^{T_2} - R\left[\log_e P\right]$$

i.e. $$\Delta S = C_P \log_e\left(\frac{T_2}{T_1}\right) - R\log_e\left(\frac{P_2}{P_1}\right) \qquad \text{...(iii)}$$

(C) *Value of S in terms of pressure and volume :*

$$T = \frac{PV}{R} \text{ and } dT = \frac{P.dV + V.dP}{R}$$

Substituting this value of $dT$ in relation (i) above, we get

$$\Delta S = \int\left[\frac{C_V}{T}\frac{(P\,dV + V\,dP)}{R} + \frac{P\,dV}{T}\right]$$

$$= \int\left[\frac{C_V(P\,dV + V\,dP)}{PV} + \frac{P\,dV\,.\,R}{PV}\right]$$

$$\left[\because PV = RT \text{ and } \frac{1}{T} = \frac{R}{PV}\right]$$

$$= \int\left[C_V\left(\frac{dV}{V} + \frac{dP}{P}\right) + (C_P - C_V)\frac{dV}{V}\right] \quad [\because R = C_P - C_V]$$

$$= \int_{(P_1,V_1)}^{(P_2,V_2)}\left[C_V\frac{dP}{P} + C_P\frac{dV}{V}\right]$$

$$= C_V\left[\log_e P\right]_{P_1}^{P_2} + C_P\left[\log_e V\right]_{V_1}^{V_2}$$

or $$\Delta S = C_V \log_e\left(\frac{P_2}{P_1}\right) + C_P\log_e\left(\frac{V_2}{V_2}\right) \qquad \text{...(iv)}$$

## NUMERICAL EXAMPLES

**Ex. 7.** *The melting point of tin is 232°C, its latent heat of fusion 14 cals/g. and specific heat of solid and molten tin 0·055 and 0·064 cal./g. K respectively. Calculate the change in entropy when 1 g. of tin is heated from 150°C to 314°C.*

**Sol.** Here the change in entropy takes place in three steps.

(i) Change in entropy when solid tin is heated from 150°C (150 + 273 = 423 K) to 232°C (505K)—melting point of tin

$$\Delta S_1 = mc\log_e\frac{T_2}{T_1} = 1 \times 0{\cdot}055 \log_e\frac{505}{423}$$

$$= 2{\cdot}3026 \times 0{\cdot}055 \log_{10}\left(\frac{505}{423}\right) = 0{\cdot}0097 \text{ cal/K}$$

(ii) Now the tin changes from solid state to liquid state at 505 K. During this change of phase

$$\Delta S_2 = \frac{dQ}{T} = \frac{m \times L}{T} = \frac{1 \times 14}{505} = 0{\cdot}028 \text{ cal./K.}$$

(iii) Now the temperature of molten tin rises from 232°C (505 K) to 314°C (587 K) in liquid phase.

$$\Delta S_3 = mc\log_e\frac{T_2}{T_1}$$

$$= 1 \times 0{\cdot}064 \log_e\left(\frac{587}{505}\right) = 2{\cdot}3026 \times 0{\cdot}064 \log_{20}\left(\frac{587}{505}\right)$$

$$= 0{\cdot}0096 \text{ cal./K.}$$

Hence the total change in entropy

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$= 0{\cdot}0097 + 0{\cdot}028 + 0{\cdot}0096 = \mathbf{0{\cdot}047 \text{ cals./K.}}$$

**Ex. 8.** *Calculate the increase in entropy when 1 kg. of ice at –10°C is converted into steam at 100°C [Specific heat of ice = 0·5 kilo calorie/kg. °C, latent heat of ice = 3·4 × $10^5$ Joule/kg, latent heat of steam = 22·68 × $10^5$ Joule/kg., J = 4·2 Joule/Calorie.*

**Solution.** Here the change of entropy takes place in four steps :

(i) Increase in entropy when the temperature of 1 kg. of ice increases from = – 10°C (263 K) to 0°C (273 K).

$$\Delta S_1 = mc\log_e\frac{T_f}{T_i}$$

$$= 1 \times 0{\cdot}5 \times 2{\cdot}3026 \log_{10}\frac{273}{263}$$

$$= 0{\cdot}5 \times 2{\cdot}3026 \times 0{\cdot}0162 = 0{\cdot}01865 \text{ kilo–calorie/K}$$

(ii) Increase in entropy when 1 kg. of ice at 0°C is converted into water at 0°C.

$$\Delta S_2 = \frac{dQ}{T} = \frac{mL}{T} = \frac{1\,kg \times 3{\cdot}4 \times 10^5\,Joule/kg}{273}$$

$$= \frac{3{\cdot}4 \times 10^5}{273}\text{ Joule/K} = 1{\cdot}245 \times 10^3 \text{ Joule/K}$$

$$= \frac{1{\cdot}245 \times 10^3}{4{\cdot}2 \times 10^3}\text{ kilo cal./K} = 0{\cdot}2965 \text{ kilo cal/K.}$$

(iii) Increase in entropy when the temperature of 1 kg. of water is raised from 0°C (273 K) to 100°C (373 K).

$$\Delta S_3 = mc\log_e\frac{T_f}{T_i} = mc \times 2{\cdot}3026 \log_{10}\frac{373}{273}$$

$$= 1 \times 1 \times 2{\cdot}3026 \times 0{\cdot}135$$

$$= 0{\cdot}3109 \text{ kilo cal./K.}$$

(iv) Increase in entropy when 1 kg. of water at 100°C (373 K) is converted into steam at the same at the same temperature

$$\Delta S_4 = \frac{dQ}{T} = \frac{mL}{T} = \frac{22{\cdot}68 \times 10^5}{373}\text{ J/K} = \frac{22{\cdot}68 \times 10^5}{373 \times 4{\cdot}2 \times 10^3}\text{ kilo cal/K.}$$

$$= 1{\cdot}4477 \text{ kilo cal./K.}$$

Therefore, total increase in entropy

$$= 0{\cdot}01865 + 0{\cdot}2965 + 0{\cdot}3109 + 1{\cdot}4477 \text{ kilo cal./K}$$

$$= \mathbf{2{\cdot}07375 \text{ kilo cal./K}}$$

**Ex. 9.** *A mass m of a liquid at temperature $T_1$ is mixed with an equal mass of the same liquid at temperature $T_2$. The system is thermally insulated. Show that the entropy change of the universe is*

$$2m\, c_P \log_e \frac{(T_1+T_2)/2}{\sqrt{(T_1 T_2)}}$$

**Sol.** When mass of the liquid at temperature $T_1$ is mixed with an equal mass of the same liquid at temperature $T_2$, the temperature of the mixture will be

$$\frac{T_1+T_2}{2}$$

Now change in entropy when the temp. of m gram of liquid changes from $T_1$ to $\frac{T_1+T_2}{2}$.

$$\Delta S_1 = \int_{T_1}^{(T_1+T_2)/2} \frac{dQ}{T} = \int_{T_1}^{(T_1+T_2)/2} mc_P \frac{dT}{T}$$

$$= mC_P \Big[\log_e T\Big]_{T_1}^{(T_1+T_2)/2}$$

$$= mc_P \log_e \frac{T_1+T_2}{2T_1}.$$

Also change in entropy when the temp. of mass $m$ of liquid changes from $T_2$ to $\frac{T_1+T_2}{2}$.

$$\Delta S_2 = \int_{T_1}^{(T_1+T_2)/2} mc_P \frac{dT}{T} = mc_P \Big[\log_e T\Big]_{T_1}^{(T_1+T_2)/2} = mc_P \log_e \frac{T_1+T_2}{2T_2}$$

Hence the entropy change of the universe

$$\Delta S = \Delta S_1 + \Delta S_2 = mc_P \log_e \frac{T_1+T_2}{2T_1} + mc_P \log_e \frac{T_1+T_2}{2T_2}$$

$$= mc_P \log_e \left[\frac{T_1+T_2}{2T_1} \times \frac{T_1+T_2}{2T_2}\right]$$

$$= mc_P \log_e \left[\frac{T_1+T_2}{2\sqrt{T_1 T_2}}\right]^2 = 2mc_P \log_e \frac{(T_1+T_2)/2}{\sqrt{(T_1 T_2)}}$$

which is necessarily positive.

**Ex. 10.** *5 kg. of water at 0°C is mixed with an equal mass of water at 80°C. Calculate the change in entropy. Specific heat of water may be assumed to be equal to 1 kilo calories/kg. × °C between 0°C at 80°C.*

**Sol.** Let the final temperature of the mixture be $t$ °C. Then,

$$5 \times 1 \times (t-0) = 5 \times 1 \times (80-t)$$

$$\therefore \quad t = 40^\circ C = 313\ K.$$

$$T_f = t + 273 = 40 + 273 = 313\ K$$

Now increase in entropy when the temperature of 5 kg. of water rises from 273 K to 313 K

$$\Delta S_1 = mc \log_e \frac{T_f}{T_i}$$

$$\Delta S_1 = 5 \times 1 \times \log_e \frac{313}{273}$$

$$= 5 \times 1 \times 2{\cdot}3026 \log_{10} \frac{313}{273} = 0{\cdot}6827 \text{ kilo cal./K.}$$

$$= 682{\cdot}7 \text{ cal./K.}$$

Also decrease in entropy when the temperature of 5 kg. of water falls from 80°C (353 K) to 313 K

$$\Delta S_2 = mc \log_e \frac{T_f}{T_i}$$

$$= 5 \times 1 \times 2{\cdot}3026 \log_{10} \frac{353}{313} = 0{\cdot}6021 \text{ kilo cal./K.}$$

$$= 602{\cdot}1 \text{ cal./K.}$$

Therefore, the net increase in the entropy of the system

$$\Delta S = \Delta S_1 - \Delta S_2 = 682{\cdot}7 - 602{\cdot}1 = 80{\cdot}6 \text{ cal./K.}$$

**Ex. 11.** *One gram molecule of a perfect gas expands isothermally to four times its initial volume. Calculate the change in its entropy in terms of the gas constant R.*

**Sol.** The work done in the expansion of the gas

$$W = \int_{V_1}^{V_2} P\, dV$$

where $V_1$ and $V_2$ are initial and final volumes of the gas.

But for a perfect gas, $PV = RT$

(R gas constant for one g. mole)

$$P = \frac{RT}{V} \quad \therefore \quad W = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \log_e \frac{V_2}{V_1}$$

Hence if $V_1 = V$; $V_2 = 4V$ i.e. $\frac{V_2}{V_1} = 4$

$$\therefore \quad W = RT \log_e 4 = 2{\cdot}3026 \times RT \log_{10} 4$$

where we have used of work (Joules for $W$ and $R$)

If a quantity of heat $dQ$ (Joules) is extracted for this work

then change in entropy $= \frac{dQ}{T} = \frac{W}{T} = \frac{2{\cdot}3026 \times RT \times 0{\cdot}6021}{T}$

$$= \mathbf{1{\cdot}386\ R\ joule/K}$$

**Ex. 12.** *3 g of nitorgen doubles in volume at constant temperature. Calculate the change in entropy. Given for nitrogen, molecular weight = 28.*

**Sol.** The change in entropy for $n$ moles of a perfect gas in terms of temperature and volume is given by

$$\Delta S = S_2 - S_1 = n\left[C_V \log_e \frac{T_2}{T_1} + R \log_e \frac{V_2}{V_1}\right]$$

Here temperature remains constant and mass of gas taken is 3 g.

∴ No. of moles, $n = \frac{m}{M} = \frac{3}{28}$

$$\Delta S = \frac{3}{28} R \log_e \frac{V_2}{V_1}$$

$$\therefore \quad \text{Change in entropy, } S_2 - S_1 = \frac{3}{28} \times 8{\cdot}3 \log_e \frac{2}{1} \left(\because \frac{V_2}{V_1} = \frac{2}{1}\right)$$

$$= \mathbf{0{\cdot}621\ joule/K}$$

**Ex. 13.** *For silver, the molar specific heat at constant pressure in the range 50 to 100 K is given by*

$$C_P = 0{\cdot}076\,T - 0{\cdot}00026\,T^2 - 0{\cdot}15 \text{ cal/K}$$

*where T is the Kelvin temperature. If 2 mole of silver is heated from 50 to 100 K, calculate (i) heat required (ii) change in entropy.*

**Sol.** If 2 moles, of silver are raised in temperature by $dT$, the quantity of heat required

$$dQ = 2 \times C_P\,dT$$

$$= 2\,(0{\cdot}076\,T - 0{\cdot}00026\,T^2 - 0{\cdot}15)\,dT$$

Since the temperature is increased from 50 K to 100 K, hence quantity of heat required for this purpose

$$Q = \int_{50}^{100} 2\,(0{\cdot}076\,T - 0{\cdot}00026\,T^2 - 0{\cdot}15)\,dT$$

$$= 2\left[\frac{0{\cdot}076\,T^2}{2} - 0{\cdot}00026\,\frac{T^3}{3} - 0{\cdot}15\,T\right]_{50}^{100}$$

$$= 2\left[0{\cdot}076\,\frac{(100^2 - 50^2)}{2} - 0{\cdot}00026\,\frac{(100^3 - 50^3)}{3} - 0{\cdot}15\,(100 - 50)\right]$$

$= \mathbf{403{\cdot}8}$ **calories.**

(ii) Change in entorpy, when silver is heated from 50 K to 100 K.

$$S_2 - S_1 = \int_{50}^{100} \frac{dQ}{T}$$

$$= \int_{50}^{100} \frac{2\,(0{\cdot}076\,T - 0{\cdot}00026\,T^2 - 0{\cdot}15)}{T}\,dT$$

$$= \int_{50}^{100} 2\left(0{\cdot}076 - 0{\cdot}00026\,T - \frac{0{\cdot}15}{T}\right)dT$$

$$= 2\left[0{\cdot}076\,T - 0{\cdot}00026\,\frac{T^2}{2} - 0{\cdot}15\,\log_e T\right]_{50}^{100}$$

$$= 2\left[0{\cdot}076\,(100 - 50) - 0{\cdot}00026\left(\frac{100^2 - 50^2}{2}\right) - 0{\cdot}15\,\log_e \frac{100}{50}\right]$$

$$= 2 \times 0{\cdot}076 \times 50 - 0{\cdot}00026 \times 150 \times 50 - 2 \times 0{\cdot}15 \times 2{\cdot}3026\,\log_{10} 2$$

$$= 7{\cdot}6 - 1{\cdot}95 - 0{\cdot}3 \times 2{\cdot}302 \times 0{\cdot}3010$$

$$= 7{\cdot}6 - 1{\cdot}95 - 2{\cdot}07$$

$= \mathbf{3{\cdot}58}$ **cals/K.**

## EXERCISES

### SHORT ANSWER QUESTIONS

1. Explain the terms "system" and "surroundings". with examples.
2. State and discuss zeroth law of thermodynamics. *(Ranchi Univ. 2004)*
3. Define 'work' in thermodynamics.
4. Explain the concept of 'internal energy'.

5. Explain the concept of 'Heat'.
6. State first law of thermodynamics on what conservation law it is based ?
7. Define molar heats $C_p$ and $C_v$ for a gas. What is relation between them ?
8. Compare $C_p - C_v = R$ with first law of thermodynamics $Q - \Delta U = W$
9. Differentiate between isothermal and adiabatic processes.
10. Write adiabatic equation for a perfect gas in terms of (i) pressure and volume (ii) temperature and volume
11. Write expressions for work done in
    (a) Isothermal process (b) Adiabatic process.
12. What is a heat engine ? Name its three components ?
13. What do you mean by efficiency of a heat engine ? On what factors does it depend ?
14. Explain reversible and irreversible processes with examples.
15. What is Carnot cycle and Carnot engine ?
16. Write expression for efficiency of Carnot engine ? On what factors does it depend ?
17. Which of the following is more effective to increase the efficiency of Carnot engine :
    (i) Increase temperature of source or
    (ii) decrease of temperature of sink, by same amount.
18. State Carnot theorem.
19. Give Clausius statement and Kelvin-Planck's statement of second law of thermodynamics. Are these statements equivalent ?
20. Define entropy. What is its S.I. unit ?
21. Comment on the statement that "Entropy, is a measure of disorder of molecular motion".
22. Explain physical significance of entropy.
23. Show that the change in entropy in reversible adiabatic process is zero.
24. State the principle of increase of entropy.
25. State second law of thermodynamics in terms of entropy.
26. State Clausius inequality regarding entropy.
27. What is the change in entropy when :
    (i) $m$ kg. of substance changes state from solid to liquid and viceversa ?
    (ii) $m$ kg of substance changes state from liquid to vapour and viceversa ?
    (iii) $m$ kg of substance is heated from temperature $T_1$ to $T_2$ ?
28. What is the change in entropy when $n$-moles of an ideal gas undergoes change in temperature (i) at constant volume and (ii) at constant pressure ?
29. What is the change in entropy when $m$ kg of ice at 0°C is converted into steam at 100°C ?

### LONG ANSWER QUESTIONS

1. Interpret each term of the equation $dQ = dU + dW$ and enunciate the law connected to it.
2. Explain the concept of internal energy of a system Formulate the first law of thermodynamics and explain its physical significance.

3. What are isobaric and adiabatic processes ? Deduce expressions for work and internal energy in each process.
4. Show that for an ideal gas having volume $V$ and pressure $P$, undergoing an adiabatic process, $PV^{\gamma}$ = constant where $\gamma$ is the ratio of specific heats of the gas at constant pressure and constant volume.
5. What are isothermal and adiabatic processes ? Show that during an adiabatic expansion of a perfect gas, pressure at any moment is given by the equation $PV^{\gamma} = K$, where $\gamma$ and $K$ are constants.
6. For a quasi-static adiabatic process of a ideal gas, prove

$$TP^{(1-\gamma)/\gamma} = \text{const.}$$

7. Show that for a perfect gas, the slope of an adiabatic is $\gamma$ times the slope of the isothermal, where $\gamma$ is the ratio of the principal specific heats of a gas.
8. Distinguish between quasi-static process, isothermal process and adiabatic process. Prove that the work done along any adiabatic between two isothermals is independent of the particular adiabatic.
9. Describe first law of thermodynamics and show that for isothermal expansion of a perfect gas

$$W = RT \log_e \frac{V_2}{V_1}$$

10. One gram mole of an ideal gas is contained in a piston cylinder assembly at initial condition $P_iV_i$. The gas is allowed to expand to a final volume $V_f$. Calculate work done when :
    (i) the pressure remains constant,
    (ii) the product $PV$ remains constant,
    (iii) the product $PV^{\gamma}$ = constant.
    In which process the work done is the least ? Justify your answer.
11. A gram mole of an ideal gas is in a piston cylinder assembly at initial condition $P_iV_i$ where $P_i$ is the initial pressure and $V_i$ is the initial volume. The gas is allowed to expand in accordance with the relation

$$PV^{n} = \text{constant.}$$

    (i) Represent qualitatively the changes on a $P-V$ diagram when the gas expands to the same final volume in accordance with the above relation for
        (1) $n = 0$
        (2) $n = 1$
        (3) $n = \gamma$
    the ratio of the two specific heats of the gas.
    (ii) Calculate the work done by the gas in each process mentioned above.
    (iii) What is the change in the internal energy of the gas in the above expansions for the case $n = 1$ and $n = \gamma$ ?
    (iv) In which process does the gas do the least amount of work.
    **[Hint :** Least work is done in adiabatic expansion].
12. Distinguish carefully between reversible and irreversible processes. State clearly the physical condition necessary for reversibility. Is it possible to realize reversibility in actual practice ?

13. What is a heat engine ? What are its essential parts ? Obtain a general expression for its efficiency.
14. When is an engine said to be reversible ? Explain why an engine with hundred percent efficiency is impossible.
15. (a) What is a heat engine ? Obtain a generai expression for its efficiency. Explain the use of indicator diagrams in discussing the performance of heat engines.
    (b) Explain what is meant by a reversible engine ?
16. Define Carnot's cycle. Explain the working of Carnot's heat engine. Calculate its efficiency when a perfect gas is the working substance. ***(Rohilkhand 2006, 2003, Meerut 2005, Kanpur 2006)***
17. Describe Carnot's heat engine with the help of suitable diagrams. Find its efficiency. Why it can not be realized in practice ?
18. Define Carnot's cycle and show how the work done in each operation is represented on a pressure volume diagram.
    Calculate the work done in each operation of the cycle when the working substance is a perfect gas.
19. Explain the factors which govern the efficiency of a heat engines. Illustrate your answer with reference to a Carnot cycle.
    Which is the more effective way to increase the efficiency of a Carnot engine : to increase $T_1$ keeping $T_2$ constant : or to decrease $T_2$, keeping $T_1$ constant ? Give reasons.
20. What are reversible and irreversible processes ? Prove that for a perfectly reversible engine, the efficiency is maximum and is independent of the nature of working substance.
21. In a $P-V$ diagram of a Carnot engine show by the shaded area which would represent.
    (i) Work done by the gas, (ii) Work done on the gas.
22. State and prove Carnot's theorem. ***(Rohilkhand 2005, Meerut 2006, Patna 2004)***
23. What is meant by a reversible engine ? Prove that no engine working between two given temperatures can be more efficient than a reversible engine working between the same two temperatures.
24. Explain the concepts of reversible and irreversible process. Obtain an expression for the efficiency of a reversible Carnot engine with a perfect gas as a working substance. Show that for same pairs of working temperatures, the efficiency of all reversible engines is the same, and is a maximum value attainable. ***(Purvanchal 2005)***
25. State the second law of thermodynamics and explain its physical significance. Derive an expression for the efficiency of Carnot's engine. ***(Delhi 2002)***
26. In a two stage heat engine-the first stage absorbs a heat $Q_1$ at a higher temperature $T_1$ performs a work $W_1$ and rejects heat $Q_2$ at a lower temperature $T_2$. The second stage absorbs heat expelled by the first, performs a work $W_2$ and rejects heat $Q_3$ at a still lower temperature $T_3$. Show that the efficiency of the combination engine is

$$\eta = \frac{T_1 - T_3}{T_1}$$

27. State Carnot's theorem and show that it is a necessary consequence of second law of thermodynamics. Prove that the efficiency of a Carnot engine using an ideal gas as a working substance is

$$\eta = \frac{T_1 - T_2}{T_1}$$

28. State the second law of thermodynamics in at least two distinctly different ways. Comment on the relation between these statements.

(Kanpur 2002)

29. Give the Kelvin-Planck statement and the Clausius statement of the second law of thermodynamics. Are these two statements equivalent to each other ? Justify your answer.

30. Define entropy. Prove that the entropy in a reversible process for ideal gas is constant but it increases in irreversible process.

(Patna Univ. 2004)

31. Give two statements of the second law of thermodynamics. Prove the Clausius inequality $\sum_i \frac{Q_i}{T_i} \le 0$. Hence develop the concept of entropy and show that the entropy of an isolated system increases in an irreversible process.

(Patna Univ. 2004)

32. Draw $T-S$ diagram for a reversible Carnot's engine and use it to calculate the efficiency of the engine.

(Ranchi Univ. 2005)

33. Define entropy. What is its physical significance ? Show that the entropy of universe tends to a maximum.

34. Show that when a substance of mass $m$ having a constant specific heat $C$ is heated from $T_1$ to $T_2$, the change in entropy is given by

$$S_2 - S_1 = mC \log_e \frac{T_2}{T_1}.$$

35. Define and explain entropy. Discuss its physical significance. Derive an expression or the entropy of $n$-moles of a perfect gas.

(Rohilkhand 2002)

36. Explain the term entropy. Show that the entropy of a system tends to a maximum. Calculate the change in entropy when $m$ gm. of a liquid of specific heat $S$ is heated from $T_1K$ to $T_2K$ and then converted into vapour without raising temperature.

37. Show that the change in entropy of an ideal gas may be written as

$$\Delta S = C_V \log_e\left(\frac{T_2}{T_1}\right) + (C_P - C_V)\log_e\left(\frac{V_2}{V_1}\right)$$

## NUMERICALS

1. Air is compressed adiabatically to half its volume. Calculate the change in its temperature. [Ans. 0·319 $T_1K$]

2. A gram molecule of helium at 20°C is suddenly subjected to a pressure ten times its initial value. Find the final temperature momentarily attained. The ratio of specific heats is 1·67. [Ans. 463·1°C]

3. Calculate the fall in temperature of helium initially at 15°C, when it is suddenly expanded to 8 times its volume. The ratio of specific heats = 1·66. [Ans. 216°C]

4. A quantity of air 27°C and atmospheric pressure is suddenly compressed to half its original volume. Find the final (i) temperature and (ii) pressure. [Ans. 123°C, 2·64 Atmos.]

5. A certain volume of gas at $10^5$ N/m$^2$ pressure and at 27°C expands isothermally until its volume is doubled and then adiabatically until its volume is redoubled. Find the final temperature and pressure of the gas ($\gamma = 1{\cdot}4$). [Ans. – 46°C, $1{\cdot}86 \times 10^4$ N/m$^2$]

6. 1 gram molecule of a monoatomic perfect gas ($\gamma = 5/3$) at 27°C is adiabatically compressed in a reversible process from an initial pressure of 1 atmosphere to a final pressure of 50 atmosphere. Calculate the resulting difference in temperature. [Ans. 1136°C]

7. An ideal gas of volume 1 litre and at pressure 8 atmosphere undergoes an adiabatic expansion until the presure drops to 1 atmosphere. Assuming $\gamma$ to remain constant at the value of 1·5, calculate the final volume and the work done in joules during the expansion. (1 atmos. = $1{\cdot}03 \times 10^5$ N/m$^2$). [Ans. 4,000 c.c., 810·4 joules]

8. Ten litres of air at 17°C and 76 cm. Hg pressure is compressed adiabatically to a volume 0·5 litre. Assuming $\gamma = 1{\cdot}41$, calculate the final temperature and pressure attained. [Ans. 717·4°C, 5192 cm. Hg]

9. Calculate the efficiency of a Carnot's cycle working between the temperatures 125°C and 15°C. [Ans. 27·6%]

10. The temperature of the sink of a Carnot engine is 27°C. If the efficiency of the engine is 40%, find the temperature of the source. [Ans. 227°C]

11. A Carnot engine works between the temperatures 100°C and 10°C Calculate its efficiency. Wen can its efficiency be 100%? [Ans. 24·1%; at sink's temperature $T_2 = 0$]

12. One of the most efficient engines ever developed operates between 2,100 K and 700 K. Its actual efficiency is 40%. What percentage of its maximum possible efficiency is this ? [Ans. 60%]

13. Carnot engine has an efficiency 0·4 when its cold reservoir is at 300K. Find the change in its hot reservoir temperature so that efficiency may become 0·6. [Ans. 250°C]

14. A Carnot engine has an efficiency of 40%. Its low temperature reservoir is at 7°C. Find the temperature of the high temperature reservoir. [Ans. 193·6°C]

15. A Carnot's engine with the sink temperature at 17°C has 50% efficiency. By how much should its source temperature be changed to increase its efficiency to 60% ? [Ans. Increased by 145K]

16. Calculate the efficiency of a Carnot's engine working between the temperatures 300°C and 15°C. If 100 calories of heat are absorbed by the engine at higher temperature, find the work done by the engine. [Ans. 49·7% 208 joules]

17. An engine works in a Carnot cycle between the temperatures 100°C and 0°C. If the work done in the cycle is 2,000 kilogram metre. Calculate how much heat measured in calories, is taken at the higher temperature. [Ans. $1{\cdot}75 \times 10^4$ calories]

18. A Carnot engine operates between the temperatures 327°C and 177°C. It absorbs 120 calories of heat per cycle. Calculate the thermal efficiency and the heat rejected per cycle to the sink. [Ans. 25%, 90 cals/cycle]

19. A Carnot's engine is operated between two reservoirs at temperature of 450K and 350K. It absorbs 100 calories of heat from the source per cycle. Calculate the amount of heat rejected

per cycle to the sink, the efficiency of the engine and the work done by the engine in each cycle. [Ans. 77·8 cals, 22·2%, 93·2 joules]

20. A Carnot engine works between ice point and steam point. It is desired to increase the efficiency by 20%.
    (a) Keeping the temperature of the source constant.
    (b) Keeping temperature of the sink constant. Calculate the new temperatures in the two cases. Which one of these you will prefer and why ?
    [Ans. (a) $T_2 = 198{\cdot}4$ K (b) $T_1 = 513{\cdot}2$K
    (c) first method is preferred because in each cycle a sufficient quantity of heat is rejected to the sink. It is difficult to maintain the sink at quite low temperature].
21. A Carnot engine working between a temperature $T$ and ice point gives an efficiency of 68%. Deduce the value of $T$. [Ans. 580K]
22. Calculate the change in entropy when 10 g of steam at 100°C cools to water at 0°C, assuming that the latent heat of steam is 538 calories per g and the specific heat of water 1 cal./g. [Ans. – 17·55 cals./K]
23. The entropy of saturated water at 100°C is 0·31 and that of saturated steam at the same temperature is 1·76 cals $\text{gm}^{-1}$ $\text{deg.}^{-1}$. What is the heat of vaporization at this temperature ? [Ans. 540·9 cals./g.]
24. Calculate the change of entropy when 100 g of water at 30°C are mixed with 200 g of water at 0°C. assuming that the specific heat of water is constant between these temperatures. [Ans. 0·3684 cal./K]
25. Find the change in entropy when 5 kg. of water at 15°C is mixed with 8 kg. of water at 40°C. Specific heat of water may be assumed to be equal to 1 kilocal./kg × °C between 15°C and 40°C. [Ans. 0·011 kilo cal./K.]
26. The specific heat of a substance varies with temperature as

$$C_P = a + bT + cT^2$$

Deduce an expression for change in entropy when $m$ g of the substance is heated from $T_1K$ to $T_2K$.

$$\left[\textbf{Ans. } m\left\{a \log_e \frac{T_2}{T_1} + b\,(T_2 - T_1) + \frac{c}{2}(T_2{}^2 - T_1{}^2)\right\}\right]$$

27. Calculate the change in entropy when 1 g of ice is mixed with 2 g of water at 55°C. Assume that the specific gravity and the specific heat of water remain constant (= 1 in both cases) between 0°C and 65°C, and latent heat of ice = 80 cal/g. [Ans. 0·337 cals./K]
28. Calculate the change in entropy per g for nitrogen when its temperature rises from 50°C to 100°C while the volume increases four fold. Given $c_v = 0{\cdot}18$ and molecular weight = 28. [Ans. 0·58 cal./K]
29. Calculate the change in entropy of 10 g of oxygen gas during a process in which the temperature changes from 10°C to 50°C and its pressure changes from 76 cm. to 100 cm mercury. The specific heat at constant pressure = 0·5 cals./g. [Ans. + 0·49 cal./K]
30. An electric current of 3 amp. is maintained for 1 second in a resistor of 10 ohm, while the temperature of the resistor is kept constant at 27°C by a steam of running water–
    (a) What is the entropy change of the resistor ?
    (b) What is the entropy change of the universe ? [Ans. (a) 0, (b) 0·3 joule $\text{deg.}^{-1}$]

31. An electric current of 10 ampere is maintained for 1 second in a resistor of 25 ohm while the temperature of the resistor is kept constant at 27°C. What is the entropy change of the resistor ? What is the entropy change of the universe ? [Ans. 0, 8·33 joule/K]
32. Find the change in entropy when 1 g of water at 0°C is heated to 100°C and converted into steam at the temperature, the specific heat of water being assumed constant and equal to 1 cal./°C and latent heat of steam at 100°C equal to 540 cal/g. [Ans. 1·76 cals./K.]
33. Calculate the change in entropy when 5 g of tin is heated from 127°C to 315°C. Given M.P. of tin = 542°C, latent heat of fusion of tin = 14 cal/g, specific heat of solid tin = 0·055 cal./g-°C, specific heat of molten tin = 0·064 cal./°C. [Ans. 0·050 cal./K]

## MULTIPLE CHOICE QUESTIONS : SELECT THE RIGHT CHOICE :

1. The internal energy of an ideal gas depends upon : *(Rohilkhand 2003)*
   (a) pressure (b) volume
   (c) temperature (d) temperature and volume both
2. The internal energy of a real gas depends upon :
   (a) pressure (b) volume
   (c) temperature (d) temperature and volume both
3. The specific heat of a gas : *(Rohilkhand 2002)*
   (a) has only two values $C_p$ and $C_V$
   (b) ~~has a unique value at a given~~ temperature
   (c) can have any value between 0 and ∞
   (d) depends upon the mass of the gas
4. During the melting of a slab of ice at 273 K at atmospheric pressure :
   (a) Positive work in done by the ice-water system
   (b) internal energy of ice-water system remains constant
   (c) internal energy of ice-water system increases
   (d) internal energy of ice-water system decreases
   [Hint : During melting of ice, volume of ice decreases, therefore work is being done on the system by atmosphere. System also absorbs heat from surroundings so internal energy $\Delta U = Q - W = Q + P\Delta V$ is positive *i.e.* $U$ increases].
5. An ideal gas is allowed to expand freely against vaccum in a rigid insulated container. The gas undergoes :
   (a) increase in its internal energy
   (b) decrease in its internal energy
   (c) neither increase nor increase in its temperature and internal energy
   (d) decrease in temperature
6. The heat given to an ideal gas under isothermal condition is used :
   (a) in raising temperature
   (b) in doing external work
   (c) in raising temperature and doing external work
   (d) in increasing internal energy

7. An adiabatic process occurs at constant : *(Rohilkhand 2002)*
(a) heat (b) pressure
(c) temperature (d) all of above

8. A polyatomic gas $\left(\gamma = \frac{4}{3}\right)$ at pressure $P$ is compressed to one-eighth of its initial volume adiabatically, then the pressure will change to :
(a) $4P$ (b) $8P$ (c) $16P$ (d) $32P$

9. The first law of thermodynamics in an isochoric process is : *(Garhwal 2001)*
(a) $\Delta U = Q - W$ (b) $\Delta U = Q$ (c) $\Delta U = W$ (d) $W = Q$

10. In a cyclic process the change in internal energy is : *(Purvanchal 2003)*
(a) Infinity (b) 0
(c) equal to area of cycle (d) can not be determined

11. The law of expansion or compression of a gas is given by $PV^n = \text{constant}$. If $n = 1$, then change is named as : *(Rohilkhand 2003)*
(a) adiabatic (b) isothermal (c) isobaric (d) isochoric

12. In an isobaric process work done ($W$) is equal to : *(Rohilkhand 2003 Imp.)*
(a) $\frac{R}{\gamma - 1}(T_1 - T_2)$ (b) $RT \log \frac{V_2}{V_1}$ (c) $P(V_2 - V_1)$ (d) zero

13. The work done in an idiabatic expansion depends an :
(a) expansion ratio only (b) temperature difference only
(c) Both (a) and (b) (d) neither (a) nor (b)

14. A highly compressed gas is adiabatically expanded Its temperature : *(Rohilkhand 2003 Imp.)*
(a) increases (b) decreases
(c) does not change (d) may change in any direction

15. Which law of thermodynamics suggests that there is a tendency for equalization of temperature throughout the system : *(Kanpur 2005, Rohilkhand 2003)*
(a) Zeroth law (b) First law (c) Second law (d) third law

16. The efficiency of a heat engine can never be :
(a) 10% (b) 40% (c) 60% (d) 100%

17. A Carnot engine works between a hot reservoir at temperature $T_1$ and a cold reservoir at temperature $T_2$. To increase its efficiency :
(a) $T_1$ and $T_2$ both should be increased
(b) $T_1$ and $T_2$ both should be decreased
(c) $T_1$ should be increased and $T_2$ decreased
(d) $T_1$ should be decreased and $T_2$ increased

18. Which is most effective to increase to efficiency of Carnot engine :
(a) Increase of temperature of source by 50°C
(b) Decrease of temperature of sink by 50°C
(c) Increase of temperature of source by 25°C and decrease of temperature of sink by 25°C
(d) All above an equally effective

19. "Heat itself cannot pass from a cold body to a Hot body". This statement is due to : *(Rohilkhand 2006)*
(a) Maxwell (b) Boltzmann (c) Kelvin (d) Clausius

20. It is not possible in a cyclic process to extract heat from a reservoir and convert completely into work. This statement is due to :
(a) Maxwell and Boltzmann (b) Kelvin and Planck
(c) Clausius (d) Wien

21. The efficiency of Carnot engine working between steam point and ice point is :
(a) 1 (b) 16.8% (c) 26.8% (d) 36.6%

22. The entropy of a system in an irreversible process
(a) increases
(b) decreases
(c) remains constant
(d) may increase or decrease depending on the nature of process

23. In an reversible process, the entropy of system : *(Kanpur 2005, Rohilkhand 2003)*
(a) Increases (b) decreases
(c) remains zero (d) remains constant

24. Which relation represents Clausius theorem
(a) $\oint_R \frac{dQ}{T} = 0$ (b) $\oint_R \frac{dQ}{T^2} \neq 0$ (c) $\oint_R \frac{dQ}{T} > 0$ (d) $\oint_R \frac{dQ}{T} < 0$

### ANSWERS

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

# 2

# THERMODYNAMIC RELATIONS WITH APPLICATIONS

## 2.1 Thermodynamic Functions and Maxwell's Relations

The thermodynamic state of a homogeneous system may be represented by means of certain selected variables, such as pressure $P$, volume $V$, temperature $T$ and entropy $S$. Out of these four variables, any two may vary independently and when known enable the others to be determined. Thus there are only two independent variables and the others may be considered as their functions.

There exist certain relations between these thermodynamical variables. The first and second laws of thermodynamics provide two relations which may respectively be stated as,

$$dQ = dU + PdV \qquad \text{...(1)}$$

or

$$dQ = TdS \qquad \text{...(2)}$$

Combining these two laws, we have

$$TdS = dU + PdV$$

$$dU = TdS - PdV.$$

This expresses the change in internal energy of the system in terms of four thermodynamical variables. However for a complete knowledge of the system, certain other relations are required. For this purpose we introduce some functions of the variables, ($P$, $V$, $T$ and $S$), known as thermodynamic potentials or the thermodynamic functions. There are four principal thermodynamic potentials which are of extreme importance in studying the equilibrium state of a thermodynamic system, and we shall discuss them one by one.

**1. Internal or Intrinsic Energy U.**

**1. Internal energy** is the energy possessed by a system due to molecular motion and molecular configuration. The energy possessed by virture of molecular motion is called internal kinetic energy $U_k$ and that possessed by virtue of molecular configuration is called internal potential energy $U_p$

*i.e.*

$$U = U_k + U_p$$

If there are no interactions among molecules, then $U_p = 0$.

The chief characteristic of internal energy is that when the system passes from one state to another, the change in the internal energy is independent of the route followed between the two states. The internal energy of a system is defined by the equation.

$$dU = dQ - dW$$

where $dW$ is the external work done and may be replaced by $PdV$ while $dQ$ may be put equal to $TdS$ by second law of thermodynamics. Thus,

$$dU = TdS - PdV \qquad \text{...(3)}$$

Obviously internal energy U is the function of independent variables S and V i.e.

$$U = U(S, V)$$

Taking its derivative for changes $dS$ and $dV$ in $S$ and $V$ respectively.

$$\therefore \qquad dU = \left[\frac{\partial U}{\partial S}\right]_V dS + \left[\frac{\partial U}{\partial V}\right]_S dV \qquad \text{...(4)}$$

Comparing (3) and (4), we get

$$\left[\frac{\partial U}{\partial S}\right]_V = T \text{ and } \left[\frac{\partial U}{\partial V}\right]_S = -P \qquad \text{...(5)}$$

These are the relations connecting the internal energy $U$ with the thermoddynamical variables, $S$, $V$, $T$ and $P$.

Now since $dU$ is a perfect differential, we must have

$$\frac{\partial}{\partial V}\left[\frac{\partial U}{\partial S}\right]_V = \frac{\partial}{\partial S}\left[\frac{\partial U}{\partial V}\right]_S$$

Using (5), we get

$$\therefore \qquad \left[\frac{\partial T}{\partial V}\right]_S = -\left[\frac{\partial P}{\partial S}\right]_V \qquad \text{...(6)}$$

This result is the *first thermodynamical relation of Maxwell.*

**2. Helmholtz's Function F.** The first and second laws of thermodynamics combined together provide

$$dU = TdS - dW$$

If we consider process in which the system exchanges heat with the surrounding and is thereby maintained at a constant temperature $T$, then $TdS = d(TS)$ and we can write

$$dU = d(TS) - dW$$

or

$$d(U - TS) = -dW$$

or

$$dF = -dW$$

where $F = U - TS$ is known as the **Helmholtz free energy** or more appropriately the **work function** (because eq. $dF = -dW$ shows that for reversible changes the work done by the system is equal to the decrease in this function $F$). Thus the Helmholtz free energy is defined by the equation,

$$F = U - TS, \qquad \text{...(7)}$$

where the value of $F$ depends only on the state of the substance and $dF$ is a perfect differential, Now

$$dF = dU - d(TS)$$

$$= dU - TdS - SdT$$

But

$$dU = TdS - PdV$$

$$\therefore \qquad dF = TdS - PdV - TdS - SdT$$

$$= -PdV - SdT. \qquad \text{...(8)}$$

Obviously $F$ is function of independent variables $V$ and $T$ *i.e.*

$$F = F(V, T)$$

Taking its derivative, we get

$$dF = \left[\frac{\partial F}{\partial V}\right]_T dV + \left[\frac{\partial F}{\partial T}\right]_V dT \qquad \text{...(9)}$$

Comparing (8) and (9) we get

$$\left[\frac{\partial F}{\partial V}\right]_T = -P \text{ and } \left[\frac{\partial F}{\partial T}\right]_V = -S. \qquad \text{...(10)}$$

and since $dF$ is *differential*

$$\therefore \quad \frac{\partial}{\partial V}\left[\frac{\partial F}{\partial T}\right]_V = \frac{\partial}{\partial T}\left[\frac{\partial F}{\partial V}\right]_T$$

Using (10), we get

$$\left[\frac{\partial S}{\partial V}\right]_T = \left[\frac{\partial P}{\partial T}\right]_V \qquad ...(11)$$

This is the *second thermodynamical relation of Maxwell.*

**3. Enthalpy or Total Heat H.** Enthalpy is an extensive thermodynamical property and is of particular significance. The *enthalpy* is that physical quantity which remains constant in *adiabatic throttling process.* It is mathematically defined as

$$H = U + PV.$$

The differentiation of which yields

$$\begin{aligned} dH &= dU + d(PV) \\ &= (T\,dS - P\,dV) + P\,dV + V\,dP \\ &= T\,dS + V\,dP \end{aligned} \qquad ...(12)$$

At a constant pressure ($dP = 0$), $dH = T\,dS = dQ$, the quantity of heat given to the system from an external source. This explains the name of **heat function** given to it.

Obviously enthalpy $H$ is the function of independent variables $S$ and $P$

*i.e.,* $$H = H(S, P)$$

Taking its derivative we get

$$dH = \left[\frac{\partial H}{\partial S}\right]_P dS + \left[\frac{\partial H}{\partial P}\right]_S dP \qquad ...(13)$$

Comparing (12) and (13), we get

$$\left[\frac{\partial H}{\partial S}\right]_P = T \text{ and } \left[\frac{\partial H}{\partial P}\right]_S = V. \qquad ...(14)$$

And since $dH$ is a perfect differential

$$\frac{\partial}{\partial P}\left[\frac{\partial H}{\partial S}\right]_P = \frac{\partial}{\partial S}\left[\frac{\partial H}{\partial P}\right]_S$$

Using (14), we get

or $$\left[\frac{\partial T}{\partial P}\right]_S = \left[\frac{\partial V}{\partial S}\right]_P \qquad ...(15)$$

This is the *third thermodynamical relation of Maxwell.*

**4. Gibb's Potential G.** The Gibb's function is mathematically defined as

$$G = H - TS \text{ or } F + PV, \qquad ...(16)$$

As enthalpy $H = U + PV$

$$\therefore \quad G = U + PV - TS$$

Differentiating $$\begin{aligned} dG &= dU + PdV + V\,dP - T\,dS - S\,dT \\ &= dQ + VdP - dQ - S\,dT \end{aligned}$$

[Since from I law $dQ = dU + PdV$
and from II law $dQ = TdS$]

$$\therefore \quad dG = V\,dP - S\,dT \qquad ...(17)$$

In an isobaric-isothermal process $dP = 0$ and $dT = 0$

$$\therefore \quad dG = 0 \text{ or } G = \text{constant}$$

Thus Gibb's function is *that physical quantity which remains constant inreversible isobaric process.*

As $$G = H - TS$$

In an irreversible process the entropy decreases and so Gibb's function always decreases. Thus Gibb's function remains constant in reversible isothermal and isobaric process and decreases in irreversible process. It never increases.

From (17) the Gibb's function is the function of independent variables $P$ and $T$ *i.e.*

$$G = G(P, T)$$

$$\therefore \quad dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT \qquad ...(18)$$

Comparing (17) and (18) we get

$$\therefore \quad \left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S$$

And since $dG$ is a perfect differential

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P$$

or $$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \qquad ...(19)$$

This is the *fourth thermodynamical relation of Maxwell.*

Thus we see that the four thermodynamical potential $U(S, V)$; $F(T, V)$; $H(S, P)$ and $G(T, P)$ lead us to four thermodynamical relations-known as Maxwell's relations, given below :

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad ...(i)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad ...(ii)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad ...(iii)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \qquad ...(iv)$$

## 2.2 Deduction from Thermodynamical Relations

1. *Clausius Clapeyron's equation.* Maxwell's second thermodynamical relation is

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Multiplying both sides by $T$, we get

$$T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

But from second law of thermodynamics $T\,\delta S = \delta Q$, therefore

$$\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

Here $\left(\frac{\partial Q}{\partial V}\right)_T$ represents the quantity of heat absorbed or liberated per unit change in volume at constant temperature. This means that at constant temperature the heat absorbed or liberated brings out simply a change in the volume of the substance. Therefore this amount of heat absorbed or liberated at constant temperature must be the *latent heat* and change in volume must be due to a *change of state.* Considering a unit mass of the substance, let $L$ be the *latent heat* when the substance changes in volume from $V_1$ to $V_2$ at constant temperature, then

$$\delta Q = L \text{ and } \delta V = V_2 - V_1.$$

Substituting these values in above expansion, we get

$$\left(\frac{L}{V_2 - V_1}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

or

$$\frac{L}{V_2 - V_1} = T\frac{dP}{dT}$$

$$\therefore \quad \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}.$$

This equation is called the *Calusius Clapeyron's latent heat equation.*

2. *Ratio of isothermal and adiabatic elasticities.* The coefficient of volume elasticity is defined as

$$E = \frac{\text{Stress}}{\text{Volume Strain}} = -\frac{dP}{dV/V} = -V\frac{dP}{dV}$$

Therefore the adiabatic elasticity $E_S$ (entropy constant) and isothermal elasticity $E_T$ (temperature constant) are given by

$$E_S = -V\left(\frac{\partial P}{\partial V}\right)_S$$

and

$$E_T = -V\left(\frac{\partial P}{\partial V}\right)_T.$$

Hence

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial P}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial V}\right)_T} = \frac{\left(\frac{\partial P}{\partial T}\cdot\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial S}\cdot\frac{\partial S}{\partial V}\right)_T} = \frac{\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial S}\right)_T\left(\frac{\partial S}{\partial V}\right)_T}.$$

But from thermodynamical relations, we have

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \Rightarrow \left(\frac{\partial P}{\partial T}\right)_S = \left(\frac{\partial S}{\partial V}\right)_P$$

and

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P$$

Using these relations, we get

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial S}{\partial V}\right)_P\left(\frac{\partial P}{\partial S}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial P}{\partial T}\right)_V} = \frac{\left(\frac{\partial S/\partial V}{\partial T/\partial V}\right)_P}{\left(\frac{\partial P/\partial S}{\partial P/\partial T}\right)_V} = \frac{(\partial S/\partial T)_P}{(\partial S/\partial T)_V}$$

or

$$\frac{E_S}{E_T} = \frac{T\left(\frac{\partial S}{\partial T}\right)_P}{T\left(\frac{\partial S}{\partial T}\right)_V} = \frac{\left(\frac{\partial Q}{\partial T}\right)_P}{\left(\frac{\partial Q}{\partial T}\right)_V} = \frac{C_P}{C_V} \qquad (\because T\delta S = \delta Q).$$

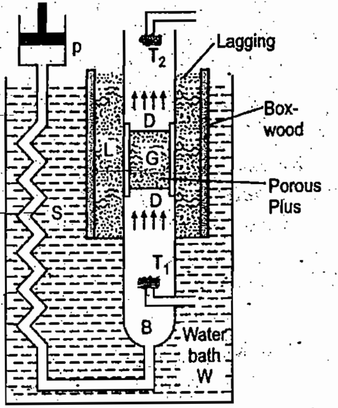
Since $\left(\frac{\partial Q}{\partial Q}\right)_Y = C_P$ and $\left(\frac{\partial Q}{\partial Q}\right)_V = C_V$.

*Thus, the ratio of adiabatic and isothermal elasticities of any substance is equal to the ratio of the heat capacities of the substance at constant pressure and constant volume.*

### 3. Joule-Kelvin Expansion : The Porous plug experiment.

Joule in 1952, in collaboration with Lord Kelvin (Thomson), devised a very sensitive technique known as *porous plug experiment* which established fully the existence of intermolecular attractions in the case of all actual gases.

*The principle of Joule-Kelvin experiment* consists in forcing a gas at a constant pressure through a porous plug thermally insulated from outside. The porous plug consists of a compressed porous material like cotton, wool or silk fiber having a number of narrow orifices in parallel. *When a gas from a constant high pressure side is made to pass through a polous plug in a region of constant low pressure, it suffers a change in temperature.* This is called the *Joule-Thomson or Joule-Kelvin effect.*



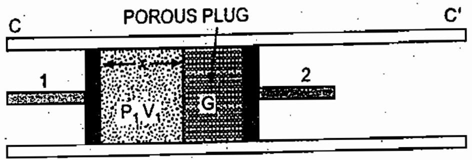
(Fig. 2.1)

*The apparatus used in porous plug experiment* is shown in Fig. 2.1. The gas under test is ~~compressed to a high~~ pressure with the help of piston $P$ and is compressed to a high pressure tube $S$ immersed in a water bath $W$ maintained at a constant temperature.

The compressed gas enters tube $B$ fitted with a porous plug $G$ of cotton wool or silk fibre, The plug is contained between two perforated brass discs $D, D$. A vessel $L$ filled with cotton-wool surrounds the tube $B$ to provide a good thermal insulation to the porous plug. When the gas flows through the plug, in suffers a large drop in pressure. When its flow becomes steady, the temperature of the gas on the two sides of the plug is measured with platinum resistance thermometers $T_1$ and $T_2$. The pressure of the incoming gas in measured by a manometer (not shown in fig) while the pressure of the out-going gas is equal to the atmospheric pressure.

### Theory of Joule-Thomson Expansion : Constancy of Enthalpy.

Let us consider a simple arrangement shown in fig. 2.2 (a) representing the porous plug experiment. $CC'$ is a cylinder with nonconducting walls having a porous plug $G$ and fitted with two non-conducting pistons 1 and 2. A fixed mass of a gas having a volume $V_1$ is filled between the piston 1 and porous plug. Let this gas be highly compressed to a pressure $P_1$ and the pressure on other side of the plug be $P_2$, the piston 2 being kept just behing the plug preventing any gas from passing through it

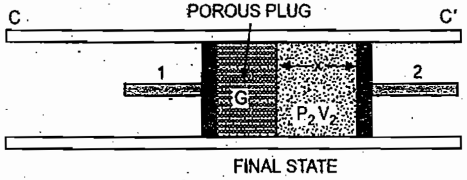


FINAL STATE

(Fig. 2.2 (a))

Fig. (a). Due to this large difference of pressure, the gas flows through the porous plug and gets throttled or 'wire drawn' *i.e.*, its molecules get further apart.

Let now piston 1 be moved slowly inwards in such a way so as to keep a *constant pressure* $P_1$ on left hand side of the plug as the gas escapes. The piston 2 will move slowly outwards so as to keep a lower constant pressure $P_2$ on the right hand side of plug. After all gas has passed through the plug the pistons 1 and 2 will be in the positions shown in fig. 2.2 (b), The gas will now occupy a greater volume say $V_2$. If $x_1$ and $x_2$ are the distances through which pistons 1 and 2 move and $A$ is the area of cross-section of the pistons, them



(Fig. 2.2 (b))

External work done on the gas by piston 1 $= P_1 \times A \times x_1$

$$= P_1V_1$$

External work done by the escaping gas on piston 2

$$= P_2 \times A \times x_2$$

$$= P_2V_2$$

∴ Net external work done by the gas in passing through the plug

$$= P_2V_2 - P_1V_1 \qquad \text{...(1)}$$

As the cylinder is thermally insulated, no heat is exchanged between the gas and its surroundings, *i.e.* $\Delta Q = 0$

Change in internal energy $= U_2 - U_1$

From I law of thermodynamics

$$\Delta Q = \Delta U + \Delta W$$

*i.e.* $$O = U_2 - U_1 + P_2V_2 - P_1V_1$$

This gives

$$U_1 + P_1V_1 = U_2 + P_2V_2 \qquad \text{...(2)}$$

$$H_1 = H_2 \qquad \text{...(3)}$$

The quantity $(U + PV)$, which is conservad, is called **enthalpy** or **total heat function** and denoted by the letter $H$. Hence in a **throtting process the initial and the final enthalpies are equal.** One is, however, not entitled to say that the enthalpy remains constant because the gas escapes under the effect of a finite pressure and it is not possible to describe the state of the gas throughout the change. It is why the Joule. Thomson effect is sometimes referred to as the iso-enthalpic effect.

It is obvious from eq. (2), if $P_2V_2 > P_1V_1$; $U_2 < U_1$. *i.e.* the internal energy of the gas will decrease on passing through the porous plug and hence a cooling will result. If any how $P_2V_2 < P_1V_1$ ; $U_2 > U_1$ *i.e.* the internal energy will increase and a heating will result. If anyhow $P_1V_2 = P_1V_1$ (*i.e.* the gas is perfect and obeys Boyle's Law). $U_1 = U_2$, the internal energy of the gas remains unchanged and its temperature remains unchanged.

**Expression for Change in Temperature in Joule Thomson Expansion.**

As all already shown during such an expansion, although there, is a pressure difference on the two sides of the porous plug, *the enthalpy H of the gas remains constant i.e.,*

$$H = U + PV = \text{Constant}$$

$$\therefore \quad dH = dU + P\,dV + V\,dP = 0$$

But since,

$$dU + PdV = dQ \qquad \text{(from first law of thermodynamics)}$$

$$= TdS \qquad \text{(from second law of thermodynamics)}$$

Therefore, $$TdS + VdP = 0 \qquad \text{...(4)}$$

If we take entropy $S$ as a function of two independent variables $P$ and $T$, the change in entropy $dS$ can be expressed as, remembering that $dS$ is a perfect differential

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP.$$

Substituting for $dS$ in eq. (4), we have

$$T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_P dP + VdP = 0 \qquad \text{...(5)}$$

Now $$T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_p = \text{specific heat at constant pressure}$$

And $$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{(from Maxwell's fourth relation)}$$

Them eq. (5) becomes

$$C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_T dT + V\,dP = 0$$

or $$C_P\,dT = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]dP$$

∴ Joule Thomson cooling $$\delta T = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]\delta P \qquad \text{...(6)}$$

Therefore, the Joule-Thomson coefficient

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \qquad \text{...(7)}$$

This expression gives the change in temperature $\partial T$ of a gas due to Joule-Thomson effect. Here $H$ stands for enthalpy, which remains constant in the process, $\delta P$ is the difference of pressure on the two sides of the porous plug and is necessarily negative as the pressure on the emergent side of the plug is lower.

**Case (i) For a perfect gas.**

Now for a *perfect gas*, the equation of state is

$$PV = RT.$$

Differentiating it with respect to $T$, taking $P$ constant, we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

or $$T\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}T = V \qquad (\because PV = RT)$$

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = 0$$

Therefore, eq. (7) gives

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = 0 \qquad \ldots(8)$$

Hence, *Joule Thomson coefficient for a perfect gas is zero.*

**Case (ii) For a real gas.**

For a *real (Vander Waals)* gas the equation of state is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT. \qquad \ldots(9)$$

Differentiating it with respect to $T$ taking $P$ constant, we have

$$\left(P + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P - \frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P (V - b) = R$$

or

$$\left[\frac{\partial V}{\partial T}\right]_P = \frac{R}{\left[P + \frac{a}{V^2}\right] - \frac{2a}{V^3}(V - b)}$$

$$= \frac{R}{\frac{RT}{V - b} - \frac{2a}{V^3}(V - b)} = \frac{R\,(V - b)}{RT - \frac{2a}{V^3}(V - b)^2} \qquad \text{[using (9)]}$$

$$T\left[\frac{\partial V}{\partial T}\right]_P = \frac{RT\,(V - b)}{RT - \frac{2a}{V^3}(V - b)^2}$$

$$= \frac{RT\,(V - b)}{RT - \frac{2a}{V^3}(V^2 + b^2 - 2Vb)}$$

As $b << V$ and the product $ab$ is very small, so we can write.

$$\frac{2a}{V^3}(V^2 + b^2 - 2Vb) \approx \frac{2a}{V^3} \cdot V^2$$

Thus

$$T\left[\frac{dV}{dT}\right]_V = \frac{RT\,(V - b)}{RT - \frac{2a}{V}} = \frac{V - b}{1 - \frac{2a}{VRT}}$$

$$= (V - b)\left[1 - \frac{2a}{VRT}\right]^{-1}$$

Expanding binomially and neglecting smaller terms, we have

$$T\left[\frac{\partial V}{\partial T}\right] = (V - b)\left[1 + \frac{2a}{VRT}\right]$$

$$= V - b + \frac{2a}{RT} \text{ neglecting smaller term } \frac{2ab}{VRT}$$

or

$$T\left[\frac{\partial V}{\partial T}\right] - V = \frac{2a}{RT} - b$$

Substituting this result in eq. (7), we have

$$\mu = \left[\frac{\partial T}{\partial P}\right]_H = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right] \qquad \ldots(8)$$

This gives the Joule-Thomson effect for an actual gas. It is clear from this expression that (i) if $\frac{2a}{RT} > b$ or $T < \frac{2a}{Rb}$ then $\left[\frac{\partial T}{\partial P}\right]_H$ is positive. But since $\partial P$ is necessarily a negative quantity (Pressure on emergent side of the plug is lower). $\partial T$ is also negative and hence the gas will be cooled on passing through the porous plug.

(ii) If $\frac{2a}{RT} < b$ or $T > \frac{2a}{RT}$, then $\left[\frac{\partial T}{\partial P}\right]_H$ is negative and hence $\partial T$ will be positive *i.e.*, *the gas will be heated* up on passing through the porous plug.

(iii) $\frac{2a}{RT} = b$ or $T = \frac{2a}{Rb}$, $\left[\frac{\partial T}{\partial P}\right]_H = 0$ *i.e.* the gas on passing through the porous plug shows *no change in temperature of inversion* and it denoted by

$$T_i = \frac{2a}{Rb}$$

For most of the gases, the ordinary working temperatures are below the temperature of inversion and hence they show a cooling effect. Temperature of inversion for hydrogen and helium are much below the ordinary temperatures and hence at these temperatures they show a heating effect. If, however, these gases are precooled below their inversion temperature before allowing to undergo a Joule–Thomson expansion, they will also show a cooling effect.

**4. Change of Temperatue during Adiabatic Process.**

(i) From first thermodynamic relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

On multiplying and dividing by $T$ the right hand side, we get

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{T}\left(\frac{\partial P}{\partial S}\right)_V$$

As $\delta Q = T\delta S$, we have

$$\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial P}{\partial Q}\right)_V$$

Since an increase in the amount of heat at constant volume always results in an increase of pressure, the term $[\partial P/\partial Q]_V$ is positive. Hence the term $[\partial T/\partial V]_S$ should be negative that is *i.e.* the temperature should decrease with an increase in volume under condition of constant entropy (adiabatic process). In other words, an adiabatic expansion must result in a fall of temperature

(ii) In a similar way, third thermodynamic relation

$$\left[\frac{\partial T}{\partial P}\right]_S = \left[\frac{\partial V}{\partial S}\right]_V$$

provides

$$\left[\frac{\partial T}{\partial P}\right]_S = T\left[\frac{\partial V}{\partial Q}\right]_P$$

Since an increase in the quantity of heat at constant pressure always results in an increase in volume the term $[\partial V/\partial Q]_P$ is positive. Hence the term $[\partial T/\partial P]_S$ must also be positive *i.e.*, the temperature must increase with an inerease in pressure under conditions of constant entropy. In other words, *an adiabatic compression always results in an increase of temperature.*

## 5. TdS Equations

(i) Let us take entropy $S$ of a thermodynamic system as a function of temperature $T$ and volume $V$

*i.e.* $$S = S(T, V)$$

Taking its perfect differential

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad \text{...(1)}$$

Multiplying throughout by $T$, we get

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \qquad \text{...(2)}$$

But $$T\left(\frac{dS}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = C_V$$

Also $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (Maxwell's II relation)

Making these substitutions in (2), we get

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad \text{...(3)}$$

(ii) Let us take entropy as a function of temperature $T$ and pressure $P$, *i.e.*

$$S = S(T, P)$$

Taking its perfect differential

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP.$$

Multiplying throughout by $T$, we get

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \qquad \text{...(4)}$$

But $T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P.$

and $$\left\{\frac{\partial S}{\partial P}\right\}_T = -\left\{\frac{\partial V}{\partial T}\right\}_P \qquad \text{[Maxwell's IV relation]}$$

Substituting these values in (4), we get

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{...(5)}$$

## 6. Energy Equation

Let a thermodynamic system undergo an infinitesimal reversible process between two equilibrium states. Its general behaviour may be expressed by the first and second laws of thermodynamics, which are

$$dQ = dU + P\,dV$$

and $$dQ = T\,dS.$$

These give $dU + P\,dV = T\,dS$

or $$dS = \frac{dU + P\,dV}{T}.$$

Making this substitution in Maxwell's 2nd relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ we get

$$\frac{1}{T}\left(\frac{\partial U + P\,\partial V}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

or $$\left(\frac{\partial U}{\partial V}\right)_T + P = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \qquad \text{...(1)}$$

This is the required energy equation. Le us apply it to gases :

**(i) Ideal gas :** For 1 mole of an ideal gas, we have

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

or $$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

or $$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V} = P.$$

Putting this in eq. (1), we get

$$\left(\frac{\partial U}{\partial V}\right)_T = 0.$$

Thus, *the internal energy of an ideal gas is independent of its volume at constant temperature.*

**(ii) Vander Waals' Gas :** For 1 mole of an actual gas, we have

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \text{...(2)}$$

or $$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

or $$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}.$$

Putting this in eq. (1), we get

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V - b} - P.$$

Putting the value of $\frac{RT}{V-b} - P$ from eq. (2), we have

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}, \qquad \text{..(3)}$$

which is positive. This means that *the internal energy of an actual gas depends on the volume at constant temperature.*

### 7. Vander Waals' Gas Under Free Expansion

Suppose 1 mole of a real gas undergoes free expansion. Let $\Delta T$ be the change in temperature corresponding to change in volume $\Delta V$. Then, by reciprocity theorem, we have

$$\left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T \qquad \text{...(1)}$$

Now, the molar specific heat at constant volume is defined as

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

By first law :

$$dQ = dU + P\,dV$$
$$= dU. \qquad \text{(at constant volume)}$$
$$\therefore \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Making this substitution in eq. (1), we get

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$$

But for a Vander Waals' gas, we have

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$
$$\therefore \quad \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\frac{a}{V^2}$$

For a finite change in volume, the change in temperature is

$$\Delta T = -\frac{1}{C_V}\frac{a}{V^2}\Delta V.$$

### 8. Heat Capacity Equations

The molar specific heats at constant pressure and at constant volume of a thermodynamic system are expressed by

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \text{ and } C_V = \left(\frac{\partial Q}{\partial T}\right)_V$$
$$\therefore \quad C_P - C_V = \left(\frac{\partial Q}{\partial T}\right)_P - \left(\frac{\partial Q}{\partial T}\right)_V$$

But $dQ = T\,dS$.

$$\therefore \quad C_P - C_V = T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V \qquad \text{...(1)}$$

Now, if the entropy $S$ is considered as a function of $T$ and $V$, then, since $dS$ is a perfect differential, we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

or

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Multiplying by $T$ throughout, we have

$$T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Substituting this in eq. (1), we have

$$C_P - C_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad \text{...(2)}$$

But $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ by Maxwell's second relation.

$$\therefore \quad C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \qquad \text{...(3)}$$

This is the required expression.

Now, from the first and second laws, we can write

$$T\,dS = dU + P\,dV$$

or

$$T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P.$$

Making this substitution in eq. (2), we have

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{...(4)}$$

This is the alternative expression.

**Perfect gas :** For one mole of a perfect gas, we have

$$PV = RT$$
$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \text{ and } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Making these substitutions in eq. (3), we get

$$C_P - C_V = \frac{R^2 T}{PV}$$

But $pV = RT$.

$$\therefore \quad C_P - C_V = R.$$

**Vander Waals' Gas :** Fofr a Van der Waals' gas, we have

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT,$$

where $a$ and $b$ are constants. This may be written as

$$\left(P + \frac{a}{V^2}\right) = \frac{RT}{V - b}.$$

Differentiating it with respect to $T$ at constant volume, we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b},$$

and differentiating with respect to $T$ at constant pressure,

$$-\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P=-\frac{RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_P+\frac{R}{V-b}$$

or
$$\left(\frac{\partial V}{\partial T}\right)_P\left[\frac{RT}{(V-b)^2}-\frac{2a}{V^3}\right]=\frac{R}{V-b}$$

or
$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{\dfrac{R}{V-b}}{\dfrac{RT}{(V-b)^2}-\dfrac{2a}{V^3}}$$

Substituting the values of $\left(\frac{\partial P}{\partial T}\right)_V$ and $\left(\frac{\partial V}{\partial T}\right)_P$ in eq. (3), we get

$$C_P-C_V=\frac{T\dfrac{R}{(V-b)}\dfrac{R}{(R-b)}}{\dfrac{RT}{(V-b)^2}-\dfrac{2a}{V^3}}=\frac{R}{1-\left(\dfrac{2a}{V^3}\right)\dfrac{(V-b)^2}{RT}}$$

Since $b << V$; we may replace $(V-b)$ by $V$ in the second power. Then, we get

$$C_P-C_V=\frac{R}{1-\left(\dfrac{2a}{V^3}\right)\dfrac{V^2}{RT}}$$

$$=R\left(1-\frac{2a}{RTV}\right)^{-1}$$

Expanding by binomial theorem and remembering that $a$ is very small, we get

$$C_P-C_V=R\left(1+\frac{2a}{RTV}\right)$$

## SOLVED EXAMPLES

**Ex. 1.** *Write down the fundamental equation of thermodynomics for a paramagnetic salt when its magnetism I is changed-in a magnetic field. Write Maxwell's relations in this case. If the paramagnetic salt is demagnetised adiabatically, derive an expression for the change in temperature.*

**Solution.** In this case the work done on the salt $= H\,dI$, where $H$ is magnetic field.

$\therefore$ The work done by the salt $= -H\,dI$.

If we assume that there is no change of volume, first law of thermodynamics give

$$dQ=dU-H\,dI. \qquad \text{...(1)}$$

From second law of thermodynamics,

$$dQ=T\,dS. \qquad \text{...(2)}$$

Combining the first and second laws, *i.e.* equations (1) and (2), the fundamental equation of thermodynamics can be written in the form

$$T\,dS=dU-H\,dI \qquad \text{...(3)}$$

Comparing this equation with equation $TdS=dU+PdV$ we see that for writing Maxwell's relations in this case $P$ should be replaced by $-H$ and $V$ by $I$ *Maxwell's relations in this case* are

$$\left.\begin{aligned}\left(\frac{\partial T}{\partial I}\right)_S&=\left(\frac{\partial H}{\partial S}\right)_I &&\text{...(i)}\\ \left(\frac{\partial S}{\partial I}\right)_T&=-\left(\frac{\partial H}{\partial T}\right)_I &&\text{...(ii)}\\ \left(\frac{\partial T}{\partial H}\right)_S&=-\left(\frac{\partial I}{\partial S}\right)_H &&\text{...(iii)}\\ \left(\frac{\partial I}{\partial T}\right)_H&=\left(\frac{\partial S}{\partial H}\right)_T &&\text{...(iv)}\end{aligned}\right\} \qquad \text{...(4)}$$

From equation [4 (iii)], we have

$$\left(\frac{\partial T}{\partial H}\right)_S=-\left(\frac{\partial I}{\partial S}\right)_H \qquad \text{...(5)}$$

Here the left hand side represents the rate of change of temperature with respect to field in adiabatic demagnetisation or magnetisation when $S$ is constant. The net change in temperature can be obtained by integrating equation (5).

Equation (5) may be written as

$$\left(\frac{\partial T}{\partial H}\right)_S=-\left(\frac{\partial I}{\partial T}\right)_H\left(\frac{\partial T}{\partial S}\right)_H=-\frac{\left(\dfrac{\partial I}{\partial T}\right)_H}{\left(\dfrac{\partial S}{\partial T}\right)_H}$$

$$=-\frac{T\left(\dfrac{\partial I}{\partial T}\right)_H}{T\left(\dfrac{\partial S}{\partial T}\right)_H}=-\frac{T\left(\dfrac{\partial I}{\partial T}\right)_H}{\left(\dfrac{\partial Q}{\partial T}\right)_H}. \qquad \text{(since } \delta Q=T\,\delta S\text{)}$$

or
$$\left(\frac{\partial T}{\partial H}\right)_S=-\frac{T}{mC_H}\left(\frac{\partial I}{\partial H}\right)_H',$$

where $C_H$ is the specific heat at constant magnetic field and $m$ is the mass of the substance.

Therefore the change in temperature $\delta T$ can be written as

$$\delta T=-\frac{T}{mC_H}\left(\frac{\partial I}{\partial T}\right)_H\delta H. \qquad \text{...(6)}$$

It is found that $\left(\frac{\partial I}{\partial T}\right)_H$ is always negative. Hence the coefficient of $\delta H$ on R.H.S. of eqn. (6) is positive. If there is decrease in $H$, $\delta H$ is negative and so is $\delta T$. Thus. there is *cooling in the process of adiabatic demagnetisation.* If $H$ falls from a value $H$ to zero, the total cooling can be obtained by integrating equation (6) provided $\left(\frac{\partial I}{\partial T}\right)_H$ and $C_H$ are known functions of $T$ and $H$.

## 2.3 Some Other Properties of Thermodynamic Potentials

It is desirable at this stage to recapitualate the more important results reached and to state some further relations involving thermodynamic potentials $U$, $F$, $H$ and $G$.

**Intrinsic energy (or internal energy) U :** It is inherent energy stored by molecules of system and is *defined* by the equation, (first law of thermodynamics)

$$dU = dQ - dW. \qquad \text{...(1)}$$

Here $dQ$ is the heat supplied to the system, $dU$ is the change in intrinsic energy and $dW$ is the external work usually expressed by the typical term $P\,dV$.

From second law of thermodynamics, $dQ = T\,dS$.

$\therefore$ Equation (1) becomes

$$dU = T\,dS - P\,dV. \qquad \text{...(2)}$$

The *internal energy* depends **only on state** of the system and is the function of independent variables $S$ and $V$.

For an *adiabatic process* $dQ = 0$, therefore equation (1),

$$dU = -dW,$$

Thus, the change in internal energy when the system goes *adiabatically* from one state to the other is equal to the external *work done on the system*. This work done is the same for all adiabatic paths by which the system can pass from one state to the other. Thus, when a system passes from one state to the other, the change in internal energy is independent of the path followed between the two states; but depends only on initial and final states.

**Enthalpy (or total heat) H :** The enthalpy $H$ is defined by the equation.

$$H = U + PV. \qquad \text{...(3)}$$

This function $H$ is often called ***total heat constant***; but the name *enthalpy*, suggested by K. Onnes, is to be preferred. This function is of particular importance in the thermodynamics of engineering.

From equation (3) it is obvious ~~that the~~ entalpy ~~is equal to~~ the sum of the internal energy and a certain amount of external work $PV$. According to Ewing the enthalpy of a substance is defined as *the external work which would be done if the substance would be imagined to start from no volume at all and to expand to its actual volume under a constant pressure equal to its actual pressure.*

Differentiating equation (3), we get

$$\begin{aligned} dH &= dU + P\,dV + V\,dP \\ &= (T\,dS - P\,dV) + P\,dV + V\,dP \qquad \text{[using eqn. (2)]} \\ &= T\,dS + V\,dP. \qquad \text{...(4)} \end{aligned}$$

Obviously the enthalpy is the function of independent variables $S$ and $P$.

If any process is carried out at constant pressure, then $dP = 0$; so that equation (4) becomes

$$dH = T\,dS = dQ.$$

Thus, is in any system the heat is supplied at constant pressure ($dP = 0$), then the change in enthalpy is equal to the heat suplied. This justified the name of term *'heat function'* or *'heat content'* in describing enthalpy $H$.

**Helmholtz function (or Helmholtz free energy) F :** Maxwell called this function as *available energy*. It is also called the *thermodyanamic potential at constant volume*. This is defined by the equation

$$F = U - TS. \qquad \text{...(5)}$$

Differentiating above equation, we have

$$\begin{aligned} dF &= dU - d\,(TS) \\ &= (T\,dS - P\,dV) - T\,dS - S\,dT. \end{aligned}$$

$$\therefore \qquad dF = -S\,dT - P\,dV.$$

The Helmholtz function is thus the function of independent variables $T$ and $V$. For a reversible *isothermal change*, $dT = 0$, therefore,

$$dF = -P\,dV = -dW,$$

*i.e.*,

$$dF = -dW.$$

This means that in *reversible isothermal changes*, the external *work* $dW$ is done wholly at the cost of Helmholtz free energy of the system. This shows why the name *free energy* is appropriate. The function $F$ is the available energy at constant temperature and corresponds exactly with the potential energy of a mechanical system. Just as a mechanical system uses up the potential energy in doing work, a thermodynamics system uses up a certain amount of this free or available energy in doing work at constant temperature. *The change in this free energy is exactly equal to the maximum work done in isothermal changes.* That is why Planck called the function $F$ as the *free energy for isothermal processes.*

From the equation (5) is follows that

$$U = F + TS. \qquad \text{...(8)}$$

This equation indicates that the internal energy of system is made up of two parts; (i) the free energy which is available energy in reversible isothermal changes, and (ii) $TS$ which of course is $U - F$, called the *latent energy or bound energy*, of the system as it can not be used in usual form.

Thus we have the relation :

$$\boxed{\textit{Intrinsic energy} = \textit{Helmholtz free energy} + \textit{Latent energy}}$$

The significance of the function $F$ can be understood in another way also. For it, consider a system that changes isothermally and reversibly from an initial state $i$ to a final state $f$, then

$$F_i = U_i - TS_i$$

and

$$F_f = U_f - TS_f$$

$$\begin{aligned} \therefore \qquad \Delta F = F_f - F_i &= (U_f - U_i) - T\,(S_f - S_i) \\ &= \Delta U - T\Delta S, \end{aligned}$$

But for a reversible process, $T\,\Delta S = \Delta Q$.

$$\therefore \qquad \Delta F = \Delta U - \Delta Q = -\Delta W \text{ (from first law).}$$

or

$$-\Delta F = \Delta W, \qquad \text{...(9)}$$

where $\Delta W$ is the reversible (and therefore maximum) work done by the system. It is obvious from equation that the *free energy F is such that its decrease gives the maximum amount of work available during an isothermal change of the system from one given state to another.*

It must be kept in mind that

(i) If the change is not isothermal, even then the free energy will change but then it will not be equivalent to the maximum work.

(ii) If the change is irreversible, but drop in free energy would exceed the output of work, *i.e.* $-\Delta F > \Delta W$.

**Gibbs function (or Gibbs free energy) G :** Gibbs function was called by Duhem the *thermodynamical potential at constant pressure.* This is defined by the equation

$$G = U - TS + PV \qquad \text{...(10)}$$

As $F = U - TS$, therefore we can write

$$G = F + PV. \qquad \text{...(11)}$$

This is the relation between Gibbs function and Helmholtz function. As enthalpy $H = U + PV$, therefore equation (10) can be written as

$$G = H - TS,$$

or

$$H = G + TS. \qquad \text{...(12)}$$

Thus

$$\boxed{\textit{Enthalpy} = \textit{Gibb's free energy} + \textit{Latent energy}}$$

Differentiating equation (10), we have:

$$dG = dU - d(TS) + d(PV)$$

$$= (dU - TdS) - SdT + PdV + VdP$$

$$= -dW - SdT + PdV + VdP.$$

If the process is *isothermal and isobaric* (*i.e.*, if $dT = 0$ and $dP = 0$), then

$$dG = -(dW - PdV) = -dA,$$

where $dA\ (= \bar{d}W - PdV)$ is the amount of work obtained exclusive of the mechanical work ($PdV$) involved in the change of the system.

Thus $$dG + dA = 0, \qquad ...(13)$$

This means that *in reversible isothermal and isobaric changes the external work, exclusive of any PdV work, is done wholly at the cost of Gibb's free energy* or the Gibb's potential G is such a function that its decrease during isothermal isobaric process is equal to the net work obtained, *i.e.*,

$$-dG = dW - PdV$$

$$= dA \text{ (net work).}$$

## 2.4 Relation of F and G with the Parameters of the System

**The Gibbs-Helmholtz Relation:** We have already defined by the Helmholtz free energy $F$ by relation.

$$F = U - TS, \qquad ...(1)$$

so that $$dF = dU - TdS - SdT = (TdS - PdV) - TdS - SdT$$

⇒ $$dF = -PdV - SdT \qquad ...(2)$$

And the Gibb's potential $G$ by the relation.

$$G = H - TS = U + PV - TS, \qquad ...(3)$$

so that $$dG = dU + PdV + VdP - TdS - S\,dT$$

$$= TdS + VdP - TdS - SdT$$

⇒ $$dG = VdP - SdT. \quad (\text{Since } dU + PdV = TdS) \qquad ...(4)$$

In many chemical changes $P$ and $V$ remain constant. In such cases $dF = dG$.

We shall now consider different processes

(i) **Isothermal Process**

$$dF_T = -PdV, \text{ or } \left(\frac{\partial F}{\partial V}\right)_T = -P. \qquad ...(5)$$

and $$dG_T = VdP, \text{ or } \left(\frac{\partial G}{\partial P}\right)_T = V \qquad ...(6)$$

*(ii)* ***Isobaric process****, i.e.,* when pressure is constant

$$dG_P = -SdT, \text{ or } \left(\frac{\partial G}{\partial T}\right)_P = -S. \qquad ...(7)$$

*Thus entropy is a measure of the rate of change of Gibb's potential with temperature at constant pressure.*

Substituting the value of $S$ from equation (7) in (3) *i.e.* $G = H - TS$, we get

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P \qquad ...(8)$$

*(iii)* ***Isochoric processes****, i.e.* when volume is constant

$$dG_V = -SdT, \text{ or } \left(\frac{\partial F}{\partial T}\right)_V = -S. \qquad ...(9)$$

*Thus entropy is a measure of the rate of change of free energy with temperature at constant volume.*

Now substituting the value of $S$ from eqn. (9) in (1) (*i.e.*, $F = U - TS$) we get

$$F = U + T\left(\frac{\partial F}{\partial T}\right)_V. \qquad ...(10)$$

Equations (8) and (10) co-relating Gibb's potential $G$ with enthalpy $H$ and Helmholtz free energy $F$ with internal energy $U$ are known as ***Gibb's Helmholtz relations.*** These are the very important thermodynamic relations because they do not involve the calculation of entropy which is often difficult. Such relations may also be derived in other forms:

Consider a system undergoing physical or chemical changes reversibly and isothermally from state 1 to state 2. Let these states be specified by the functions $U_1, H_1, S_1, F_1, G_1$ and $U_2, H_2, S_2, F_2, G_2$. Then

$$F_1 = U_1 - S_1 \text{ and } F_2 = U_2 - TS_2$$

∴ $$\Delta F = F_2 - F_1 = (U_2 - U_1) - T(S_2 - S_1) = \Delta U - T(S_2 - S_1).$$

Substituting for $S_2$ and $S_1$ from equation (9), we have

$$\Delta F = \Delta U + T\left[\left(\frac{\partial F_2}{\partial T}\right)_V - \left(\frac{\partial F_1}{\partial T}\right)_V\right]$$

or $$\Delta F = \Delta U - T\left[\frac{\partial(\Delta F)}{\partial T}\right]_V. \qquad ...(11)$$

Similarly $$G_1 = H_1 - TS_1 \text{ and } G_2 = H_2 - TS_2.$$

Therefore $$\Delta G = \Delta H - T(S_2 - S_1)$$

Substituting for $S_2$ and $S_1$ from equation (7), we have

$$\Delta G = \Delta H + T\left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right]$$

or $$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P. \qquad ...(12)$$

These relations are generally used particularly while applying thermodynamics to chemical processes.

**Gibb's Helmholtz Equation for a Reversible Cell.**

The Gibb's Helmholtz equation for the e.m.f. of a cell may obtained as follows:

Let a quantity of charge $dq$ pass through a reversible cell in the direction of discharge, the volume of cell remaining constant. The work done by the cell

$$dW = Edq \qquad ...(1)$$

where $E$ is e.m.f. *i.e.* work done per unit charge, of the cell at the temperature $T$ of the experiment.

For a thermodynamic system $dW = pdV$

Thus here $E$ takes the place of $p$ and $q$ that of volume $V$.

The first and second laws of thermodynamics are

$$dQ = dU + dW \text{ (I law)}$$

and $$dQ = TdS \text{ (II law)}$$

Combining these laws

$$TdS = dU + dW$$

i.e. $$TdS = dU + Edq \qquad \ldots(2)$$

The free energy $F$ is given by

$$F = U - TS$$

$\therefore$ $$dF = dU - d(TS) = dU - TdS - SdT$$

Using (2), we get

i.e. $$dF = -Edq - SdT \qquad \ldots(3)$$

i.e. $F$ is the function independent variables $q$ and $T$.

$$F = F(q, T)$$

Taking its perfect derivative

$$dF = \left[\frac{\partial F}{\partial q}\right]_T dq + \left[\frac{\partial F}{\partial T}\right]_q dT \qquad \ldots(4)$$

Comparing (3) and (4), we get

$$\left[\frac{\partial F}{\partial q}\right]_T = -E \text{ and } \left[\frac{\partial F}{\partial T}\right]_q = -S \qquad \ldots(5)$$

Taking second derivatives

$$\frac{\partial^2 F}{\partial T \partial q} = -\left[\frac{\partial E}{\partial T}\right]_q \text{ and } \frac{\partial^2 F}{\partial q \partial T} = -\left[\frac{\partial S}{\partial q}\right]_T$$

As $F$ is a prefect differential, we get

$$\left(\frac{\partial E}{\partial T}\right)_q = \left(\frac{\partial S}{\partial q}\right)_T \qquad \ldots(6)$$

This is analogous to Maxwell's second relation

As $$dQ = TdS \text{ i.e. } dS = \frac{dQ}{T}.$$

$\therefore$ $$\left[\frac{\partial S}{\partial q}\right]_T = \frac{1}{T}\left[\frac{\partial Q}{\partial q}\right]_T \qquad \ldots(7)$$

Also $$dQ = dU + dW = dU + Edq$$

Substituting volume of $dQ$ in (7), we get

$$\left[\frac{\partial S}{\partial q}\right]_T = \frac{1}{T}\left[\frac{\partial U + E\partial q}{\partial q}\right]_T$$

$$= \frac{1}{T}\left[\left(\frac{\partial U}{\partial q}\right)_T + E\right]$$

Substituting this in equation (6), we get

$$\left[\frac{\partial E}{\partial T}\right]_q = \frac{1}{T}\left[\left\{\frac{\partial U}{\partial q}\right\}_T + E\right]$$

i.e. $$-\left[\frac{\partial U}{\partial q}\right]_T = E - T\left[\frac{\partial E}{\partial T}\right]_q \qquad \ldots(8)$$

This is Gibb's-Helmholtz equation for a reversible cell.

The e.m.f. of cell $E$ is given by

$$\boxed{E = T\left[\frac{\partial E}{\partial q}\right]_q - \left[\frac{\partial U}{\partial q}\right]_T} \qquad \ldots(9)$$

In this equation $\left[\frac{\partial U}{\partial q}\right]_T$ respresents the loss of energy by the cell per unit charge passing through it. This loss of energy is derived from the stored chemical energy.

As current passes through the cell, a chemical reaction takes place, thereby releasing energy which enables the current to pass through an external resistance and develop heat energy or to run a motor and do work. It the chemical reaction takes place by itself, the internal energy released would appear is the **heat of reaction**, given by

$$Q = Fv\left[\frac{\partial U}{\partial q}\right]_T \qquad \ldots(10)$$

where v is the valency and $F$ is **Faraday Constant** = 96500 coulomb/g-equivalent.

Using (8), this may be expressed as

$$Q = Fv\left[E - T\left\{\frac{\partial E}{\partial T}\right\}_q\right] \qquad \ldots(11)$$

Thus by measuring the e.m.f. and its temperature coefficient, the heat of chemical reaction may be evaluated.

The e.m.f. measurements may be carried out by a sensitive potentiometer.

For a **Daniell cell.**

At 0°C or T = 273K; $E = 1{\cdot}096V$,

$$\frac{\partial E}{\partial T} = 3{\cdot}4 \times 10^{-5}\ V/\text{deg},\ v = 2$$

The equation of reaction is

$$Zn + CuSO_4(aq.) = [Cu] + ZnSO_4(aq.) + Q$$

Substituting observed values

$$Q = 96500 \times 2\,[1{\cdot}096 - 273 \times 3{\cdot}4 \times 10^{-5}]\text{ joule}$$

$$= \frac{96500 \times 2\,[1{\cdot}096 - 0{\cdot}009\ 282]}{4{\cdot}2}\text{ cal.}$$

$$= \frac{193000 \times 1{\cdot}086718}{4{\cdot}2} = 49937\text{ cal.}$$

This is in close agreement with experimental value 50130 cal.

## 2.5 Thermodynamic Equilibria

A system is said to be in state of *mechanical equilibrium* if there is no unbalanced force in the interier of the system and also none between the system and its surrountings. If this condition is not satisfied then either the system or system and surroundings both will undergo a change of state which ceases only when the mechanical equilibrium is attained. If a system in mechanical equilibrium does not show any tendency to undergo a spontaneous change of internal structure *e.g.*, a chemical reaction, it is said to be in a state of *chemical equilibrium*. A system not in chemical equilibrium undergoes a change of state until chemical equilibrium is reached. Similarly if there in no spontaneous change in the co-ordinates of a system which is in mechanical and chemical equilibrium and separated from its surroundings by a diathermic wall, it is said to be in *thermal equilibrium*. In thermal equilibrium all parts of a system are at the same temperature which is that of the surroundings. If this condition is not satisfied, a change of state takes place which ceases only when thermal equilibrium is reached. A system is said to be in a state of *thermodynamic equilibrium*, if the conditions for all the three (mechanical, chemical and thermal) types of equilibrium are satisfied and there is no tendency for any change of state either of the system or of the surroundings. The state of thermodynamic equilibrium can be described in terms of microscopic co-ordinates that do not involve time. *Thus, a system may be said to be in thermodynamics equilibrium if its state does not change in any with time.*

We shall now determine the general laws which govern the physical or chemical changes taking place in a system. The thermodynamic functions are particularly useful in determining the progress of a change in a system or its atainment of equilibrium. Let us suppose a system in contact with surroundings. Let there be an exchange of heat between them due to which there is a change in their entropies. Let $dS$ and $dS'$ be the intropy changes in the system and surrounding respectively. Then from the second law of thermodynamics (principle of increase of entropy).

$$dS + dS' \geq 0, \qquad \ldots(1)$$

where equality sign refers to reversible or quasi-static changes while inequality sign holds for natural (irreversible) changes. Further, if we regard the changes in the surroundings as reversible and consider that the surroundings supply heat $dQ$, then

$$dS' = -\frac{dQ}{T}$$

Let $dU$ be the increase in internal energy of the system and $dW$ the work done by the system, then from the first law of thermodynamics,

$$dQ = dU + dW.$$

Hence $$dS' = -\frac{dU + dW}{T}$$

Substituting this value of $dS'$ in eqn. (1), we have

$$dS - \frac{dU + dW}{T} \geq 0$$

or $$T\,dS - dU - dW \geq 0. \qquad \ldots(2)$$

It represents the general condition for a change in a thermodynamic system. It is obvious than

(i) For a real process to occur,

$$T\,dS - dU - dW > 0.$$

(ii) For a reversible changes of the system,

$$T\,dS - dU - dW = 0.$$

We shall now attempt to simplify this relation by imposing certain restraints and take up some special cases :

**(a) Adiabatic Equilibrium :** If the system is thermally isolated from its surroundings $dQ = 0$, and the condition for change in thermodynamic system redues to

$$dS \geq 0, \qquad \ldots(3)$$

where the quality sign holds for a reversible change and the inequality sign for a natural process. We shall now discuss two cases separately. If *the change takes place at constant volume*, $dW = P\,.\,dV = 0$. Further, since $dQ = 0$, $dU$ is also equal to zero and, we have

$$dU = 0,\ dV = 0,\ dS \geq 0.$$

The inequality sign is for real changes and the equality sign refers to the condition of equilibrium. As the entropy of an isolated system tends to increase, it goes on increasing till equilibrium is approached, *i.e.*, at equilibrium entropy becomes maximum. Thus, in all adiabatic changes of a system, the states of stable equilibrium is reached when entropy is maximum—it can not be a minimum for then the changes would take place quickely. Hence, at equilibrium $dS = 0$, when

$$dV = 0,\ dU = 0$$

or in another form $S = S_{\max}$ when $U =$ constant, $V =$ constant. ...(4)

The entropy may have several maxima and hence there may be several states of stable equilibrium. The equilibrium is absolutely stable for which the entropy is an absolute maximum.

*Now if the adiabatic change takes place at constant pressure*, $dU$ and $dW$ do not vanish individually but their sum is zero. Since $dW = P\,dV$, we may write

$$dU + P\,.\,dV = 0$$

or $$dU + d\,(P\,.\,V) = 0 \qquad [\text{as } P \text{ is constant}]$$

or $$d\,(U + PV) = 0$$

or $$dH = 0,$$

where $U + PV = H$ is the enthalpy or total heat. Thus, the equilibrium conditions are given by

$$dS = 0,\ dP = 0,\ dH = 0. \qquad \ldots(5)$$

**(b) Isothermal Equilibrium :** In order to derive the general conditions of isothermal equilibrium, we have to consider the two cases in which, while the infinitesimal change is taking place, the system is kept at constant volume or at constant pressure. *If the change takes place at constant volume*, the work done by the system $dW = P\,dV = 0$ and equation (2) can be written as

$$T\,dS - dU \geq 0$$

or changing sign $$dU - T\,dS \leq 0.$$

Since $T$ is constant $T\,dS = d\,(TS)$ and we have

$$d\,(U - TS) \leq 0 \text{ or } dF \leq 0.$$

That is, in a real process, if the system yiels no work $dF < 0$, *i.e.*, Helmholtz free energy $F$ decreases. There exists a minimum of free energy beyond which no spontaneous changes of state are possible. When equilibrium is attained, free energy becomes minimum and $dF = 0$, *i.e.*, in an infinitesimal virtual change, free energy must remain unaltered. Thus, the conditions of equilibrium are given by

$$dF = 0, \text{ when } dT = 0,\ dV = 0, \qquad \ldots(6)$$

or in another from

$$F = F_{\min} \text{ when } T = \text{constant},\ V = \text{constant} \qquad \ldots(7)$$

*Thus, at a state of equilibrium, the Helmholtz free energy assume a minimum value.*

Let us now consider the second case, *i.e.*, *when the infinitesimal virtual change is carred out at constant pressure*, the work done

$$dW = P\,dV = d\,(PV).$$

Hence equation (2) can be written as

$$T\,dS - dU - d\,(PV) \geq 0$$

or $$dU + d\,(PV) - d\,(TS) \leq 0$$

or $$d\,(U + PV - TS) \leq 0$$

or $$dG \leq 0.$$

That is in a real process, Gibb's potential $G$ decreases. There exists a minimum of Gibb's potential beyond which spontaneous changes are no longer possible. When equilibrium is reached Gibb's potential is minimum and $dG = 0$. Thus, for an isothermal equilibrium at constant pressure, the conditions of equilibrium are given by

$$dG = 0, \text{ when } dT = 0,\ dP = 0, \qquad \ldots(8)$$

or in another form

$$G = G_{\min}, \text{ when } T = \text{constant}, P = \text{constant} \qquad \text{...(9)}$$

Thus, an isothermal isobaric system is in equilibrium, if the Gibb's function is a minimum. Thus, the conditions of thermodynamic equilibrium are given by equations from (3) to (9).

Further according to Le Chatelier's law when a *system in eqilibrium is subjected to a constraint, a change takes place within the system tending to annul the effect of the constraint and to restore equilibrium.* In general, *every system in equilibrium is conservative and tends to remain unchanged.*

## 2.6 Theorem of Maximum Work

Let us consider a thermal isolated system consisting of several bodies not in thermal equilibrium with one another. While equilibrium is being established, the system may do work, on some external objects. The transition to equilibrium may, however, occur in different ways and the final equilibrium states will also be different. In particular the energy and entropy of the final equilibrium states will be different. The total work done on the external objects by non-equilibrium system will depend on the manner in which equilibrium is established. The question is how the equilibrium state must be reached in order that the system should do the maximum possible amount of work. Here we must exclude any work done by a general expansion of the system, since this work could also be done by a system in equilibrium and here we have to consider the work done by system not in equilibrium. Therefore, we shall assume that the total volume of the system is unchanged by the process (although it may vary during the process).

Let the original energy of the system be $U_0$ and the energy in the equilibrium state, as a function of the entropy in the equilibrium state, be $U(S)$. As the system is thermally insulated, the work done by the system is just the change in energy

*i.e.*
$$|W| = U_0 - U(S).$$

Here we have written as $|W|$, since $W < 0$, according to the convention as the work is done by the system.

Differentiating $|W|$ with respect to entropy $S$ of the final state at the constant volume, we get

$$\frac{\partial |W|}{\partial S} = -\left(\frac{\partial U}{\partial S}\right)_V$$

From first and second laws of thermodynamics

$$dU = TdS - PdV.$$

$$\Rightarrow \qquad \left(\frac{\partial V}{\partial S}\right)_V = T$$

$$\frac{\partial |W|}{\partial S} = -T$$

where $T$ is the temperature of the final state.

It is obvious that the derivative $\frac{\partial |W|}{\partial S}$ is negative, *i.e.*, $|W|$ decreases with increasing $S$. As the entropy of a thermally isolated system can not decrease The maximum possible value of $|W|$, therefore, occurs if entropy $S$ remains constant througout the process.

Thus, we conclude that the *system does maximum work when its entropy remains constant, i.e., when the process of reaching equilibrium is reversible.* This is called the **theorem of maximum work.**

## 2.7 Nernst's heat Theorem or the Third law of Thermodynamics

In 1906, Nernst proposed a general principle supported by a series of experimental tests on the problem of atomic heat at low temperature. It was proposed as *'the new heat theorem'* but is importance is so great that it is now frequently called the *third law of thermodynamics.* According to it, *"The heat capacities of all solids tends to zero as the absoluted zero of temperature is approached and that the internal energies and entropies of all substances become equal there, approaching their common value asymptotically."* This simple statement of Nernst follows neither from the first law (law of conservation of energy) nor from the second law (law of transmutability of energy) and is thus of the nature of a new law, usually called the *third law of thermodynamics.*

This theorem is useful in explaining the nature of bodies in neighbourhood of absolute zero temperature. Its importance lies in the fact that it permits the calculations of absolute values of entropy and the physical interpreatation of thermodynamic properties such as Helmholtz and Gibbs free energies etc. It can be conceived that as the temperature of a system tends to absolute zero, its entropy tends to a constant value which is independent of pressure and state of agregation etc. We may put it equal to zero so that the entropy of energy substance become normalized in an absolute way.

Now for isochoric process, we have Gibbs Helmholtz relation

$$F = U + T\left(\frac{\partial F}{\partial T}\right)_V \qquad \text{[Refer equation (10) section 2.4]}$$

We can express this relation taking two finite states as,

$$F_2 - F_1 = U_2 - U_1 + T\left\{\frac{\partial}{\partial T}(F_2 - F_1)\right\}_V \quad \ldots\ldots$$

or
$$F^* = U^* + T\left(\frac{\partial F^*}{\partial T}\right)_V \qquad \text{...(1)}$$

where $F^*$ now denotes the decrcase in free energy during the molecular reaction and $U^*$ is the decrease in inrenal energy. In order to determine the value of $F^*$. we should have therefore the knowledge of variation of $F^*$ with $T$. Thus how $F^*$ varies with temperature, particularly at low temperatures, is of considerable importance. We know, however, that $\frac{dU^*}{dT} = \Sigma\, nc$ where $c$ is the specific heat of the components taking part in the reaction and $n$ is the number of molecules, the sign $\Sigma$ denoting the summation over the number of molecules in a substance. If we consider the lowest limit of temperature, as propositioned by the Nernst heat theorem (*NHT*), to be zero, we have

$$U^* = \int_0^T \Sigma\, nc\, dT + \text{constant},$$

If at $T = 0$, the value of constant is obtained as $U_0{}^*$, then since $\left[\int \Sigma\, nc\, dT\right]_{T=0} = 0$, the value of constant is obtained as $U_0{}^*$.

Hence
$$U^* = U_0{}^* + \int_0^T \Sigma\, nc\, dT \qquad \text{...(2)}$$

Now *in order to calculate* $F^*$, differentiating equation (1) taking $F$ to be a function of temperature alone, we get

$$\frac{dF^*}{dT}=\frac{dU^*}{dT}+T\left(\frac{\partial^2 F^*}{\partial T^2}\right)_V+\frac{dF^*}{dT}$$

or

$$\frac{d^2F^*}{dT^2}=-\frac{1}{T}\frac{dU^*}{dT}=-\frac{1}{T}\Sigma nc$$

By integration, we have

$$\frac{dF^*}{dT}=-\int_0^T\frac{\Sigma nc}{T}dT+\text{constant.} \quad \text{...(3)}$$

Again, at $T=0, \int\frac{\Sigma nc}{T}dT=0$, because $c=0$ and thus we have the value constant equal to $\left(\frac{dF^*}{dT}\right)_0$, so that equation (3) gives

$$\frac{dF^*}{dT}=-\int_0^T\frac{\Sigma nc}{T}dT+\left(\frac{dF^*}{dT}\right)_0 \quad \text{...(4)}$$

The first term in this equation is easily calculated since variation of $c$ with $T$ is known from Debye's theory of specific heats. But the evaluation of second terms *i.e.*, integration constant presents difficulties. An accurate knowledge of its value is necessary for the determination of $\frac{dF^*}{dT}$ as well as of $F^*$ but there was no clue available, theoretical or experimental, for its determination. At this point Nernst put forward his Heat Theorem as a way out of this complification. Now $\left(\frac{dF^*}{dT}\right)_0=\Delta S_0$, the change in the entropy value of the system at the absolute zero when a unit reaction is permitted to take place. Nernst formulated that *"the entropy change in any isothermal reversible process of condensed system approaches zero as the temperature at which the process occurs approaches zero" i.e.,*

$$\left\{\frac{dF^*}{dT}\right\}_0=\Delta S_0=0 \quad \text{...(5)}$$

Therefore, combining equations (1), (2), (4) and (5), we get

$$F^*=U^*+T\left\{\frac{\partial F^*}{\partial T}\right\}_V=U_0{}^*+\int_0^T\Sigma nc\,dT-T\int_0^T\frac{\Sigma nc}{T}dT \quad \text{...(6)}$$

This relation enables us to determine the value of $F^*$ at any temperature. From this relation.

At $T=0$, $\quad F_0{}^*=U_0{}^*$ ...(7)

From which it follows that

$$\left(\frac{dF^*}{dT}\right)_0=0 \text{ and } \left(\frac{dU^*}{dT}\right)_0=0$$

This is why the functions $F^*$ and $U^*$ become equal at absolute zero although at $T\neq 0$, they are not so. This obviously represents an expression of Nernst Theorem as enunciated above. Thus mathematical relation

$$\lim_{T=0}\left(\frac{\partial F^*}{\partial T}\right)=\lim_{T=0}\left(\frac{\partial U^*}{\partial T}\right)=0 \quad \text{...(8)}$$

may be called the *Heat Theorem of Nernst,*

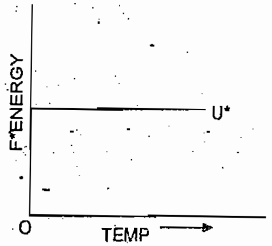


Fig. 2.5 (a)

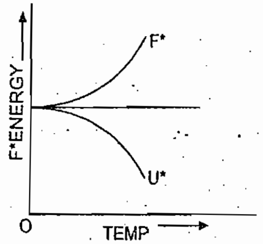


Fig. 1.6 (b)

According to Berthelot $F^*$ was equal to $U^*$ at all temperatures. The empirical principle of *Thomson and Barthelot states that, "Every chemical transformation which takes place without the intervention of external energy tends towards the production of that substance or systems of substance which will give the greatest development of heat i.e.* **that process is realized which is most exothermic."** Expressing mathematically, this principle of maximum work is equivalent to writing $F^*=U^*$ or $F^*-U^*=0$ as shown in fig. 2.3 (a) But Gibbs and Helmholtz found it to be erroneous and showed that $F^*-U^*=T\left\{\frac{\partial F^*}{\partial T}\right\}$ *i.e.*, $F^*=U^*$ only at the absolute zero temperature. Nernst went still further and showed that not only is $F^*=U^*$ at the absolute null-point but both $\frac{dF^*}{dT}$ and $\frac{dU^*}{dT}$ vanish there (absolute null). Thus the $F^*$ and $U^*$ curves becomes horizontal and coincide at the absolute zero *i.e.*, they have a common tangent which is horizontal as shown in fig. 2.3 (b). As is obvious the equality holds true for some range above and in the neighbourhood of absolute zero. If we know the curve for $U^*$ we may thus deduce the curve for $F^*$ either by a graphical method or by calculation.

**Alternative statements of the third law :** Just as there are several ways of stating the second law of thermodynamics, so are there also several ways of stating the third law. Nernst himself had originally stated that. *"No entropy change takes place when pure crystalline solid reacts at absolute zero."* Planck went a step further and formulated that not only does the total entropy change of a system vanish at absolute zero but that the entropies of the phases of the system becomes zero. He enunciated the third law as, *"The entropy of a solid or a liquid is zero at the absolute zero of temperature."* But perhaps by far the best statement of the law is due to Lewis and Randall both from the point of view of accuracy and as a generalization. The third law has been stated by them as, *"Every system has a finite positive entropy, but at the absolute zero of temperature the entropy becomes zero and does so in the case of a pure crystalline substance."*

The above statement is confined to pure crystalline solids because theoretical argument and experiment evidence have shown that the entropy of solutions and supercooled liquids is not zero even at absolute zero. For example, ice always has a residual entropy at the absolute zero. It also does not apply to the amophous class of substances like glass etc. These exceptions may however, be understood in terms of the definition of entropy that it is measure of disorder. Thus if any type of disorder remains at 0K, the entropy will remain larger that zero. In a glassy solid, the atomic arrangement is essentially similar to that in a liquid which is less regular than the structure of a crystal. Thus it is very reasonable that a glassy material may not approach zero entropy at 0K. This has been found true by Gibson and Giauque for a supercooled liquid *i.e.*; glassy glycerine of which the entropy at 0K was 5·6 cal/mole per *K* greater than that of crystalline glycerine. For perfect crystalline solids the law has been verified repeatedly and at present little doubt remains about the general validity of the above statement of the law.

It may be noted that it has now become possible to calculate the absolute value of entropy of pure substances from thermal data alone. The variation of entropy with temperature at constant pressure is given by the equation

$$dS = \frac{C_P\,dT}{T}$$

Further since the third law states that $\underset{T\to 0}{\text{Lt}}\; S = 0$ *i.e.*, the entropy can be represented by a definite integral instead of an indefinite one and we get

$$\int_{S=0}^{S=S} dS = \int_{T=0}^{T=T} \frac{C_P\,dT}{T}$$

or

$$S = \int_0^T \frac{C_P\,dT}{T} \qquad \text{...(1)}$$

which may be regarded as *mathematical statement of the third law* (or the theorem of Nernst). It is obvious that the *entropy of a substance at any temperature must be greater than its entropy at absolute zero.*

The third law has also been stated alternatively in a more elegent fashion in the following form :

*"It is impossible by any producer, no matter how idealized, to reduce any system to the absolute zero of temperature in a finite number of operations."* This is also called the principle of unatainability of absolute zero. It is to be noted that some writers take this statement to be more fundamental.

## 2.8 Consequences of the Third Law

From third law, we can arrive at a number of generalizations. We shall summarize here a series of the most simple consequences of this law as regards homogeneous substances.

**(1) The coefficient of thermal expansion of a pure solid :** The Nernst heat theorem leads to an interestng conclusion that the coefficient of expansion of a chemically homogeneous solid or liquid must be equal to zero in the limit when the temperature approaches the absolute zero. From Maxwell's second and fourth relations, we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

and

$$\left\{\frac{\partial S}{\partial P}\right\}_T = -\left\{\frac{\partial V}{\partial T}\right\}_P.$$

But in accordance with Nernst theorem, the entropy of a perfect crystalline solid is zero at 0K regardless of the pressure and volume. Thus, the quantities on the left hand side of these two equations should be zero, and, therefore

$$\lim_{T\to 0}\left\{\frac{\partial P}{\partial T}\right\}_V = 0,$$

and

$$\lim_{T\to 0}\left\{\frac{\partial V}{\partial T}\right\}_P = 0,$$

showing that the *pressure and volume coefficients tend to zero at the absolute zero of temperature.* The expansion coefficients of copper and silver have been determined upto very low temperature. The extrapolation of the curves—expansion versus temperture, to absolute zero confirms the conclusion. Actually it appears to approach zero asymptoticaly with zero slope.

**(2) The specific or molar heats $C_P$ and $C_V$ :** The specific heat at constant pressure ($C_P$) and constant volume ($C_V$) are defined by the equations

$$C_P = T\left\{\frac{\partial S}{\partial T}\right\}_P,\; C_V = T\left\{\frac{\partial S}{\partial T}\right\}_V$$

By integration. we obtain

At constant pressure,

$$S = \int_0^T \frac{C_P\,dT}{T},$$

and At constant volume,

$$S = \int_0^T \frac{C_V\,dT}{T}$$

where the integration constant has been put equal to zero by assuming the lower limit of integration to be equal to zero in accordance with Nernst's third law. Now, the third law implies that the entropy increase from 0K to any temperature $T$ must be finite *i.e.*, the value of $S$ must be finite at all temperatures. This means that at absolute zero, $C_P$ and $C_V$ must be zero. If it is not so, *i.e.*, $C_P$ and $C_V$ are finite, then $S$ can not be finite as demanded by the third law. Hence

$$\lim_{T\to 0} C_P = 0 \text{ and } \lim_{T\to 0} C_V = 0,$$

*i.e., all specific heats vanish at absolute temperature.* These results have been fully confirmed by experiments.

**(3) Temperature of change of phase :** We know that in a reversible change of phase at constant temperature and pressure, there is change in the Gibb's potential $G$ of a system and hence if $G_1$ and $G_2$ be its value for different phases in equilibrium, we have

$$G_1 = G_2. \qquad \text{...(1)}$$

Now according to Nernst's heat theorem, the entropy for a pure crystalline solid at temperature $T$ is given by

$$S = \int_0^T \frac{C_P\,dT}{T}. \qquad \text{...(2)}$$

where $C_P$ is the specific heat at constant pressure of a condensed system.

Now since Gibb's potencial is given by the equation

$$G = U + PV - TS = H - TS.$$

Substituting its value in equation (1) with the help of (2) with proper suffix, we get

$$H_1 - T\int_0^T \frac{C_{P_2}}{T}\,dT = H_2 - T\int_0^T \frac{C_{P_2}}{T}\,dT,$$

or

$$H_2 - H_1 = T\int_0^T (C_{P_2} - C_{P_1})\cdot\frac{dT}{T}. \qquad \text{...(3)}$$

For any change of state, the difference in the total heat ($H$) is the two states is obviously the latent heat, *i.e.*, $H_2 - H_1 = L$ and eqn. (3), then provides

$$L = T\int_0^T (C_{P_2} - C_{P_1})\cdot\frac{dT}{T} \qquad \text{...(4)}$$

Now, $H = U + PV$, so that $dH = dU + P\,dV + V\,dP \Rightarrow dH = dQ + V dP$

or $$dQ = dH - V\,dP.$$

Expanding $dH$ in terms of the variation in temperature and pressure, we get

$$dQ = \left(\frac{\partial H}{\partial T}\right)_P \cdot dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP.$$

If pressure is constant, $dP = 0$, so that the second term on the right hand side of this equation is zero. Therefore, dividing by $dT$, we have

$$\left\{\frac{dQ}{dT}\right\}_P = C_P = \left\{\frac{dH}{dT}\right\}_P$$

$$\therefore \qquad C_{P_2} - C_{P_1} = \left[\frac{d\,(H_2 - H_1)}{dT}\right]_P = \frac{dL}{dT} \qquad (\because H_2 - H_1 = L).$$

Substituting this value in equation (4) above, we have

$$L = T\int_0^T \frac{1}{T}\cdot\frac{dL}{dT}\,dT \qquad \text{...(5)}$$

The relation is a very important one and enables us to determine the melting point or the boiling point of a substance when its latent heat as a function of temperature is known.

**(4) Slope of the melting curve of solid helium :** Let us consider that a phase change takes place at a temperature $T$ and a pressure $P$ and that the two phases can co-exist at the absolute zero. From Clausius Clapeyron's equation, we get

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V},$$

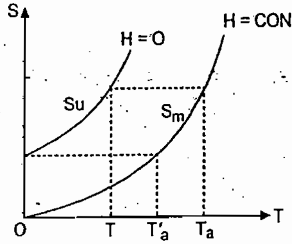
where $\Delta S$ and $\Delta V$ stand for the changes in entropy and molecular volume respectively.

$\therefore$ Now, according to Nernst's heat theorem, $\Delta S \to 0$ when $T \to 0$ and since in general $\Delta V \neq 0$, we have

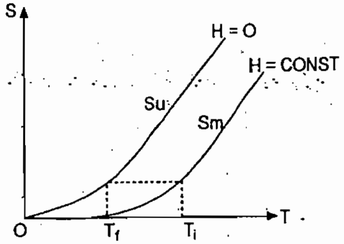
$$\lim_{T \to 0} \frac{dP}{dT} = 0.$$

indicating thereby that the slope of pressure versus temperature curve tends to zero as $T \to 0$. Solid helium furnished a good example of obeying the third law and of its entropy tending to zero as $T \to 0$ because the slope of melting curve of solid helium is actually zero as the temperature approached the absolute zero.

**(5) The 'unattainability' of absolute zero :** It is a consequence of Nernst heat theorem that the absolute zero of temperature can never be reached by any physically realizable process. In order to demonstrate the unattainability, we consider the most efficient means of cooling, *i.e.*, the adiabatic demagnetization. Let us first suppose that the temperature-entropy curve have the form as shown in Fig. 2.4 (a) We shall first discuss that the nature of the curve near absolute zero are contrary of Nernst heat theorem. As entropy is a measure of disorder, in any case $S_u$ (entropy of unmagnetized salt, *i.e.* when $H = 0$) will be greater than $S_m$ (entropy of magnetized salt). If we now consider demagnetization to take place adiabatically and reversibly at temperature $T_a$, we proceed along an adiabatic (isentropic) curve, *i.e.* along a horizontal line till the point of intersection with $S_u$ curve is reached which determines the final temperature. If, however, the initial temperature is $T_a'$ or lower, we would attain the absolute zero by the time $S_u$ curve is



(Fig. 2.4 (a))



(Fig. 2.4 (b))

reached. But according to Nernst heat theorem, there can be no entropy difference between the forms at zero point, *i.e.*, the curve $H = 0$ must also pass through the origin at $T = 0$ as shown in Fig. 2.4 (b) If we now start with magnetized state at the initial temperature, $T_i$ and process along a horizontal line ($S$ = constant) until the demagnetized state on the curve $H = 0$ is reached, we attain a temperature $T_f$ which is definitely lower than $T_i$ but as is seen, the absolute zero is certainly not attained. It is obvious from the diagram that *no adiabatic process initiated at non-zero temperature can lead to zero temperature.*

We can make this point still more clear mathematically. Suppose that a reversible process by which state (1) becomes state (2) is to be used to achieve absolute zero. Then the entopies of the initial and final states are given by

$$S_1(T_1) - S_1(0) = \int_0^{T_1} \frac{C_{P_1}}{T}\,dT, \qquad \text{...(i)}$$

and —

$$S_2(T_2) - S_2(0) = \int_0^{T_2} \frac{C_{P_2}}{T}\,dT, \qquad \text{...(ii)}$$

But according to Nernst's theorem,

$$S_2(0) = S_1(0). \qquad \text{...(iii)}$$

Moreover, only an adiabatic process is acceptable because there is no heat reservoir at a lower temperature to accept that from the system and for an adiabatic reversible process, we have

$$\Delta S = S_2(T_2) - S_1(T_1) = 0. \qquad \text{...(iv)}$$

Combining equations (i) to (iv), we get

$$\int_0^{T_1} \frac{C_{P_1}}{T}\,dT = \int_0^{T_2} \frac{C_{P_2}}{T}\,dT. \qquad \text{...(v)}$$

If now $S_2$ is zero, right hand side of equation (v) is zero as the limits of definite integral are equal and we have

$$\int_0^{T_1} \frac{C_{P_1}}{T}\,dT = 0 \qquad \text{...(vi)}$$

which on the face of it is impossible because if the process starts at a real positive temperature $T_1$, eqn. (vi) can not be satisfied as $C_{P_1}$ is greater than zero at all temperatures. Thus Nernst postulate does imply that no simple adiabatic process can lead from a non-zero to a zero temperature.

One may think that the process by which absolute zero is to be reached might be irreversible. Since in an irreversible process entropy increases, we have

$$\Delta S = S_2(T_2) - S_1(T_1) > 0$$

or
$$\int_0^{T_2} \frac{C_{P_2}}{T}\, dT > \int_0^{T_1} \frac{C_{P_1}}{T}\, dT$$

which can not be satisfied at all if $T_2 = 0$. It is therefore impossible to reach absolute zero by a process that is reversible or irreversible, even if repeated again and again. Temperatures as low as 0·001 K have been attained in the laboratory but absolute zero is itself unattainable. The following conclusion may therefore be drawn from the third law :

*The absolute zero temperature can not be reached by any finite process; it may only be reached asymptotically.*

## 2.9 Phase, Component and Variation

In order to consider the equilibrium between mixtures of various substances, we shall first define and explain the terms involved, which are :

**Phase :** It is a greek word meaning 'appearance' and is defined *as a physically distinct but homogeneous part of a system which is separated from other parts of the system by definite bounding surface.* Thus, *each different, physically homogeneous part of a system is called a phase.* For example, in water system consisting ice, water and its vapour, ice is the solid phase, water is the liquid phase and vapour is the gaseous phase. A system containing water and its vapour has two phases—the liquid phase and the vapour phase. All homogeneous solutions are one phase systems and similarly a gaseours mixture is always a single phase. Every solid, however, constitutes a separate phase. A system composed of two or more phases is called a *heterogeneous system.*

**Component :** For any system, the number of components is defined as *the number of distinct chemical species involved.* It must not be confused with the constituents of the system as all the constituents need not be components. The *smallest number of independently variable constituents by which the composition of every phase of the system can be expressed determines the number of components.*

The water system, for example, consists of one component as the composition of each of the three phases *i.e.*, solid, liquid and vapour can be expressed in terms of the single constituent water.

**Degrees of freedom or the variance :** By the degrees of freedom or variance of a system is meant *the smallest number of independent variables (such as temperature, pressure and concentration) that must be specified in order to define the system completely i.e.*, the number of factors which can be varied independently without altering the number of phases. A system consisting of one phase of water (*i.e.* solid, liquid or gas) requires temperature and pressure to be specified to define completely the state of the system and hence it has two degrees of freedom *i.e.*, it is *bivariant.* If a quantity of water is in equilibrium with its vapour (two phases in equilibrium) then we may specify either temperature or the pressure to define the system completely *i.e.*, it is *univariant* or the system possesses only one degree of freedom. When three phases can coexist at triple point, it is a self defined system and does not need any factor to be specified or the degree of freedom is zero for this system and hence it is called an *invariant* system.

## 2.10 Gibb's Phase Rule

**A general theorem on the maximum number of possible phases :** There exists a definite relation in a system between the number of degrees of freedom, the number of components and the number of phases present. This relation was first established by W. Gibb's in 1876 and is known as the *Gibb's phase rule.* It is a principle of widest generality and expresses the behaviour of a heterogeneous system in equilibrium which is not affected by gravity, electrical or magnetic forces or by surface action and is influenced only by pressure, temperature and concentration.

To arrive at a formulation of a phase rule, let us consider a hetrogeneous system consisting of $n$ different componets in $r$ phases. We shall find, here, the maximum value of $r$ determined by the number of independent components and indicate the components by subscripts and the phases by superscripts attached to the letters. Thus the mass of the $i^{th}$ component in $k^{ith}$ phase is represented by $M_i^k$.

Now a system is said to be in equilibrium, if the temperature and pressure are constant throughout. Thus we consider the system to be isothermal-isobaric rather than an isolated one. In this case the *Gibb's potential*

$$G = U - TS + PV \qquad \ldots(1)$$

should be minimum for eqilibrium. Of the quantities entering in equation (1), $T$ and $P$ are entirely independent of mass of the system while $U$, $V$ and $S$ are proportional to the mass for a given temperature and pressure. From this it is obvious that $G$ is also proportional to the mass. Thus in this case

$$G = G\,(M_1, M_2, M_3 \ldots M_n). \qquad \ldots(2)$$

It is obvious that if all the masses are multiplied by $q$, we have

$$G\,(qM_1, qM_2, qM_3, \ldots qM_n) = qG\,(M_1, M_2 \ldots, M_n), \qquad \ldots(3)$$

This equation defines a homogeneous function of first degree in the masses.

Differentiating above equation with respect to $q$, we get

$$\frac{dG}{dq} = \frac{\partial G}{\partial (qM_1)} \cdot \frac{d\,(qM_1)}{dq} + \frac{\partial G}{\partial (qM_2)} \cdot \frac{d\,(qM_2)}{dq} + \ldots + \frac{\partial G}{\partial (qM_n)} \cdot \frac{d\,(qM_n)}{dq} = G\,(M_1, M_2 \ldots M_n)$$

or
$$M_1 \frac{\partial G}{\partial (qM_1)} + M_2 \frac{\partial G}{\partial (qM_2)} + \ldots + M_n \frac{\partial G}{\partial (qM_n)} = G\,(M_1, M_2 \ldots M_n)$$

If we set $q = 1$ in above equation according to our case, we have

$$M_1 \frac{\partial G}{\partial M_1} + M_2 \frac{\partial G}{\partial M_2} + \ldots + M_n \frac{\partial G}{\partial M_n} = G\,(M_1, M_2, \ldots M_n) \qquad \ldots(4)$$

This is the Euler theorem* of homogeneous function of first degree in the masses for our case. In this equation the R.H.S. is a homogeneous function of first degree in the masses. In order that L.H.S. is such a function also, the derivatives $\frac{\partial G}{\partial M_i}$ must be homogeneous functions of degree zero, *i.e.*, the *derivatives may be the functions only of the ratios of the masses.*

Like energy and entropy the thermodynamical function such as Helmholtz free energy $F$, Gibbs function $G$ and enthalphy $H$ are additive, *e.g.*, the Gibbs potential of the entire system is equal to the sum of Gibbs functions of its phases. Thus if we distinguish the Gibbs potentials of the several phases by primes (dashes), we have for the entire system

$$G = G' + G'' + \ldots + G^r. \qquad \ldots(5)$$

The condition of equilibrium is

$$\delta G = \delta G' + \delta G'' + \delta G''' + \ldots \delta G^r = 0 \qquad \ldots(6)$$

with the supplementary condition $\delta T = 0$ and $\delta P = 0$. In addition to these conditions the mass of each component (substance) must remain unaltered; the distribution of a given substance among the various phases may change, but the total mass of the substance remains constant. The we have the following $n$ auxiliary conditions :

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* The Euler theorem for homogeneous function $f$ $(x, y, z\ldots\ldots$ of $n^{th}$ degree) is $df\,(x, y, z, \ldots\ldots) = x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} + \ldots$

$$\left.\begin{array}{c} \delta M_1' + \delta M_1'' + \ldots + \delta M_1^r = 0 \\ \delta M_2' + \delta M_2'' + \ldots + \delta M_2^r = 0 \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \delta M_n' + \delta M_n'' + \ldots + \delta M_n^r = 0 \end{array}\right\} \quad \ldots(7)$$

considering, now the variation of $G(M_1, M_2, M_3, \ldots M_n)$, while $T$ and $P$ are held constant, we obtain

$$\delta G = \frac{\partial G'}{\partial M_1'}\delta M_1' + \frac{\partial G'}{\partial M_2'}\delta M_2' + \ldots + \frac{\partial G}{\partial M_n'}\delta M_n' + \frac{\partial G''}{\partial M_1''}\delta M_1'' + {}_1'' + \frac{\partial G''}{\partial M_2''}\delta M_2''$$

$$+ \ldots + \frac{\partial G''}{\partial M_n''}\delta M_n' + \ldots + \frac{\partial G^r}{\partial M_1^r}\delta M_1^r + \frac{\partial G^r}{\partial M_2^r}\delta M_2^r + \ldots + \frac{\partial G^r}{\partial M_n^r}\delta M_n^r = 0. \quad \ldots(8)$$

Here the variations are not arbitrary, but satisfy conditions (7). We, therefore apply the method of Lagrangian undermined multiplier, for that multiplying equations (7) by $\lambda_1, \lambda_2, \ldots \lambda_n$ and adding them to principal equation (8), we get

$$\left.\begin{array}{l} \left(\frac{\partial G'}{\partial M_1'} + \lambda_1\right)\delta M_1' + \left(\frac{\partial G}{\partial M_2'} + \lambda_2\right)\delta M_2' + \ldots + \left(\frac{\partial G'}{\partial M_n'} + \lambda_n\right)\delta M_n' \\ + \left(\frac{\partial G}{\partial M_1''} + \lambda_1\right)\delta M_1'' + \left(\frac{\partial G}{\delta M_2''} + \lambda_2\right)\delta M_2'' + \ldots + \left(\frac{\partial G''}{\partial M_n''} + \lambda_n\right)\delta M_n'' \\ \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \\ + \left(\frac{\partial G^r}{\partial M_1^r} + \lambda_1\right)\delta M_1^r + \left(\frac{\partial G^r}{\partial M_2^r} + \lambda_2\right)\delta M_2^r + \ldots + \left(\frac{\partial G^r}{\partial M_n^r} + \lambda_n\right)\delta M_n^r = 0 \end{array}\right\} \quad \ldots(9)$$

If above equation to be satisfied, the coefficients of $\delta M_i^K$ must vanish separately. Then we have the following equations, *nr* in number to be satisfied.

$$\left.\begin{array}{l} \left(\frac{\partial G'}{\partial M_1'} + \lambda_1\right) = 0, \left(\frac{\partial G'}{\partial M_2'} + \lambda_2\right) = 0; \ldots, \left(\frac{\partial G'}{\partial M_n'} + \lambda_n\right) = 0 \\ \left(\frac{\partial G''}{\partial M_2''} + \lambda_1\right) = 0, \left(\frac{\partial G''}{\partial M_2''} + \lambda_2\right) = 0, \ldots, \left(\frac{\partial G''}{\partial M_n''} + \lambda_n\right) = 0 \\ \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \\ \left(\frac{\partial G^r}{\partial M_1^r} + \lambda_1\right) = 0, \left(\frac{\partial G^r}{\partial M_2^r} + \lambda_2\right) = 0, \ldots, \left(\frac{\partial G^r}{\partial M_n^r} + \lambda_n\right) = 0 \end{array}\right\} \quad \ldots(10)$$

In above *nr* equations there are *n* Lagrangian multipliers and the derivatives depend on $T$, $P$ and $(n-1)$ mass ratios, *i.e.*, on $(n+1)$ variables. As $T$ and $P$ are the common temperature and pressure of the phases and $r$ is the number of phases, we have in all $[n + r(n-1) + 2]$ independent variables. As the number of equations must certainly not be greater than the number of independent variables, we must have,

$$nr \le n + r(n-1) + 2$$

or

$$r \le n + 2. \quad \ldots(11)$$

*Thus in a system consisting of n independent components, not more than $(n+2)$ phases can be in equilibrium simultaneously, i.e., in any system the number of phases may be, at the most two greater than the number of independent components. This is called Gibb's phase rule.* It gives the maximum number of possible phases in equilibrium simultaneously in a system. According to this rule a system consisting of single substance, can have three phases at the most.

If the number $r$ of co-existing phases is less than $(n+2)$, then $(n+2-r)$ of the variables can take arbitrary values, *i.e.*, we can vary arbitrarily any $(n+2-r)$ variables without destroying the equilibrium; the order of variables must, of course, be varied in a definite manner. The number of variables which can be arbitarily varied without destroying the equilibrium is called the number of *thermodynamic degrees of freedom* of the system. If this is denoted by $f$, the phase rule may be written as

$$f = n + 2 - r \quad \ldots(12)$$

or

$$r + f = n + 2. \quad \ldots(13)$$

*i.e., the sum of number of phases and the number of degrees of freedom exceeds the number of components by two.* This is the celebrated *phase rule of Gibbs.*

**Application of phase rule :** To illustrate the applications of phase rule, we may take a system of one component, say water. Thus $n = 1$. Under ordinary circumstances, there are three possible phases :

(a) Suppose that the system contains *only one phase*, say the liquid, then $r = 1$ and we have

$$f = n - r + 2 = 1 - 1 + 2 = 2$$

That is there are two degrees of freedom or the system is *bivariant*. Therefore, both pressure and temperatue can be varied simulatanceously without any change taking place in the nature of the phase pressent.

(b) If the system contains *two phases* in equilibrium, say water and its vabour, then $r = 2$ and we have

$$f = n - r + 2 = 1 - 2 + 2 = 1,$$

*i.e.*, there is only one degree of freedom or the system is *univariant*. It means that at an arbitrarily fixed temperature, the pressure at which water and its vapour are an equilibrium, is determined by the thermodynamical conditions of equilibrium and that if we change the pressure arbitrarily, one of the two phases will disappear.

(c) If all the three phases co-exist, then $r = 3$ and we have

$$f = 1 - 3 + 2 = 0,$$

*i.e.*, there is no degree of freedom or the system is *invariant*. It means that the ice-water-vapour can remain in equilibrium only at some definite temperature and pressure. If either the pressure or the temperature be changed one of the three phases will disappear. The point at which the three phases co-exist in equilibrium is called the *triple point* and at this point all the three curves (lines), repressenting the equilibrium between solid-liquid, liquid-vapour, and vapour-solid, intersect. For water co-ordinates of the point on a $P$ and $T$ diagram are $T = 0{\cdot}0075°\text{C}$, $P = 4{\cdot}58$ mm. of mercury.

The phase rule has its more important applications in dealing with systems possessing two or more components *e.g.* when a freezing mixture is formed by mixing salt with ice or when a salt is dissolved in water (aqueous salt solution). It also finds its ready application in physical chemistry as well as in metallurgy.

## 2.11 Chemical Potential

One is well familiar with the term potential as used in mechanical and electrical system. Each potential has got a capacity factor and the work done on the system is expressed by the product of this capacity factor with the change in potential. For example in case of gravitational potential $gh$. the mass is the capacity factor and hence the work done is given by $mg(h_2 - h_1)$. In case of a electrostatic system the work done in moving a charge $q_1$ from a position of potential $V_1$ to another of potential $V_2$ is given by $q(V_2 - V_1)$ where the charge $q$ is the capacity factor. In similar way, we can define the capacity and potential quantities for a chemical system. Here we choose the mole as the capacity factor and molar free energy as the potential (known as chemical potential). Then to transfer $n$ moles of a substance from a state of molar free energy $F_1$ to a state of molar free energy $F_2$, an amount of work $n(F_2 - F_1)$ is required. *A chemical substance that is free to move from one place to another, will move spontaneously from a state of higher chemical potential to a state of lower chemical potential.* In the position of equilibrium, the chemical potential is constant throughout the entire system.

Let us now consider a general heterogeneous system consisting of an independent components in several co-exising phases. To start with, it is convenient to describe a given phase by its chemical composition, which is specified by the number of mole $N_i$ of each species $i$, its volume $V$ and its entropy $S$. Then, any of the properties of the phase can be considered as a function of the independent variables $S$, $V$ and the number of moles of the constitutents 1, 2, 3,..., $i$,.... For example, if we consider the internal energy and recognize that it does depend upon the mass of substance which are used to form the system, then we may set the energy to be a function of the entropy ($S$), volume ($V$) and the number of moles of each component, so that

$$U = U(S, V, N_1, N_2, \ldots N_i, \ldots, N_n), \qquad \ldots(1)$$

where $N_i$ is the number of particles of $i$th component (kind). Infinitesimal changes in these $(n+2)$ variables will lead to an infinitesimal change $dU$ in the energy of the system. By the usual rule of calculus we get

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V; N_1, N_2, N_3, \ldots,} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N_1, N_1, N_2, \ldots,} dV + \left(\frac{\partial U}{\partial N_1}\right)_{S; V, N_2, N_3, \ldots,} dN_1$$

$$+ \left(\frac{\partial U}{\partial N_2}\right)_{S, V, N_1, N_3, \ldots,} dN_2 \ldots + \left(\frac{\partial U}{\partial N_i}\right)_{S, V, N_1, N_2 N_3, \ldots,} dN_i + \ldots$$

This expession may be shortened by the use of a summation symbol, so that

$$dU = \left\{\frac{\partial U}{\partial S}\right\}_{V, N} dS + \left\{\frac{\partial U}{\partial V}\right\}_{S, N} dV + \sum_{n=1}^{n} \left\{\frac{\partial U}{\partial N_i}\right\}_{S, V, N_i} dN_i, \qquad \ldots(2)$$

where the subscript $N$ means that the number of particles of each component is held fixed and the subscript $N_i$ means that the number of particles of each component except for the $i$th component is held constant.

Now when the composition is constant, the system is a simple one of unvarying composition and we have [Refer equation (3) section 2.1]

$$dU = T\,dS - P\,dV. \qquad \ldots(3)$$

Comparing coefficients of $dS$ and $dV$ from equations (2) and (3), we get

$$\left\{\frac{\partial U}{\partial S}\right\}_{V, N} = T \text{ and } \left\{\frac{\partial U}{\partial V}\right\}_{S, N} = -P,$$

and we introduce a new symbol, $\mu_i$ to the partial derivative $\left\{\frac{\partial U}{\partial N_i}\right\}_{S, V, N_i}$ so that

$$\left\{\frac{\partial U}{\partial N_i}\right\}_{S, V, N_j} = \mu_i. \qquad \ldots(4)$$

The quantity $\mu_i$ is so important to considerations of chemical equilibrium that is given a special name and is called the *chemical potential* of the component $i$ in the given phase. With these relations, we can rewrite equation (2) in the compact form as

$$dU = TdS - PdV + \sum_{i=1}^{n} \mu_i\, dN_i \qquad \ldots(5)$$

The chemical potential $\mu$ may be expressed in terms of other thermodynamic functions as well. For example, the *Helmholtz free energy* F may be written as a function of temperature $T$, volume $V$ and $n$ independent variables $N_1, N_2, N_3, \ldots, N_i \ldots N_n$, *i.e.*

$$F = F(T, V, N_1, N_2, \ldots, N_i, \ldots, N_n). \qquad \ldots(6)$$

Infinitesimal changes in these $(n+2)$ variables cause an infinitesimal change $dF$ in the Helmholtz free energy of the sysem. Thus we have

$$dF = \left\{\frac{\partial F}{\partial T}\right\}_{V, N} dT + \left\{\frac{\partial F}{\partial V}\right\}_{T, N} dV + \sum_{i=1}^{n} \left\{\frac{\partial F}{\partial N_i}\right\}_{T, V, N_j, \ldots} dN_i. \qquad \ldots(7)$$

If as a result of a change in the system, there is no alteration in the number of molecules of the various constituents, that is to say, all the $dN$'s are zero or the system is a closed one, then equation (7), becomes

$$dF = \left\{\frac{\partial F}{\partial T}\right\}_{V, N} dT + \left\{\frac{\partial F}{\partial V}\right\}_{T, N} dV \qquad \ldots(8)$$

It has been previously shown [equation (8), section 2.1] that for such a change,

$$dF = -SdT - PdV. \qquad \ldots(9)$$

Equating coefficients in (8) and (9), it follows, therefore, that

$$\left\{\frac{\partial F}{\partial T}\right\}_{V, N} = -S \text{ and } \left\{\frac{\partial F}{\partial V}\right\}_{T, N} = -P;$$

and writing $\mu_i$ for the partial derivative $\left\{\frac{\partial F}{\partial N_i}\right\}_{T, V, N_i}$, we have

$$dF = -S\,dT - PdV + \sum_{i=1}^{n} \mu_i\, dN_i \qquad \ldots(10)$$

$$= -SdT - PdV + \mu_1\, dN_1 + \mu_2\, dN_2 + \ldots \qquad \ldots(11)$$

where, we have

$$\mu_1 = \left\{\frac{\partial F}{\partial N_1}\right\}_{T, V, N_2 \ldots} \qquad \ldots(12)$$

and

$$\mu_2 = \left\{\frac{\partial F}{\partial N_2}\right\}_{T, V, N_1} \ldots \text{etc.}$$

*The chemical potentials are thus the rate of change of free energy per mole, at constant volume and temperature.*

Likewise chemical potentials can be expressed in terms of thermodynamical functions-enthalphy $H(S, P, N_1, N_2, N_i, \ldots, N_n)$ and Gibb's function $G(T, P, N_1, N_2, \ldots, N_i, \ldots, N_n)$ and we may write

$$dH = T\,dS + V\,dP + \sum_{i=1}^{n} \mu_i\, dN_i, \qquad \ldots(13)$$

where
$$\mu_i=\left\{\frac{\partial H}{\partial N_i}\right\}_{S,P,N_j} \qquad \ldots(14)$$

and
$$dG=-S\,dT+V\,dP+\sum_{i=1}^{n}\mu_i\,dN_i, \qquad \ldots(15)$$

where
$$\mu_i=\left\{\frac{\partial G}{\partial N_i}\right\}_{S,V,N_j} \qquad \ldots(16)$$

The above formulae show that

*Chemical potential,*

$$\mu_i=\left\{\frac{\partial U}{\partial N_i}\right\}_{S,V,N_j}=\left\{\frac{\partial H}{\partial N_i}\right\}_{T,V,N_j}=\left\{\frac{\partial H}{\partial N_i}\right\}_{S,P,N_j}=\left\{\frac{\partial G}{\partial N_i}\right\}_{T,P,N_j} \qquad \ldots(17)$$

*i.e., the chemical patential of any component (substance) in the system (mixture) can be obtained by differenting any of the thermodynamic functions U, F, H and G with respect to the corresponding unmber of particles keeping other thermodynamic variables fixed.*

In particular the chemical potential may be expressed by

$$\mu_i=\left\{\frac{\partial G}{\partial N_i}\right\}_{T,P,N_j} \qquad \ldots(18)$$

which is probably the most important of these equations because the independent variables are temperature, pressure and the number of moles of each component.

~~The~~ chemical potentials ~~are~~ thus expressed ~~as~~ functions of pressure, temperature and the ratios of the number of particles of different components of the system. These number of particles in $\mu_i$ can appear only as ratios, since $G$ is a homogeneous function of first order in $N_i$ therefore the chemical potentials must be homogeneous functions of zero order in these variables.

As $G$ is homogeneous function of first order, we have using Euler's theorem,

$$G=\sum_i N_i\frac{\partial G}{\partial N_i}=\sum_i \mu_i\,N_i. \qquad \ldots(19)$$

If the system is in an external field which is constant in time, the different parts of the system are under different conditions. One of the conditions of equilibrium of such a system is that the temperature should be constant throughout, but the pressure will vary from point to point. In such a case the other condition of equilibrium is that the chemical potential of each component of the sytem is constant.

*Thus, a system in an external field will be in equilibrium if the temperature and the chemical potential of each component of the system is constant throughout, i.e.*

$$dT_i=0 \text{ and } d\mu_i=0. \qquad \ldots(20)$$

## 2.12 Vapour Pressure Relation : The chemical constant

Experiments indicate that the saturated vapour pressure of a gas increases with an increase in temperature and, therefore the vapour pressure $P$ must be a function of temperature $T$, *viz.* $P=f(T)$, where $f(T)$ must be of such a form that it increases with rise in temperature. The results of vapour pressure measurements are all based on the famous Clausius Clapeyron equation which in the case of vaporisation of a substance may be written as

$$\frac{dP}{dT}=\frac{L}{T(V_g-V_l)}$$

where $V_g$ and $V_l$ represent the volume of one gram mole of the vapour and liquid respectively, $L$ the molecular latent heat of vapourisation and $P$ the vapour pressure at temperature $T$.

If the vapour in equilibrium with the liquid is assumed to behave as a perfect gas and the volume of the liquid is neglected in comparison with that of the vapour (since $V_l << V_g$), then we may write $V_g=\frac{RT}{P}$ and the Clapeyron's equation becomes

$$\frac{dP}{dT}=\frac{L}{TV_g}=\frac{L}{T\cdot\frac{RT}{P}}=\frac{LP}{RT^2}$$

or
$$\frac{dP}{P}=\frac{L}{RT^2}dT.$$

The integration of this relation gives

$$\log_e P=\frac{1}{R}\int\frac{L}{T^2}dT+i, \qquad \ldots(1)$$

where $i$ is the integration constant independent of $T$ and is called the *vapour-pressure constant* or the *chemical constant.*

It is found of immense importance in verifying Nernst's heat theorem and also in the study of heterogeneous system and chemical equilibria.

The above integral can not be solved in a simple manner as the variation of $L$ with $T$ is not a simple one. Hence a number of attempts, both theoretical and empirical, have been made to find a correct expression for $P$ as a function of $T$. The best approach to the problem is however, from equilibrium condition. When two phases of the same substance are in equilibrium, their Gibbs thermodynamical potentials have the same value in both phases, *i.e.*, $G_1=G_2$, where $G$ is given by

$$G=U+PV-TS$$

the symbols having their usual meanings. Thus, Gibbs thermodynamical potential may be considered both in condensed and vapour phase. But instead of using the Gibbs potential, we will use an equivalent function $\psi$ given by the relation

$$\psi=-\frac{G}{T}=\psi\frac{U+PV-TS}{T}=S-\frac{U+PV}{T} \qquad \ldots(2)$$

and for equilibrium, we shall have

$$(\psi)_{condensed}=(\psi)_{vapour}. \qquad \ldots(3)$$

We shall now find these quantities separately. For the condensed phase, we have

$$S=\int_0^T\frac{\partial S}{\partial T}dT+\int_0^T dP+(S_0)_{cond.}$$

where $(S_0)_{\text{cond.}}$ is the value of entropy of the condensed phase at absolute zero. Since $\int_0^T\frac{\partial S}{\partial P}dP$, change of entropy with change of vapour pressure, is generally very small for condensed phases, we may neglect it and have

$$S=\int_0^T\frac{\partial S}{\partial T}dT+(S_0)_{cond.}=\int_0^T C_P\frac{dT}{T}+(S_0)_{cond.} \qquad \left[\text{Since } C_P=\left(\frac{\partial Q}{\partial T}\right)_P=T\left(\frac{\partial S}{\partial T}\right)_P\right] \qquad \ldots(4)$$

Let us now find the value of $(U+PV)$. We know that

$$d(U+PV)=dU+P\,dV+V\,dP$$

$$= \frac{dQ}{dT}\,dT + V\,dP = C_P\,dT + V\,dP \qquad [\because\ dQ = dU + P\,dV]$$

$$\therefore \qquad U + PV = \int_0^T C_P\,dT + \int_0^T V\,dP + (U + PV)_0 = \int_0^T C_P\,dT + (U_0)_{\text{cond.}}$$

because $P_0$, $V_0$ and $\int_0^T V\,dP$ are negligible small and hence omitted. Here $(U_0)_{\text{cond.}}$ is the energy of the condensed phase at absolute zero.

Substituting the values of $S$ and $(U + PV)$ from equations (4) and (5) in (2), we get

$$(\psi)_{cond.} = \int_0^T C_P\,dT + (S_0)_{cond.} - \frac{1}{T}\int_0^T C_P\,dT - \frac{(U_0)_{cond.}}{T}$$

$$= -\frac{(U_0)_{cond.}}{T} + \int_0^T \frac{dT}{T^2}\int_0^T C_P\,dT + (S_0)_{cond.} \qquad \ldots(6)$$

where all the quantities refer to the condensed phase.

Let us now calculate $\psi_{vapour}$. For it we have from eqn. (2)

$$\frac{\Psi}{R} = \frac{S}{R} - \frac{U + PV}{RT} \qquad \ldots(7)$$

But from equation (6) for vapour phase also, we have

$$U + PV = \int_0^T C_P\,dT + (U)_{vap.},$$

where now all the terms refer to vapour phase. Now, if we assume ideal behaviour for the vapour and if the vapour be monoatomic (which is specially true in case of metals), we have $C_P = \frac{5}{2}R$. Then

$$\frac{U + PV}{RT} = \frac{(U_0)_{vap.}}{RT} + \frac{1}{RT}\cdot\frac{5}{2}RT = \frac{(U_0)_{vap.}}{RT} + \frac{5}{2}. \qquad \ldots(8)$$

Now, the expression for the value of entropy of a perfect monoatomic gas is given from statistical mechanics to be

$$S = Nk \log \frac{V}{Ng}(2\pi mk\,T)^{3/2} + \frac{5}{2}Nk + S_0$$

or

$$\frac{S}{R} = \log \frac{V}{Ng}(2\pi mk\,T)^{3/2} + \frac{5}{2} + \frac{S_0}{R} \qquad \text{(since } Nk = R\text{)}$$

where $S_0$ is the value of entropy at the absolute zero.

Performing the conversion with the help of equation of state $PV = NkT$, so that $\frac{V}{N} = \frac{kT}{P}$ and anticipation quantum theory, where $g = h^3$, we get

$$\frac{S}{R} = \log \frac{kT}{Ph^3}(2\pi mkT)^{3/2} + \frac{5}{2} + \frac{S_0}{R}$$

or

$$\frac{S}{R} = \frac{5}{2}\log T - \log P + \log\left[\frac{(2\pi m)^{3/2}\,k^{5/2}}{h^3}\right] + \frac{5}{2} + \frac{S_0}{R} \qquad \ldots(9)$$

Substituting in equation (7) the values obtained in (8) and (9) we get $\frac{\Psi}{R}$ for vapour phase for a monoatomic gas to be

$$\left\{\frac{\Psi}{R}\right\}_{vap.} = \frac{5}{2}\log T - \log P + \log\frac{(2\pi m)^{3/2}\cdot k^{5/2}}{h^3} + \frac{5}{2} + \left\{\frac{S_0}{R}\right\}_{vap.} - \frac{(U_0)_{vap}}{RT} - \frac{5}{2}$$

$$= \frac{5}{2}\log T - \log P + \log\frac{(2\pi m)^{3/2}\cdot k^{5/2}}{h^3} + \left\{\frac{S_0}{R}\right\}_{vap.} - \frac{(U_0)_{vap.}}{RT} \qquad \ldots(10)$$

Equating $\left\{\frac{\Psi}{R}\right\}_{cond}$ to $\left\{\frac{\Psi}{R}\right\}_{vap.}$ from (6) and (10), we get

$$\frac{1}{R}\left[\frac{(U_0)_{cond.}}{T} + \int_0^T \frac{dT}{T^2}\int_0^T (C_P)\,dT + (S_0)_{cond.}\right]$$

$$= \frac{5}{2}\log T - \log P + \log\frac{(2\pi m)^{3/2}\,.\,k^{5/2}}{h^3} + \left\{\frac{S_0}{R}\right\}_{vap.} - \frac{(U_0)_{vap.}}{RT}$$

or

$$\log P = -\frac{(U_{vap} - U_{cond.})}{RT} + \frac{5}{2}\log T - \frac{1}{R}\int_0^T \frac{dT}{T^2}\int_0^T C_P\,dT$$

$$+ \log\frac{(2\pi m)^{3/2}\,.\,k^{5/3}}{h^3} + \frac{(S_{vap.} - S_{cond.})_0}{R}$$

Putting $(U_{vap.} - U_{cond.}) = \Sigma\,S_0$, we get

$$\log P = -\frac{L_0}{RT} + \frac{5}{2}\log T - \frac{1}{R}\int_0^T \frac{dT}{T^2}\int_0^T C_P\,dT + \log\frac{(2\pi m)^{3/2}\,.\,k^{5/2}}{h^3} + \frac{\Sigma\,S_0}{R}$$

If pressure is measured in atmosphere and logarithms to the base 10 are used, we have

$$\log_{10} P = \frac{L_0}{2{\cdot}30\,RT} + \frac{5}{2}\log_{10} T - \frac{1}{2{\cdot}30\,R}\int_0^T \frac{dT}{T^2}\int_0^T C_P\,dT$$

$$+ \log_{10}\frac{(2\,\pi\,m)^{3/2}\,.\,k^{5/2}}{h^3} + \frac{\Sigma\,S_0}{2{\cdot}30\,R} - \log_{10}(1{\cdot}013 \times 10^6)$$

The term $\log_{10}(1{\cdot}013 \times 10^6)$ occurs on account of the fact that one atmospheric pressure is equal to $1{\cdot}013 \times 10^6$ dynes/cm$^2$. Putting $m = Mm_H$ ($M =$ molecular weight, $m_H =$ weight of the $h = 6{\cdot}62 \times 10^{-27}$ erg-sec, $2{\cdot}30\,R = 4{\cdot}273$ and $\log_{10}(1{\cdot}013 \times 10^6) = 6{\cdot}906$, (in C.C.S. system) we get the final expression

$$\log P = -\frac{L_0}{4{\cdot}373T} + \frac{5}{2}\log T - \frac{1}{4{\cdot}573}\int_0^T \frac{dT}{T^2}\int_0^T C_p\,dT - 1{\cdot}59 + 1{\cdot}5\log M \qquad \ldots(11)$$

where we have put $\Sigma S_0 = 0$ in accordance of Nernst heat theorem.

The only term independent of $T$ in eqn. (11) is $[1{\cdot}5\log M - 1{\cdot}59]$ and this can be identified by the constant $i$ in eqn. (1) chemical constant. Hence the value of *chemical constant for a perfect monoatomic gas* is given by

$$i = 1{\cdot}5\log_{10} M - 1{\cdot}59 \qquad \ldots(12)$$

where $M$ is the molecular weight of the substance. The values of chemical constants of many substances have now been determined accurately. The above eqn. (12) may also be written in the following form

$$i = i_0 + 1{\cdot}5\log_{10} M$$

where $i_0 = -1{\cdot}59$ is a universal constant. Theoretical value of $i_0$ can be compared with the experimentally determined values. Table below gives the experimental values of $i_0$.

| Substance | Experimental values of $i_0$ |
|---|---|
| Neon | —1·56 |
| Argon | —1·61 |
| Sodium | —1·41 |
| Potassium | —1·47 |
| Zinc | —1·50 |
| Cadmium | —1·51 |
| Mercury | —1·63 |
| Hydrogen | —1·57 |

It will be observed that except in the case of sodium and potassium, the agreement between theory and experiment is quite good. The difference in case of sodium and potassium may be due to the presence of some small proportion of diatomic molecules in the vapours. According to Schottky, it may reveal that the statistical weights of an atom in the solid and vapour states are not the same.

## EXERCISES

### SHORT ANSWER QUESTIONS

1. Name the thermodynamic variables and thermodynamic functions.
2. What is the basic characteristics of all the four thermodynamic functions.
3. Define Internal energy. Express change in internal energy in terms of independent variables $S$ and $V$.
4. Define Helmholtz function $F$. Express change in Helmholtz function in terms of independent variables $V$ and $T$.
5. Define enthalpy. Express change in enthalpy in terms of independent variables $S$ and $P$.
6. Define Gibb's function. Express change is Gibb's function in terms of variables $P$ and $T$.
7. Explain the Gibb's function $G$ and prove that $G$ is constant in an isothermal-isobaric process. **(Mumbai 2004)**
8. State and prove Gibb's Helmholtz equation.
9. Using Maxwell's relations show that internal energy of an ideal gas is independent of volume at constant temperature.
10. Using Maxwell's relations show that the internal energy of Vander Waal's gas depends on volume at constant temperature.
11. Obtain Clausius Clapeyron's equation using Maxwell's thermodynamical relation. **(Rohilkhand 2006, 2003)**
12. Prove heat capacity relation.

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$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P.$$

13. Using Maxwell's thermodynamic relations, prove that

$$\frac{\partial H}{\partial U} = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T$$

where $H = U + PV$ **(Mumbai 2004)**

14. Using Maxwell's thermodynamic relations, prove that the ratio of adiabatic to isochoric pressure coefficients of expansion is equal to $\frac{\gamma}{\gamma-1}$ where $\gamma = \frac{C_P}{C_V}$. **(Mumbai 2003)**
15. State the theorem of maximum work.
16. Define chemical potential.

### LONG ANSWER QUESTIONS

1. (a) Define various thermodynamic potentials, stating the conditions under which each is specially useful.
   (b) Derive the four thermodynamic relations of Maxwell from the thermodynamic potentials $U$, $F$, $H$ and $G$. **(Kanpur 2005, Mumbai, 2003, Rohilkhand 2006)**
2. Define the free energy functions $F$ and $G$ and explain the importance of these functions. Derive from them the corresponding thermodynamic relations of Maxwell.
3. Explain the meaning of Helmholtz free energy. Show that in a natural isothermal change at constant volume, Helmoltz free energy decreases. **(Mumbai 2001)**
4. Employing a function $G$ defined by $G = H - TS$ and a function H defined by $H = U + PV$, prove that

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P.$$

5. Explain the meaning the importance of *extrinsic energy* and *Helmholtz free energy* Prove that relation

$$F = U + T\left(\frac{\partial F}{\partial T}\right)_V$$

where $F$ is the free energy and $U$ is the internal energy of the system.

6. State Maxwell's thermodynamic relations between pressure, volume, temperature and entropy of a homogeneous system. Hence deduce that the ratio of adiabatic and isothermal elasticities for any substance is equal to $C_p/C_V$.
7. Explain Gibb's function $G$ and prove that $G$ remains constant in an isothermal and isobaric process.
8. Prove that thermodynamic relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

and hence prove that

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

9. (b) Prove that for any substance.

$$TdS = C_p\,dT - T\alpha\,VdP$$

Where α is coefficient of volume expansion.

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

*(Ranchi Univ. 2005)*

10. Prove the thermodynamical relations

(i) $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

(ii) $T\,.\,dS = C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

11. A function $(H)$ is defined by $H = U + PV$ and function $(F)$ is defined as $F = U - TS$, show that

$$H = F - T\left(\frac{\partial F}{\partial T}\right)_V - V\left(\frac{\partial F}{\partial V}\right)_T \text{ and } G = F - V\left(\frac{\partial F}{\partial V}\right)_T.$$

*(Mumbai 2004)*

where $G$ is Gibb's free energy.

12. (a) Show hat for a homogeneous fluid

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

where symbols have their usual meanings.

(b) Hence prove that

(i) for a perfect gas

$$C_P - C_V = R.$$

*(Rohilkhand 1992)*

(ii) For a real gas $C_P - C_V = R\left[1 + \frac{2a}{RTU}\right]$

*(Mumbak 2000)*

13. Deduce the thermodynamical relations :

(i) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$; (ii) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

14. Using Maxwell's thermodynamical relations, prove that

(i) $E_S/E_T = C_P/C_V$

(ii) $C_P - C_V = TE\alpha^2 V$

where the symbols have their usual meanings.

15. What do you mean by enthalpy $H$ and Gibb's function G. Show that

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

[Hint : $dH = dU + P\,.\,dV + V\,.\,dP$

$= TdS - PdV + PdV + VdP = TdS + VdP$

$\therefore \quad \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$ ]

16. Using Helmholtz's free energy F and the Gibb's free energy G prove that

$$T = \left(\frac{\partial U}{\partial S}\right)_V ; P = -\left(\frac{\partial U}{\partial V}\right)_S$$

and $\quad \left(\frac{\partial H}{\partial P}\right)_T - V = -T\left(\frac{\partial V}{\partial T}\right)_P$

where the letters have their usual meanings.

17. What is Joule-Thomson process. Derive an expression for the Joule Thomson coefficient in an isenthalpic process. Hence show that the effect is the resultant of the deviations from Joule's law and Boyle's law. *(Rohilkhand 2005, Mumbai 2002)*

18. (a) Discuss briefly the general conditions for thermodynamical equilibrium.

19. Define the entropy of a substance and show that if the entropy of a pure substance at the absolute zero of temperature is zero, then its specific heat and its temperature coefficient of volume expansions must also be zero.

20. Describe and explain Nernst's heat theorem. Give its important applications.

21. State Nernst's third law of thermodynamicas. Deduce the predictions that this law makes as regards the limiting values of coefficient of thermal expansions and molar specific heats $C_P$ and $C_V$ as temperature tends to 0K for homogeneous system. Also prove that change of pressure required to produce a finite change in temperature is unbounded as temperature tends to 0K.

22. State the third law of thermodynamics in terms of entropy differences. Show that it leads to unattainability of absolute zero temperature in a finite number of steps.

23. State the third law of thermodynamics in terms of entropy differences. Show that it leads to unattainability of absolute zero temperature in a finite number of steps. Will the same hold if we simply take the quantum theory result that specific heat tends to zero as T tends to zero? *(Rohilkhand 2004)*

24. Prove from the third law that the absolute zero temperature can only be reached asymptotically.

25. What do you mean by a heterogeneous system. Discuss in this respect the term—phase, component and variance. Show that in any system, the number of phase may be at the most two greater than the number of independent components.

26. Discuss Gibb's phase rule. Mention some of its important applications.

27. What is the chemical potential of a system? Show that the chemical potential of any component in the system may be obtained by differentiating any of the thermodynamic functions with respect to the corresponding number of particles keeping other thermodynamic variables fixed.

28. Show that the integration of the expressions for $dF$, $dU$ and $dH$ for constant value of the intensity factors lead in each case to the equation

$$G = \sum_i \mu_i N_i$$

Discuss its significance in connection with the equilibrium of two states of the same substance under various conditions.

29. It temperature and volume are taken as independent variables, showthat

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N_i} \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad \text{and} \quad \mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_j}$$

where the subscript $N$ means that the number of particles of each component is held fixed and the subscript $N_j$ means that the number of particles of component except for the $i$th component is held constant.

30. What is chemical constant? Deduce an expression for the same in case of a monoatomic gas.

## MULTIPLE CHOICE QUESTIONS : *SELECT THE RIGHT CHOICE*

1. Which law of thermodynamics suggests that there is a tendency for the equalization of temperature throughout the system. *(Rohilkhand 2003)*
   (a) Zeroth law (b) First law (c) Second law (d) Third law
2. Helmholtz free energy is : *(Rohilkhand 2003)*
   (a) $U+TS$ (b) $H+TS$ (c) $H-TS$ (d) $U-TS$
3. Gibbs Potential is defined as : *(Kanpur 2005, 2001)*
   (a) $G=U-PV+TS$ (b) $G=U+PV+TS$
   (c) $G=U-PV-TS$ (d) $G=U+PV-TS$
4. If a thermodynamic process remains isothermal as well as isobaric, then which of the following functions remains constant : *(Rohilkhand 2003)*
   (a) Internal energy (b) Helmholtz function
   (c) Enthalpy (d) Gibb's function
5. Clausius Clepeyron equation is :
   (a) $\frac{dP}{dT}=\frac{\Delta S}{\Delta V}$ (b) $\frac{dP}{dT}=\frac{1}{\Delta S\,\Delta V}$ (c) $\frac{dP}{dT}=\frac{T\Delta S}{\Delta V}$ (d) $\frac{dP}{dT}=\frac{\Delta V}{T\Delta S}$
   when $\Delta S$ = change in entropy during the change of state and $\Delta V$ is change in volume in two phases.
6. If the ratio of isothermal and adiabatic elasticities is $\frac{E_S}{E_T}$, then which of the following is true :
   (a) $\frac{E_S}{E_T}=\frac{C_P}{C_V}$ (b) $\frac{E_S}{E_T}=\frac{C_V}{C_P}$ (c) $\frac{E_S}{E_T}=C_P\,.\,C_V$ (d) $\frac{E_S}{E_T}=\sqrt{\left(\frac{C_P}{C_V}\right)}$
7. The value of $C_P-C_V$ for an ideal gas is : *(Rohilkhand 2002)*
   (a) $TE\,\alpha^2V$ (b) $TE\alpha V^2$ (c) $T^2E\alpha V$ (d) $TE\alpha^2V^2$
8. The relation between $C_P$ and $C_V$ for a real gas is :
   (a) $C_P-C_V=R$ (b) $C_P-C_V=R^{-1}$
   (c) $C_P-C_V=R\left(1+\frac{2a}{RTV}\right)$ (d) $C_P-C_V=R\left(1+\frac{2a}{RbV}\right)$
9. Maxwell's thermodynamic relation is : *(Rohilkhand 2003)*
   (a) $\left(\frac{\partial S}{\partial T}\right)_V=\left(\frac{\partial P}{\partial V}\right)_T$ (b) $\left(\frac{\partial T}{\partial V}\right)_S=-\left(\frac{\partial P}{\partial S}\right)_V$ (c) $\left(\frac{\partial T}{\partial V}\right)_S=\left(\frac{\partial P}{\partial S}\right)_V$ (d) $\left(\frac{\partial P}{\partial T}\right)_S=\left(\frac{\partial V}{\partial S}\right)_T$
10. Joule Thomson effect depends upon :
    (a) initial temperature only (b) pressure difference only
    (c) both (a) and (b) (d) neither (a) nor (b)
11. The temperature of inversion of a gas is :
    (a) $\frac{a}{Rb}$ (b) $\frac{2a}{Rb}$ (c) $\frac{8a}{27Rb}$ (d) $\frac{27}{8}\frac{Rb}{a}$

12. Hydrogen and helium at normal temperature show : *(Rohilkhand 2003)*
    (a) Heating effect
    (b) Cooling effect
    (c) Sometimes cooling and sometimes heating effect
    (d) no effect
13. At absolute zero temperature, all the processes are carried out without change in entropy. This statement is referred to as : *(Rohilkhand 2006)*
    (a) Zeroth law of thermodynamics (b) First law of thermodynamics
    (c) Second law of thermodynamics (d) Nernst heat theorem
14. Joule Thomson coefficient is :
    (a) $\left(\frac{\partial T}{\partial P}\right)_H=\frac{1}{C_P}\left(\frac{2a}{RT}-b\right)$ (b) $\left(\frac{\partial T}{\partial P}\right)_H=\frac{1}{C_P}\left(\frac{2b}{RT}-a\right)$
    (c) $\left(\frac{\partial T}{\partial P}\right)_H=C_P\left(\frac{2a}{Rb}-T\right)$ (d) $\left(\frac{\partial T}{\partial P}\right)_H=\frac{1}{C_V}\left(\frac{2a}{Rb}-T\right)$
15. The chemical potential is expressed as :
    (a) $\mu_i=-\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j}$ (b) $\mu_i=\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j}$ (c) $\mu_i=\left(\frac{\partial G}{\partial T}\right)_{P,N}$ (d) $\mu_i=\left(\frac{\partial G}{\partial P}\right)_{T,N}$
16. If $r$ is number of existing phases, $f$ degrees of freedom and $n$ the number of components in a system, then Gibb's phase rule is :
    (a) $r+f=n$ (b) $r+f=n+1$ (c) $r+f=n+2$ (d) $r+f=n-1$

### ANSWERS

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. (d) | 2. (d) | 3. (d) | 4. (d) | 5. (a) | 6. (a) | 7. (a) | 8. (c) |
| 9. (b) | 10. (c) | 11. (b) | 12. (a) | 13. (d) | 14. (a) | 15. (b) | 16. (c) |

# 3

# CONCEPTS OF THERMAL RADIATION

## 3.1 Thermodynamics and Radiation

Thermodynamic laws are also applicable to systems other than the material one. These, for example, have been applied to establish important principle of the theory of radiation. Radiation as we know today, is a mean of transferring energy by tranverse electromagnetic waves and is similar in nature to light, radio waves, ultraviolet rays and X-rays. One of the 'kind' of radiation is *matter radiation* such as cathode rays and molecular beams etc., but here we shall deal with the *energy radiations* only such as heat and light etc. which can propagate through space even without a material medium.

We all know that a body will emit visible radiation if it is hot enough. Bodies when heated emit radiant energy, the quantity and quality of which depend, for any given body, on the temperature of the body. The close relationship between temperature and radiation is implied by the fact that a white hot body is hotter than a red-hot one. Thus the rate at which an incandescent lamp filament emits radiation increases rapidly with a rise in the filament temperature and the emitted light goes on becoming whiter. If, however a body is maintained at a constant temperature, then the nature of the body is not changed by the continuous emission of radiation. The radiation is then called a *temperature radiation* which is a heat effect and is entirely different from electrical or chemical effects. The radiation inside the isothermal enclosure in equilibrium with the walls at a specific temperature occupies a certain volume and exerts pressure. Hence its state can be described by means of thermodynamic coordinates pressure, volume. temperature and density, As a result thermodynamics, which disregards the interior structure of a system, can well be applied for the studies of the properties of radiation. In the following sections we shall apply the thermodynamic considerations to these temperature radiation.

## 3.2 Radiation and Thermal Radiation

We receive heat from the sun which is millions of kilometres away from the earth. After a few thousands kilometres there is only empty space with no material medium. If there is, density does not exceed one or two molecules per cubic centimetre. The presence of matter of this density can be entirely ignored. Therefore, process, by which we receive heat from the sun, cannot be either conduction or convection which require an intervening material medium. The process is termed as radiation. Heat travelling by radiation is called ***radiant heat or thermal radiation***.

During this process, heat from the sun passes through air around the earth; but the air is not heated. Maxwell defined the ***radiation as the transfer of heat from a hot body to a cooler body without appreciable heating of the intervening medium (or space).***

This statement does not mean that an intervening medium will not be heated when thermal radiation falls on it or passes through it. Infact the bodies may absorb radiant heat to a greater or lesser degree when the radiations fall on them or pass through them and thereby get heated to a greater or lesser extent. The examples of such substances are glass, wood, metal etc. On the other hand some substances allow radiant heat to pass through them without being heated to any great extent. The examples of such substances are quartz, rock salt, fluorspar etc.

Conclusively we can say that when heat is propagated by radiation, no material medium is necessary for the transmission and if there is any material medium, it is not necessary that it should first get itself heated (as in the case of conduction and convection) before it could assist the propagation of thermal radiation, More-over it had been shown that heat is a form of energy like light. *The propagation of heat by radiation consists merely the transfer of energy which can take place even in empty space.*

**Properties of thermal Radiation :** The investigations show that thermal radiation has following properties :

(1) Thermal radiation travels through empty space with the velocity of light.
(2) Thermal radiation like light, travels in straight lines.
(3) Thermal radiation, like light, obeys the inverse square law of distance.
(4) Thermal radiation is reflected and refracted like light.
(5) Thermal radiation exhibits the phenomenon of interference, diffraction and polarisation like light.

From the above properties of thermal radiation, it is clear that, it has the same nature as light. The only difference is that its average wavelength is greater than that of visible light. Therefore, the **thermal radiation** is called the **infra red radiation.** The spectrum af radiations given out by hot body may be formed, by using the prisms of rock-salt. **KCl** etc. or diffraction grating of large spacings, just as the spectrum of visible radiation is formed by using ordinary glass prism or grating.

The thermal radiations can not be detected by the eye or the photographic plate but they can be detected by the **bolometer,** which depends on the change of electrical resistance with temperature or **thermopile** which is just a series of thermocouples connected properly to produce an e.m.f proportional to incident energy.

## 3.3 Some Definitions

**1. Total energy density :** ***Total energy density of radiations at any point is the total radiant energy per unit volume around that point for all the wavelenghts taken together.*** This is generally expressed by $u$, its unit is joule $m^{-3}$.

**2. Spectral energy density :** ***Spectral energy density for a particular wavelength is the energy per unit volume per unit range of wavelength. This is denoted by $u_\lambda$.***

**3. Emissive power.** *The spectral emissive power of a body at a particular wavelength is the radiant energy emitted per unit time per unit surface area of the body within a unit wavelength range.*

**4. Absorptive power :** *The absorptive power of a body at a particular temperature and for a particular wavelength is defined as the ratio of the radiant energy absorbed per unit surface area per unit time to the total energy incident on the same area of the body in unit time within a unit wavelength range.* It is denoted by $a_\lambda$.

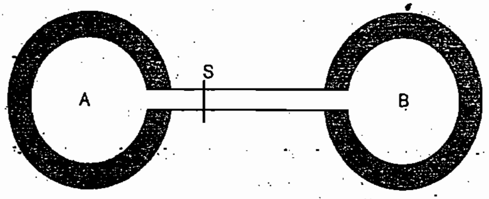
## 3.4 Energy Density of Radiation in an Isothermal (Uniform Temperature) Enclosure

In general the nature of radiation and the amount of radiation per unit area per second *i.e.*, the quality and quantity of radiation depends on the temperature as well as on the nature of the surface. If, however, ***we consider a non-conducting enclosure maintained at a constant temperature (non conducting isothermal enclosure), the quality and the quantity of radiation***

***inside such an enclosure depend only on its temperature and are entirely independent of both the nature of the walls and the nature of the bodies which may be inside it.*** This can be proved as follows :

Let us suppose two enclosures $A$ and $B$ having walls of different materials; but maintained at the same constant temperature $T$. Let each one be filled with radiant energy. Suppose that the density of radiant energy (radiant energy per unit volume) depends on the temperature as well as on the nature of the walls.

Let us also suppose that the density of radiant energy is greater in $A$ than that in $B$.



(Fig. 3.1)

Let the enclosures $A$ and $B$ be joined by a tube fitted with a screen $S$ transparent to all radiations. Evidently more radiations will fall on the screen from $A$ than from $B$ and hence on the whole, there will be a flow of radiation from $A$ to $B$. After some-time, let the enclosures be separated and allowed to attain equilibrium again with their new energy densities. The energy density in $A$ is less than before and hence its walls will, therefore, lose heat into the enclosure and cool down till equilibrium is again attained. On the other hand, the energy density in $B$ is greather than before, therefore, its walls will absorb energy from within and get heated. This means that a difference of temperature will be produced between $A$ and $B$, although they were originally at one temperature. Alternatively we have created a difference of temperature between the two enclosures $A$ and $B$ without any expenditure of energy. Using ~~$B$ as~~ hot body (source) of a heat engine and $A$ as a cold body (sink) we can obtain work without expenditure of any energy which is contrary to the second law of thermodynamics. Therefore our original assumption that the energy density of radiation in $A$ is greater than in $B$ is incorrect and hence the energy densities in $A$ and $B$ must be identical. Thus we can say that **the energy density of the raditation in a uniform temperature enclosure depends on its temperature and is entirely independent of the nature of the walls.**

Now let us suppose that the bodies $A$, $B$ and $C$ are placed inside an isothermal enclosure. Experience shows that each body will attain the temperature of the enclosure irrespective of its nature or original temperature. As the bodies, $A$, $B$ and $C$ are at the same temperature as that of the enclosure, each body must radiate energy at the same rate and exactly of same kind as it absorbs. In other words we can say that ***the bodies contained inside the enclosure have no effect on the quality or quality of the radiant energy filled-in the enclosure.***

## 3.5. Black-Body

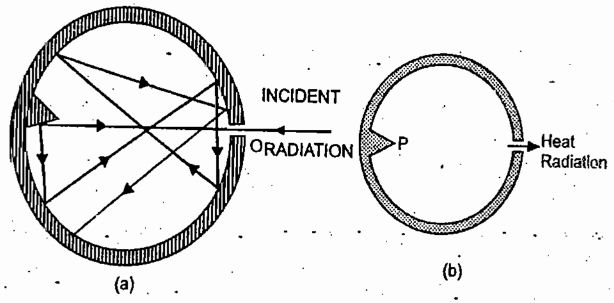
A perfectly black body is one which absorbs all the heat radiations, of whatever wavelength, incident on it. It neither reflects nor transmits any of the incident radiation and, therefore appears black whatever be the colour of incident radiation.

Let a black-body be placed in an isothermal enclosure. The body will emit the full radiations of the enclosure after it is thermal equilibrium with the enclousre. These radiations are independent of the nature of the substance. Clearly the radiation from an isothermal enclosure is identical with that from a black-body at the same temperature. Therefore, the heat radiations in as isothermal enclosure are termed as **black-body radiations.**

In practice no substance possesses strictly the proparties of a black-body. Lamp black and the Platinum black are the nearest approach to a black body. However the bodies showing close approximation to perfectly black body can be constructed.

**Black-Body in Practice :**

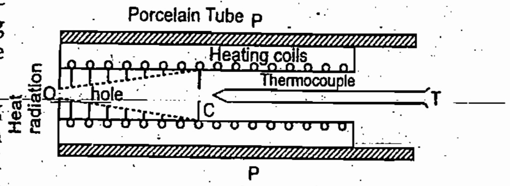
**(a) Ferys' black-body :** It consists of a hollow copper sphere blackened inside with a small fine hole $O$ in the surface. When the radiations enter the hole, they suffer a number of reflections at the inner walls of the sphere until it is completely absorbed. To avoid direct reflection of the radiation from the inner surface, a pointed projection is made in front of the hole as in fig. 3.2 (a). Thus the small hole acts as a black-body absorber. When this sphere is placed in a bath at a fixed temperature, the heat radiations come out of the hole as shown in fig 3.2 (b). It is to be noted that only the hole and the walls of the sphere, acts as a black-body radiator.



(a) (b)

(Fig. 3.2)

**(b) Wien's black-body.** It consists of a long hollow metallic cylinder $C$ blackened inside with heating coils around it. The cylinder is surrounded by concentric porcelain tubes. Heat radiations emerge out of the hole. The radiations from the inner surface pass through a number of limiting diaphragms. The temperature of central part of the cylinder is measured by a thermocouple. The hole acts as a black-body radiator.



(Fig. 3.3)

## 3.6. Kirchhoff' Law and its Important Applications

Kirchhoff's law states that *the ratio of the emissive power to the absorptive power for a given wavelength at a given temperature is the same for all bodies and equal to the emissive power of a perfectly black body at that temperature.*

**Proof.** Let us consider a body placed in an isothermal enclosure. Let $dQ$ be the amount of radiant energy, of wavelength lying between $\lambda$ and $\lambda + d\lambda$, incident on unit surface area per second. If $a_\lambda$ is the absorptive power of the body for the wavelength $\lambda$ and at the temperature of enclosure, then the amount of radiant energy absorbed by unit surface area of the body per second will by $a_\lambda \, dQ$ the remainder of the incident energy $(1 - a_\lambda)\, dQ$ will be reflected or transmitted.

If $e_\lambda$ is the emissive power of the body for wavelength $\lambda$ at the temperature of the enclosure, then the total radiation lying between wavelength $\lambda$ and $\lambda + d\lambda$ emitted by unit surface area of the body per second is $e_\lambda \, d\lambda$. As the body is in temperature equilibrium with the enclosure, energy radiated by the body must be equal to that received by it, *i.e.*,

$$(1 - a_\lambda)\, dQ + e_\lambda \, d\lambda = dQ$$

or

$$e_\lambda \, d\lambda = a_\lambda \, dQ$$

or $$\frac{e_\lambda}{d\lambda} = \frac{dQ}{d\lambda} \quad \ldots(1)$$

But $\frac{dQ}{d\lambda}$ depends only on temperature, therefore $\frac{e_\lambda}{a_\lambda}$ is the same for all substances for a given temperature, *i.e., the ratio of emissive power to the absorptive power for radiation of given wavelangth is same for all bodies at a given temperature.*

If the body under consideration is perfectly black, the absorptive power $a_\lambda = 1$ for all wavelengths and $e_\lambda$ has maximum value which we denote, by $E_\lambda$. Therfore for such a body, we have

$$E_\lambda\, d\lambda = dQ$$

or $$E_\lambda = \frac{dQ}{d\lambda} \quad \ldots(2)$$

Comparing (1) and (2), we have for any body

$$\frac{e_\lambda}{a_\lambda} = E_\lambda \quad \ldots(3)$$

*i.e., the ratio of the emission power to absorptive power is equal to emissive power of a perfectly black-body at a given temperature which is Kirchhoff's law.*

**Applications :** Kirchhoff's law tells us that *good absorbers are good emitters.* If a body absorbs radiation of a particular wavelength strongly, it also emits the same radiation strongly.

1. When a polished metal ball having a black spot on its surface is heated to a high temperature, the black spot appears more brightly than the polished surface. The reason is that the black spot, which absorbs radiation more strongly than the polished surface at ordinary temperature, emits more strongly at high temperature. Similarly, a piece of red glass, which absorbs green light strongly, glows with a green light when heated.

2. The best example of Kirchhoff's law is provided by the emission and absorption spectra of sodium vapour. When the sodium vapour is heated to a temperature high enough to emit visible radiation, its emission spectrum consists of two yellow lines. On the other hand, when white light is passed through a cooler sodium vapour and then seen through a spectroscope, the continuous spectrum of the white light is found to consist of two dark lines in exactly the same position at the yellow lines in the emission spectrum. Thus sodium vapour which emits two yellow lines strongly is also a good absorber of light of these two wave-lengths.

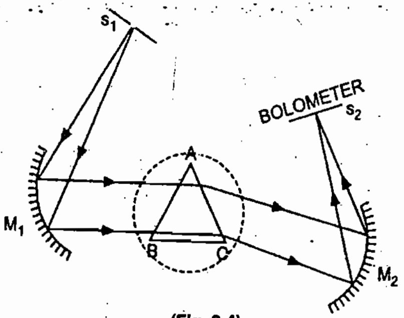
3. It explained the origin of Frauhofer dark lines in sun's spectrum. The sun consists of a central glowing mass which gives the continuous spectrum, It is surrounded by a cooler atmosphere which contains various elements like hydrogen, nitrogen, sodium, caesium, copper, etc. in the gaseous state. When radiation from the central mass passes through the surrounding atmosphere, the various elements absorb those wave-lengths which they can emit at a higher temperature. As a result those wave-lengths are missing from the sun's spectrum and we see dark lines in their places.

4. Kirchhoff's law is responsible for the development of the science of spectrum analysis. It established that atoms of each element give a spectrum which is characteristic of that element alone. Hence if the characteristic spectral lines of an element are seen is a spectrum, it is certain that the element is present in the substance of which the spectrum is being taken.

## 3.7. Black Body Radiations

Lummer and Pringsheim investigated the distribution of energy among the radiation emitted by a black-body at different temperatures.

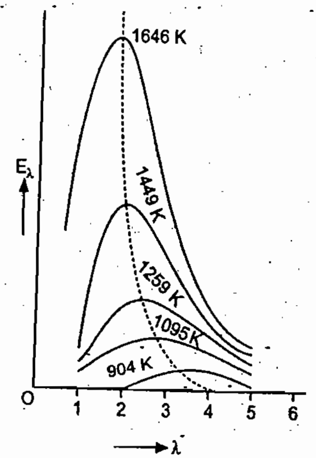
The experimental arrangement of Lummer and Pringsheim is shown in fig. 3.4. Their black-body was a small aperture of an electrically **heated** chamber whose temperature was measured by a thermocouple.



(Fig. 3.4)

The radiations from the black-body pass through the slit $S_1$ and fall on the reflector $M_1$. After being reflected, the parallel beam of radiation falls on a rock-salt or fluorspar prism *ABC* placed on the turn table of the spectrometer. The emergent light is focused by the reflector (concave mirror) $M_2$ on a line bolometer placed behind the slit $S_2$. The bolometer is connected to a sensitive galvanometer. The turn table is rotated slowly so that different parts of the radiation spectrum successively fall on the bolometer and the corresponding deflections in galvanometer connected in the bolometer circuit are read. The intensity of each line is proportional to the deflection in the galvanometer. Then a curve (fig. 3.5) is drawn between intensity and the wavelength.

Experiment is repeated by heating the body to different temperatures and the curves are drawn for various temperatures.



(Fig. 3.5)

**Result.**

The curves show :

(i) The energy is not uniformly distributed in the radiation spectrum of a black-body.

(ii) At a given temperature, the intensity of radiations increases with increase of wavelength and becomes maximum at a particular wavelength. By further increasing the wavelength, the intensity of heat radiations decreases.

(iii) An increase is temperature causes a decrease in $\lambda_m$ where $\lambda_u$ is the wavelength for which the energy emitted is maximum; such that $\lambda_m T =$ constant. This is called Wein's displacement law. This constant is called **Wien's displacement constant** and has a value $0{\cdot}2986 \times 10^{-2}\ mK$.

(iv) An increase in temperature causes an increase in energy emission for all wavelengths.

(v) The area under each curve represents the total energy emitted by the body at a particular temperature for the range of wavelengths considered. This area increases with increase of temperature. It is found that area is directly proportional to the fourth power of absolute temperature *i.e.,* $E \propto T^4$ which is **Stefan's law.**

## 3.8. Diffuse Radiations and Radiation Pressure

The radiation is said to be diffused if it travels in all possible directions. Consider the diffused radiations in an isothermal enclosure.

Let a photon of energy $h\nu$ move with velocity of light $c$. According to the theory of relativity this energy of the photon is equivalent to a mass $m$ given by

$$mc^2 = h\nu$$

$$m = \frac{h\nu}{c^2}$$

Then the momentum of the photon = mass × velocity.

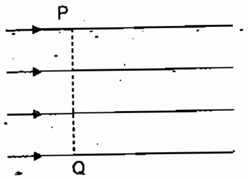
$$= \frac{h\nu}{c^2}c = \frac{h\nu}{c}$$

$$= \frac{e}{c}, \text{ } e \text{ being energy of a photon,}$$

Now the momentum incident on the surface perpendicular to the direction of incident photon beam per unit area per second is given by

$$p = \Sigma\frac{e}{c}$$

$$= \frac{\Sigma e}{c} \qquad \text{...(1)}$$



(Fig. 3.6)

but $\Sigma e$ = total energy incident on the surface per unit area per second $= E$ (say).

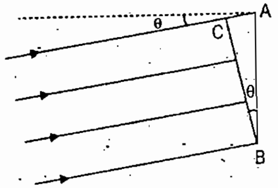
∴ The pressure on surface = Rate of change per unit area.

= momentum incident normally per unit area per second.

$$p = \frac{\Sigma e}{c} = \frac{E}{c} \qquad \text{...(2)}$$

where $\Sigma e = E$ = energy incident on the surface per unit area per second.

Let $u$ be the energy density of diffuse radiation in the enclosure having surface $AB$ of area $S$.



(Fig. 3.7)

Let the beam of diffuse radiation make an angle (θ) with the normal to the surface $AB$ The energy incident on the normal surface $BC$ per unit area per second $= uc$.

If $S'$ is the surface area of the plane $BC$, the energy incident on the surface $BC$ per second $= uc \,.\, S'$.

But surface area of the plane $BC$, $S'$ = (surface area of plane $AB$) × $\cos\theta = S\cos\theta$

∴ The energy incident on the surface $BC$ per second

$$= uc\,S\cos\theta.$$

From fig. 3.7 it is obvious that the total energy crossing the plane $BC$ per second is equal to the energy incident on the plane $AB$ per second.

Therefore, the energy incident on the plane $AB$ per second

$$= uc\,S\cos\theta.$$

So the energy incident on the plane $AB$ per unit area per second $= \frac{uc\cos\theta}{S} = uc\cos\theta$.

Therefore, the momentum incident the surface $AB$ per unit area per second

$$= \frac{uc\cos\theta}{c} = u\cos\theta$$

The component of this momentum in a direction normal to the surface $AB = (u\cos\theta)\cos\theta$

$$= u\cos^2\theta. \qquad \text{...(3)}$$

If all this momentum is absorbed, then eqn. (3) gives the total rate of change of momentum per second per unit area normal to the surface $AB$, *i.e.*, the pressure of radiation on the surface $AB$ is given by

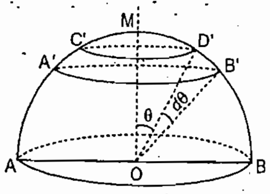
$$p = u\cos^2\theta \qquad \text{...(4)}$$

In the case of diffuse radiations, the radiation is incident from all possible directions with equal probability. To find the pressure of diffuse radiations. WE have to consider all possible values of θ given by

$$p = u\,\overline{\cos^2}\,\theta \qquad \text{...(5)}$$

where $\overline{\cos^2\theta}$ represents averaged $\cos^2\theta$ over all directions.

Consider the radiation to be equivalent to a large number of beams of equal intensity, say $N$, distributed uniformly over all directions.



(Fig. 3.8)

In order to calculate $u\cos^2\theta$ imagine a hemisphere of radius $r$ (fig. 3.8) round the centre $O$ of the element $AB$. Now from the surface of the hemisphere cut out a ring shaped element $(A'\,B'\,C'\,D')$ by means of two cones of semi angles θ and $\theta + d\theta$ drawn from $O$ as apex and $OM$ (which is perpendicular to $AB$) as axis.

The area of this ring $= 2\pi r\sin\theta\, r\,d\theta = 2\pi r^2\sin\theta\,d\theta$.

As $N$ beams are considered to be uniformly distributed over the surface of the hemisphere which is equal to $2\pi r^2$.

The number of beams passing through the area of the ring,

$$dN = \frac{2\pi r^2\sin\theta\,d\theta}{2\pi r^2}N = N\sin\theta\,d\theta. \qquad \text{...(6)}$$

Fraction of beams incident between angles θ and $\theta + d\theta$

$$= \frac{dN}{N} = \sin\theta\,d\theta$$

The pressure $dp$ due to beams incident between angles θ and $\theta + d\theta$ is therefore, written as

$$dp = \frac{dN}{N}u\cos^2\theta = \sin\theta\,d\theta.\,u\cos^2\theta$$

$$= u\cos^2\theta\sin\theta\,d\theta. \qquad \text{...(7)}$$

For all possible rings within the hemisphere θ may vary from 0 to $\frac{\pi}{2}$, therefore pressure $p$ is given by

$$p = \int_0^{\pi/2} u\cos^2\theta\sin\theta\,d\theta$$

$$u = \int_0^{\pi/2}\cos^2\theta\sin\theta\,d\theta \qquad \text{...(8)}$$

Now put $\cos\theta = x$

$$\therefore \qquad -\sin\theta\,d\theta = dx$$

$$\therefore \quad p = u\int_1^0 x^2(-dx) = u\int_0^1 x^2\,dx$$

$$= u\left[\frac{x^2}{3}\right]_0^1 = \frac{u}{3}.$$

$$\therefore \quad \boxed{\textbf{Pressure of diffuse radiation} = \frac{1}{3} \times \textbf{energy density.}}$$

## 3.9. Stefan-Boltzmaan Law :

It states that *the rate of emission of radiant energy by unit area of perfectly black-body is directly proportional to the fourth power of its absolute temperature.* It symbols

$$E = \sigma T^4$$

where $\sigma$ is a constant and is called *Stefan's constant.*

The law in the above form refers to the emission only the not to the net loss of heat by body after exchange with the surroundings. It simply deals with the amount of heat emitted by the body by virtue of its temperature irrespective of what it receives from the surroundings. The law can be extended to represent the net loss of heat and may be enunciated as follows :

A black-body at absolute temperature $T$ surrounded by another black-body at absolute temperature $T_0$ not only loses an amount of energy $\sigma T^4$ but also gains $\sigma T_0^4$, thus the amount of heat lost by the former per unit time is given by

$$E = \sigma(T^4 - T_0^4)$$

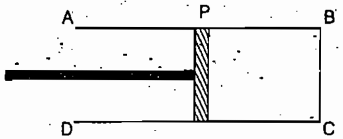
The law is known as *Stefan Boltzmann's law* as Boltmann deduced is thermodynamically.

**Thermodynamical Proof :**

Let us consider a cylindrical enclosure $ABCD$ of uniform cross-section with perfectly reflecting walls and provided with a perfectly reflecting piston $P$. Let it be filled with diffuse radiations of energy density $u$ at uniform temperature $T$.

If $V$ is the volum of the enclosure ; then the total internal energy of radiations inside the enclosure is given by

$$U = uV \qquad \text{...(1)}$$



(Fig. 3.9)

Let a small amount of heat $dQ$ flow in the enclosure form outside and at the same time the piston moves out so that the volume changes by a small amount $dV$. In this process the temperature and as a result the energy density $u$ changes by an infinitesimal amount. If $dU$ is the change in internal energy of radiation and $dW$ is the external work done by radiation in the expansion of volume by an amount $dV$, then by the first law of thermodynamics

$$dQ = dU + dW.$$

But $U = uV$ and $dW = pdV$, $p$ being the pressure of radiation.

$$dQ = d(uV) + p\,dV$$

But the pressure of diffuse radiation $p = \frac{1}{3}u$ therefore.

$$dQ = d(uV) + \frac{1}{3}u\,dV$$

$$= u\,dV + V\,du + \frac{1}{3}u\,dV$$

$$= V\,du + \frac{4}{3}u\,dV. \qquad \text{...(2)}$$

If $dS$ is the change in entropy of the radiation, then from second law of thermodynamics, we have

$$dS = \frac{dQ}{T} \qquad \text{...(3)}$$

Substituting value of $dQ$ from (2) in (3), we have

$$dS = \frac{V}{T}du + \frac{4u}{3T}dV. \qquad \text{...(4)}$$

From this expression it is clear that $S$ is function of two independent variables $u$ and $V$, *i.e.*,

$$S = f(u, V)$$

$$dS = \frac{\partial S}{\partial u}du + \frac{\partial S}{\partial V}dV \qquad \text{...(5)}$$

Comparing (4) and (5), we get

$$\frac{\partial S}{\partial u} = \frac{V}{T} \text{ and } \frac{\partial S}{\partial V} = \frac{3u}{4T} \qquad \text{...(6)}$$

As $dS$ is a perfect differential, we have

$$\frac{\partial^2 S}{\partial u\,\partial V} = \frac{\partial^2 S}{\partial V\,\partial u}$$

$$\frac{\partial}{\partial u}\left(\frac{\partial S}{\partial V}\right) = \frac{\partial}{\partial V}\left(\frac{\partial S}{\partial u}\right) \qquad \text{...(7)}$$

Substituting the values of $\frac{\partial S}{\partial T}$ and $\frac{\partial S}{\partial u}$ from (6) in (7), we get

$$\frac{\partial}{\partial u}\left(\frac{4u}{3T}\right) = \frac{\partial}{\partial V}\left(\frac{V}{T}\right) \qquad \text{...(8)}$$

As $T$ is independent of $V$ and is a function of $u$ only, on differentiating (8), we get

$$\frac{4}{3T} - \frac{4u}{3T^2}\frac{\partial T}{\partial u} = \frac{1}{T}$$

$$\frac{1}{3T} = \frac{4u}{3T^2}\frac{\partial T}{\partial u}$$

$$\frac{\partial u}{u} = 4\frac{\partial T}{T}$$

Integrating we have

$\log u = 4 \log T + \log A$, $\log A$ being constant of integration

This gives

$$u = AT^4 \qquad \text{...(9)}$$

But it can be shown that the total rate of emission of radiant energy per unit area is related to the energy density by the relation

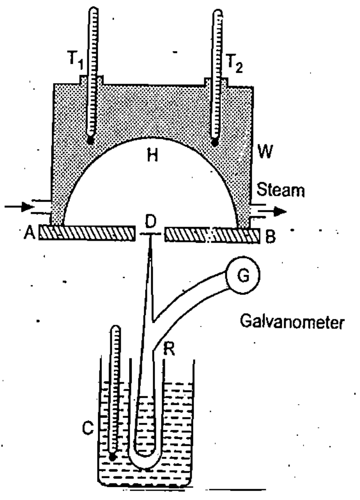
$$E = \frac{1}{4}uc$$

$$\therefore \quad E = \frac{1}{4}AcT^4 \text{ or } E = \sigma T^4 \qquad \text{...(10)}$$

where $\sigma$ is a constant called Stefan's constant. The value of Stefan's constant is $5{\cdot}672 \times 10^{-8}$ joule $\text{m}^{-2}\,\text{sec}^{-1}\,(\text{K})^{-4}$.

## 3.10 Determination of Stefan's constant

The apparatus used for determination of Stefan's constant consists of a hollow metallic hemisphere $H$ blackened inside and placed in a wooden box $W$, lined with tin which serves as a steam chamber. Steam can be passed in the chamber when desired and then in steady state the temperature of hemisphere remains constant, equal to that of steam and may be measured by thermometers $T_1$ and $T_2$. The hemisphere $H$ rests symmetrically on a platform $AB$ which has a small hole at its centre. A small silver disc $D$ blackened at its top surface can be fitted or taken out from the hole. One junction of the silver-constantan couple is soldered to the lower surface of $D$; while the other is placed in the water bath or sand container $C$. A sensitive galvanometer (G) is introduced in thermocouple circuit with resistance $R$ in series.



(Fig. 3.10)

**Theory :** When the inner surface of $H$ is heated by passing steam, it acts as a black body radiator. The disc $D$ absorbs the radiation emitted by $H$ and its temperature rises continuously, thus causing a difference of temperature in the two junctions of the thermocouple.

If $T_1$ is the steady state temperature of $H$ and $T_0$ is that of disc $D$, when it is just exposed to radiation from $H$.

Then by Stefan-Boltzmann law the **net energy gained by the disc per second = *EA***

$$= \sigma (T_1^4 - T_0^4) A \text{ joule, } A \text{ being area of disc,}$$

$$= \frac{\sigma (T_1^4 - T_0^4) A}{J} \text{ kilocal.}$$

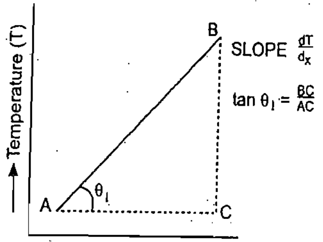
If $m$ is the mass of disc, $c$ its specific heat in kilocal (°C)$^{-1}$ (kg)$^{-1}$ and $dT/dt$ it rate of rise of temperature at $T_0$, then the energy gained by the disc per second would be $mc\,(dT/dt)$; hence we must have

$$mc \frac{dT}{dt} = \frac{\sigma (T_1^4 - T_0^4) A}{J}$$

or
$$C = \frac{Jmc}{A (T_1^4 - T_0^4)} \frac{dT}{dt} \text{ watt m}^{-2}\text{K}^{-4} \qquad \ldots(1)$$

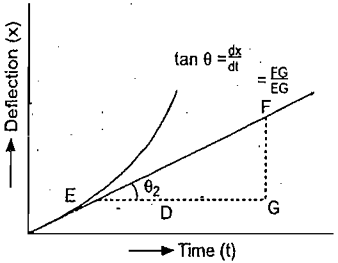
Now it remains to evaluate $dT/dt$; which is done as follows :

**(i) Calibration of Thermo-couple :** Before passing steam in the chamber, the silver disc is kept in position in the hole. The water or sand bath (C) is heated to a suitable temperature Due to temperature difference of junctions of thermocouple, the galvanometer gives deflection. The resistance $R$ is so chosen that the deflection does not go beyond the scale of galvanometer. Now the deflection $x$ of the galvanometer is noted for different temperatures $T$ of the bath when falling. The graph is plotted between temperature $T$ on $Y$ axis and deflection $x$ on $X$-axis. The graph is in the form of a straight line whose slope ($tan\, \theta_1$) gives $dT/dx$. During this part the disc acts as a cold junction of thermocouple.



(Fig. 3.11)

**(ii) Determination of $dT/dt$ :** The disc is removed from the hole and steam is passed through chamber $W$. When temperature of chamber becomes steady, the disc is again positioned in the hole of chamber. The disc now absorbs radiation from chamber and so its temperature rises. Therefore, deflection in galvanometer increases. A graph is plotted between deflection $x$ and time $t$. A point $E$ near the origin is chosen and a tangent is drawn from $E$ on the graph. The slope of tangent (tan $\theta_2$) gives $dx/dt$.



(Fig. 3.12)

Thus
$$\frac{dT}{dt} = \frac{dT}{dx} \times \frac{dx}{dt} = \tan\theta_1 \times \tan\theta_2$$
$$= \frac{BC}{AC} \times \frac{FG}{EG}$$

Thus the value of $dT/dt$ at temperature corresponding to point $E$ is obtained. Knowing constants $m$, $c$ and $A$ of disc, temperatures $T_1$ of steam chamber, $T_0$ the room temperature. ; $\sigma$ may be evaluated from (1).

## 3.11 Adiabatic Expansion of Black-body Radiation :

Imagine an enclosure of perfectly reflecting walls and capable of expanding. Let it be filled with diffuse black body radiations of energy density $u$ at a uniform temperature $T$ and let this radiation be in equilibrium with a tiny piece of matter of negligible thermal capacity. If the radiation is caused to expand adiabatically, there is no exchange of energy between the walls and the radiation and the work done on the surroundings is accomplished at the expense of the internal energy of both the radiation and the piece of matter. The energy density of the radiation inside the enclosure now falls and so the temperature of piece of matter also decreases as the radiation is always in equilibrium with it during expansion. The final temperature of the tiny matter piece can now be calculated in the following manner :-

Let $V$ be the volume of the enclosure, then total internal energy of radiations,

$$U = u\,V.$$

Let us now suppose that the walls of the enclosure move out-wards slowly with uniform velocity, so that the radiation inside it expand adiabatically. If $dV$ is the change in volume of the enclosure, the work done by the pressure of radiation on the walls of the enclosure is $p\,dV$ which is drawn from internal energy of radiation. If $dU$ is the change in internal energy, then by first law of thermodynamics, for adiabatic change ($dQ = 0$), we have

$$dU + p dV = dQ = 0.$$

or
$$d(uV) + \frac{1}{3} u dV = 0 \qquad \left(\text{since } U = uV \text{ and } p = \frac{1}{3} u\right)$$

or
$$u dV + V du + \frac{1}{3} u dV = 0.$$

or
$$\frac{4}{3} u dV = - V du$$

or
$$\frac{4}{3}\frac{dV}{V}=-\frac{du}{u}$$

Integrating, we get
$$\frac{4}{3}\log V=-\log u+\text{ constant}$$

or
$$\log V^{4/3}\,.\,u=\text{ constant}$$

But $u=AT^4$ from equation (7) of section 3·10.

∴
$$V^{4/3}\,.\,T^4=\text{ constant}$$

or
$$V^{1/3}\,.\,T=\text{ constant,} \qquad \text{...(1)}$$

or
$$VT^3=\text{ constant}$$

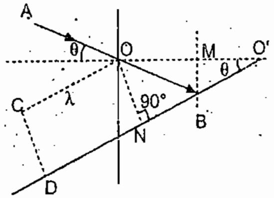
*i.e.*
$$VT^3=V'T'^3. \qquad \text{...(2)}$$

where $T'$ is the new temperature corresponding to volume $V'$. This relation is useful in the study of spectral distribution of energy. According to it, if the volume of black-body radiation is increased adiabatically by a factor 8, the radiation will then be capable of existing in equilibrium with matter at a temperature one-half of the initial temperature.

It should be noted that the black (full) radiation inside the enclosure remains black after a reversible adiabatic expansion.

## 3.12 Spectral Distribution of Radiation Energy

**Wien's law.** The Stefan-Boltzmann law expresses the relationship between the total energy and the temperature of the blackbody radiation. This law does not give the actual distribution of energy in the different parts of the spectrum. Several theoretical attempts have been made to obtain it from thermodynamical laws. The first, notable success in this direction was acheieved by Wien who, with the application of thermodynamical principles, provided a relation expressing the intensity of radiation between wavelengths $\lambda$ and $\lambda+d\lambda$ as a function of the wave length $\lambda$ and the temperature $T$ of the source.



(Fig. 3.13)

In order to derive Wiew's law, consider a spherical enclosure whose walls reflect perfectly but diffusely. Let it be full of radiations of energy density $u$ at a uniform temperature $T$. Let the walls of the enclosure move outwards slowly with a uniform velocity $v$, so that the radiations inside it undergo a reversible adiabatic expansion. The temperature $T$ of the radiation is then related to the volume $V$ of the spherical enclosure through equation (1) of section 3·12 which is
$$V^{1/3}\,.\,T=\text{ constant.} \qquad \text{...(1)}$$

Let us now find a change in the wave-length suffered by a ray on reflection at slowly moving walls of the enclosure. Let $AO$ be the ray of wave-length $\lambda$ incident at an angle $\theta$ on the wall as shown in fig. 3.13. Let a particular wave-crest strike the wall as $O$. The crest will be reflected along $OC$. If $OC=\lambda$, then as the reflected wave-crest reaches $C$, the next will reach at $O$ in time $T$. $T$ being time period of wave-motion. During this time the wall has traversed a distance $OM=vT$. Therefore, the path followed by second wave-crest will be $OBD$. Then increase in wavelength due to one reflection
$$=OB+BN=O'B+BN=OO'\cos\theta$$

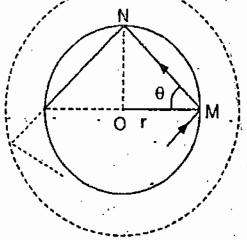
$$=2\,(OM)\cos\theta=2vT\cos\theta$$
$$=\frac{2v\lambda}{c}\cos\theta \qquad \text{...(2)}$$
$$\left(\text{since } T=\frac{\lambda}{c},\ c\text{ being velocity of radiation}\right)$$

To calculate the number of reflections per second let us consider a ray striking the spherical wall at angle $\theta$ and reflected along $MN$ making an angle $\theta$ with the normal.

The distance traversed by the beam before it suffers the next reflection
$$=MN=2r\cos\theta.$$

Therefore, the time between two successive reflections
$$=\frac{2r\cos\theta}{c}$$

∴ The number of reflections per second $=\dfrac{c}{2r\cos\theta}$



(Fig. 2.14)

If $\delta r$ is the increase is radius in time $\delta t$, then the number of reflections in time $\delta t$
$$=\frac{c}{2r\cos\theta}\,.\,\delta t=\frac{c}{2r\cos\theta}\,.\,\frac{\delta r}{v}. \qquad \text{...(3)}$$

∴ Change in wave-length in time $\delta t$,

$\delta\lambda=$ Change in wave-length in one reflection × Number or reflections in time $\delta t$
$$=\frac{2v\lambda}{c}\cos\theta\times\frac{c}{2r\cos\theta}\,.\,\frac{\delta r}{v}\ \text{[using (2) and (3)]}$$
$$=\lambda\frac{\delta r}{r}$$

∴
$$\frac{\delta\lambda}{\lambda}=\frac{\delta r}{r}. \qquad \text{...(4)}$$

Volume of sphere,
$$V=\frac{4}{3}\pi r^3.$$

∴ Change in volume of sphere,
$$\delta V=\frac{4}{3}\pi\,.\,3r^2\,.\,\delta r$$

∴
$$\boxed{\frac{\delta V}{V}=\frac{3\,\delta r}{r}} \qquad \text{...(5)}$$

or
$$\frac{\delta r}{r}=\frac{1}{3}\frac{\delta V}{V}$$

Substituting this value of $\delta r/r$ in equation (4), we get
$$\frac{\delta\lambda}{\lambda}=\frac{1}{3}\frac{\delta V}{V} \qquad \text{...(6)}$$

Integrating, we get $\quad \log\lambda=\dfrac{1}{3}\log V+\log K,\quad$ where $\log K$ is the integration constant.

This gives
$$\lambda=KV^{1/3}$$

or $$V^{1/3}=\frac{\lambda}{K} \qquad \text{...(7)}$$

Substituting this in equation (1), we get

$$\frac{\lambda}{K}T=\text{ constant.}$$

or $$\lambda T=\text{ constant.} \qquad \text{...(8)}$$

This is usual *form of Wien's displacement law.* According to it if the radiation of a particular wave-length at a certain temperature is adiabatically altered to another wave length, the temperature changes in the inverse ratio.

Let us now suppose that the radiations lying between wavelength $\lambda$ and $\lambda+d\lambda$ are isolated in the enclosure and let these alone be subjected to adiabatic expansion. Let $u_\lambda\, d\lambda$ be the energy density of these radiations. The total energy density of these radiations,

$$U=u_\lambda\, d\lambda\, V.$$

$\therefore$ When these radiations alone are expanded adiabatically, then work done in adiabatic expansion

$$\Delta W=p\cdot\Delta V=\frac{1}{3}u_\lambda\, d\,\lambda.\,\Delta V.$$

From first law of thermodynamics, we have $\Delta U+\Delta W=\Delta Q$

$$\Delta\,(u_\lambda\, d\lambda\, V)+\frac{1}{3}u_\lambda\, d\lambda\,.\,\Delta V=\Delta Q=0\ (\text{since here }\Delta Q=0)$$

or $$\Delta u_\lambda\,.\,d\lambda\,.\,V+u_\lambda\,\Delta d\lambda\,.\,V+u_\lambda\, d\lambda\,.\,\Delta V+\frac{1}{3}u_\lambda\, d\lambda\,.\,\Delta V=0$$

or $$\Delta u_\lambda\, d\lambda\,.\,V+u_\lambda\,.\,\Delta d\lambda\,.\,V+\frac{4}{3}u_\lambda\, d\lambda\,.\,\Delta V=0.$$

Dividing throughout by $u_\lambda\,.\,d\lambda\,.\,V$, we have

$$\frac{\Delta u_\lambda}{u_\lambda}+\frac{\Delta d\lambda}{d\lambda}+\frac{4}{3}\frac{\Delta V}{V}=0. \qquad \text{...(9)}$$

Since $d\lambda$ changes in the same way as $\lambda$, we have

$$\frac{\Delta d\lambda}{d\lambda}=\frac{\Delta\lambda}{\lambda}.$$

Substituting this in equation (9), we get

$$\frac{\Delta u_\lambda}{u_\lambda}+\frac{\Delta\lambda}{\lambda}+\frac{4}{3}\frac{\Delta V}{V}=0. \qquad \text{...(10)}$$

Also from equation (6), we have

$$\frac{1}{3}\frac{\Delta V}{V}=\frac{\Delta\lambda}{\lambda}.$$

Substituting this in equation (10), we get

$$\frac{\Delta u_\lambda}{u_\lambda}+\frac{\Delta\lambda}{\lambda}+\frac{4\Delta\lambda}{\lambda}=0.$$

or $$\frac{\Delta u_\lambda}{u_\lambda}=-\frac{5\Delta\lambda}{\lambda}$$

Integrating, we get $\log u_\lambda=-5\log\lambda+\log C$, where $\log C$ is constant of integration. This gives

$$\log\,(u_\lambda\,.\,\lambda^5)=\text{ constant or }u_\lambda\lambda^5=u'_\lambda\lambda'^5 \qquad \text{...(11)}$$

where $u_\lambda'$ is the density of radiation of wave-length $\lambda'$ (to which the radiation of wave-length $\lambda$ has been transformed by expansion at temperature $T'$.

Therefore,

$$\frac{u_\lambda}{u_\lambda'}=\frac{\lambda'^5}{\lambda^5}=\frac{T^5}{T'^5} \qquad \{\because \lambda T=\lambda' T'\}$$

Obviously, $u_\lambda$ must be a function of $T$, hence the constant in equation (11) must contain $T$. Also we know that the constant is such that it remains constant throughout in such process of adiabatic expansion. From equation (8) we know that for such process $\lambda T$ is constant. Then we may say that the constant in equation (11) must be function of $\lambda T$.

Then equation (11) may be written as

$$u_\lambda\,\lambda^5=A'f(\lambda T), \qquad \text{where } A' \text{ is any constant}$$

$$u_\lambda\, d\lambda=\frac{A'}{\lambda^5}f(\lambda T)\, d\lambda. \qquad \text{...(12)}$$

As emissive power $E_\lambda$ is proportional to energy density $u_\lambda$, we have $E_\lambda\, d\lambda \propto u_\lambda\, d\lambda$.

$\therefore$ Equation (12) gives $$E_\lambda\, d\lambda=\frac{A}{\lambda^5}f(\lambda T)\, d\lambda. \qquad \text{...(13)}$$

This equation is called the *Wien's distribution law.* Here $E_\lambda\, d\lambda$ denotes the amount of energy contained in the spectral region from wave-length $\lambda$ to $\lambda+d\lambda$ emitted by a black-body at temperature $T$.

Equation (13) may be written as

$$E_\lambda\, d\lambda=\frac{A\,T^5}{\lambda^5\,T^5}f(\lambda T)\, d\lambda$$

$$=AT^5\,(\lambda T)^{-5}f(\lambda T)\, d\lambda$$

or $$E_\lambda\, d\lambda=AT^5\,F\,(\lambda T)\, d\lambda, \qquad \text{...(14)}$$

where $$F\,(\lambda T)=(\lambda T)^{-5}f\,(\lambda T).$$

Equation (14) represents another from of *Wien's distribution law.*

In terms of ν, *Wien's distribution law,* using equation (14) may we written as

$$E_\nu\, d\nu=AT^5\,F\,(\lambda T)\left(-\frac{c}{\nu^2}d\nu\right)\quad\left(\textit{since }\lambda=\frac{c}{\nu}\text{ so }d\nu=-\frac{c}{\nu^2}d\nu\right)$$

$$=BT^3\left(\frac{\nu}{T}\right)^{-2}F'\left(\frac{\nu}{T}\right)d\nu \qquad \text{...(15)}$$

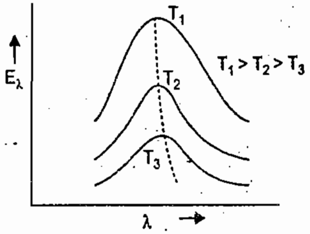
Here $E_\nu\, d\nu$ represents the amount of energy contained in the spectral region from frequency ν and ν + $d\nu$ emitted by a black body at temperature $T$.

As $E_\lambda$ is proportional of $u_\lambda$ and $\lambda T=\lambda' T'$, we have using equation (11)

$$\frac{E_\lambda}{E_\lambda'}=\frac{T^5}{T'^5} \qquad \text{...(16)}$$

It is now apparent that if the distribution energy at any temperature $T$ is given, the distribution at any other temperature $T'$ can be found with the help of

$$\left.\begin{aligned} \lambda T &= \lambda' T' \\ \text{and} \qquad \frac{E_\lambda}{T^5} &= \frac{E_\lambda'}{T'^5} \end{aligned}\right\} \qquad \text{...(17)}$$



(Fig. 3.15)

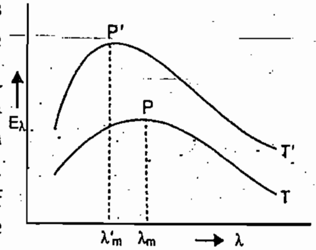
When $T' > T$, then the distribution of energy at temperature $T'$ can be obtained graphically by shortening each λ in the ratio $(T/T')$ (so that $\lambda T$ remains constant) and increasing the corresponding $E_\lambda$ in the ratio $(T'/T)^5$. The curve at $T'(>T)$ becomes higher, but more closed up such that the total area representing the intensity is changed in the ratio $(T'/T)^4$. It is found the corresponding to highest point $P$ (*i.e.*, the point of maximum emission) in the first curve at temperature $T$, there is a highest point in the second curve at temperature $T'$, such that

$$\lambda_m T = \lambda'_m T'.$$

This equation states that the *product of the wave-length corresponding to maximum energy of emission* (*i.e.*, $\lambda_m$) and the absolute temperature $T$ is constant.

*i.e.*, $$\lambda_m T = constant\ b = 0{\cdot}2898 \text{ cm K}. \qquad \text{...(18)}$$

This is called *Wien's displacement law.*



(Fig. 3.16)

The Wien's displacement law was subjected to experimental tests. Lummer and pringsheim have obtained the experimental $E_\lambda - \lambda$ curves at various temperatures. These graphs have been shown in Fig. 3.15. The wavelengths are plotted in microns ($10^{-6}$ cm) as abscissa and $E_\lambda$ in arbitrary units as ordinate. It is seen that $E_\lambda$ has a maximum value at a certain wave-length $\lambda_m$ at a given temperature. An increase in temperature caused a decrease in $\lambda_m$, *i.e.* the maximum emission gets displaced towards shorter wave-length with rise of temperature in accordance of Wien's law. The curve corresponding to a higher temperature lies above that at the lower temperature and hence area under each curve increases with increase of temperature. It is found that the area bounded by the curve and the axis of λ is proportional to $T^4$. Since this area represents the total energy density, the result is in complete agreement with the Stefan Boltzmann law. Thus Wien's law is found quite satisfactory when applied to short waves but for long waves and at higher temperature it does not confirm to the experimental results.

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## SOLVED EXAMPLE

**Examples. 1.** *The radiation from the moon gives two maxima at*

$$\lambda = 4700 \text{ Å } (0{\cdot}47\ \mu) \text{ and } \lambda = 14000 \text{ Å } (14\ \mu).$$

*What conclusions do you draw from this ?*

**Solution.** The first maximum (0·47 μ) coincides with the maximum in solar radiation and is obtained because sun's radiations are reflected from moon's disc. The other maximum (14 μ) is due to moon's own radiation.

From these data we can calculate the temperature of the sun and of the moon using Wien's displacement law

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$$\lambda_m \cdot T = b = 0{\cdot}2898 \times 10^{-2} \text{ mK}$$

When $$\lambda_m = 0{\cdot}47\ \mu = 0{\cdot}47 \times 10^{-6} \text{ m}$$

$$T_8 = \frac{0{\cdot}2898 \times 10^{-2}}{0{\cdot}47 \times 10^{-6}} = 6166 \text{ K},$$

which gives the temperature of the sun.

When $\lambda_m = 14\mu = 14 \times 10^{-6}$ m, we get the temperature of the moon

$$T_m = \frac{0{\cdot}2898 \times 10^{-2}}{14 \times 10^{-6}} = 207 \text{ K}.$$

## 3.13 Number of resonators per unit volume lying in the frequency range ν and ν + *d*ν

Consider the radiation to be enclosed in a hollow cubic enclosure, the walls of which are perfectly reflecting. According to electromagnetic theory the radiation is supposed to consist of a number of waves. These waves travel in all possible directions in the enclosure and undergo multiple reflections from the various walls of the enclosure. Inside the enclosure stationary vibrations are formed with the walls as nodal points as a result of the interference of the reflected waves with the corresponding incident waves. The formation of stationary vibrations can be understood by an analogy with vibrations of a stretched string with both end points fixed. It is well known that the end points of the string are two nodes of stationary vibrations and only certain discrete frequencies of vibrations are allowed. If $l$ is the length of the string, the allowed wavelength are given by

$$\lambda = \frac{2l}{n};\ n = 1, 2, 3, 4, \ldots, \infty \qquad \text{...(1)}$$

The corresponding allowed frequencies are

$$\nu = \frac{c}{\lambda} = \frac{nc}{2l};\ n = 1, 2, 3, 4, \ldots, \infty,$$

where $c$ is the speed of the waves.

Every allowed frequency is called a *mode of vibration*. The allowed modes of vibration inside the cube can be calculated just as in the case of strings. But in this case the waves are confined to a three-dimensional space. We therefore, have to think a three dimensional picture with the walls of the cube as nodal planes. Let each side of the cube be $a$. If we take the three intersecting edges of the cube as X, Y and Z-axes of a cartesian co-ordinate system and cos α, cos β, cos γ as direction cosines of the direction of propagation of a particular wave, then the projections of the edges of the cube on the direction of propagation of the wave are $a \cos\alpha$, $a \cos\beta$, $a \cos\gamma$ respectively. In this case only those waves will be allowed for which all the faces of the cube form nodal planes. For this the allowed wavelengths have to satisfy three conditions of the kind of equation (1) in which $l$ is replaced by $a \cos\alpha$, $a \cos\beta$ and $a \cos\gamma$ resprectively. Thus an allowed wave length λ must satisfy

$$\lambda = \frac{2a \cos\alpha}{n_1},\ \lambda = \frac{2a \cos\beta}{n_2} \text{ and } \lambda = \frac{2a \cos\gamma}{n_3} \qquad \text{...(2)}$$

where, $n_1$, $n_2$ and $n_3$ are positive integers.

Now according to trigonometric condition of direction cosines

$$\cos^2\alpha + \cos^2\beta + \cos^2\beta = 1. \qquad \text{...(3)}$$

Substituting values of cos α, cos β and cos γ from equations (2) in (3), we get

$$\frac{n_1^2\lambda^2}{4a^2}+\frac{n_2^2\lambda^2}{4a^2}+\frac{n_3^2\lambda^2}{4a^2}=1.$$

or

$$n_1^2+n_2^2+n_3^2=\left(\frac{2a}{\lambda}\right)^2.$$

As $\lambda=\frac{c}{\nu}$, we have

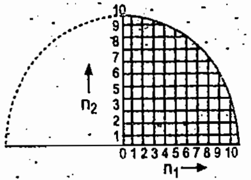
$$n_1^2+n_2^2+n_3^2=\left(\frac{2a\nu}{c}\right)^2 \qquad \text{...(4)}$$

This equations gives the allowed frequencies (or modes of vibration) inside the cube. According to this only those frequencies are allowed for which equation (4) hold with various choices or positive integral values of $n_1, n_2$ and $n_3$. Each choice of the value of $n_1, n_2$ and $n_3$ corresponds to a frequency (or a mode of vibration). The total number of modes of vibration are the total number of possible sets $(n_1, n_2, n_3)$. The number of modes of vibration within the frequency interval ν and ν + $d\nu$ can be found with the help of equation (4).

For convenience let us first count the modes of vibration in an analogous two dimensional problem. The two dimensional analogue of equation (4) is

$$n_1^2+n_2^2=\left(\frac{2a\nu}{c}\right)^2 \qquad \text{...(5)}$$

If we plot a graph with $n_1$ along $X$-axis and $n_2$ along $Y$-axis for a given value of ν $\left(i.e., \text{ of } \frac{2a\nu}{c}\right)$ we get the points lying on a circle; since equation (5) represents a circle of radius $\frac{2a\nu}{c}$. Such a graph is shown in fig. 3·17 for $\frac{2a\nu}{c}=10$. In the graph the abscissa and ordinates have been drawn corresponding to all possible integral values of $n_1$ and $n_2$ upto 10. Every intersection of these abscissa and ordinates represents an allowed set of values of $n_1$ and $n_2$, and hence a mode of vibration. The points on the circle correspond to the frequency ν, while those lying inside the circle correspond to frequencies less than ν. As only positive values of $n_1$ and $n_2$ are allowed, we have to consider the intersections only in positive quadrant. The lines drawn divide the quadrant in a number of unit squares.



(Fig. 3.17)

Every point of intersection can be associated with one square. As the area of each square is unity, therefore, the number of squares is equal to the area inside the quadrant of the circle. Thus the number of modes of vibration with frequencies less than ν is equal to the area of a quadrant of a circle represented by equation (5). This area is $\frac{1}{4}.\pi r^2=\frac{1}{4}.\pi\left(\frac{2a\nu}{c}\right)^2=\frac{\pi a^2\nu^2}{c^2}$ Similarly we can state that the number of modes of vibration within frequency interval ν and ν + $d\nu$ is equal to the area in the positive quadrant lying between two circles of radii $\frac{2a\nu}{c}$ and $\frac{2a(\nu+d\nu)}{c}$.

The area is

$$\frac{1}{4}\pi\left[\left\{\frac{2a(\nu+d\nu)}{c}\right\}^2-\left(\frac{2a\nu}{c}\right)^2\right]=\frac{1}{4}\pi\cdot\frac{8a^2\nu}{c^2}=\frac{2\pi a^2\nu^2 d\nu}{c^2}.$$

Now considering the case of three dimensions, we see that the circle is replaced by a sphere and a mesh of squares is replaced by a mesh of cubes. The number of modes of vibrations within frequency renge ν + $d\nu$ is now equal to the volume of the constant $\left(\frac{1}{8}\text{th}\right)$ of a spherical shell with the radii

$$\frac{2a\nu}{c} \text{ and } \frac{2a(\nu+d\nu)}{c}$$

This volume is $\frac{1}{8}\left\{\frac{4}{3}\pi(r+dr)^3-\frac{1}{8}\pi r^3\right\}=\frac{1}{8}.4\pi r^2 dr$

$$=\frac{1}{8}.4\pi\left(\frac{2a\nu}{c}\right)^2\frac{2a d\nu}{c}=\frac{4\pi a^2\nu^2}{c^3}d\nu.$$

But $a^3=V=$ volume of the cube.

Therefore, the modes of vibrations inside cubical enclosure within frequency range ν and ν + $d\nu=\frac{4\pi V\nu^2 d\nu}{c^3}$.

Thus the number of modes of vibration per unit volume with in frequency range ν and $d\nu=\frac{4\pi\nu^2 d\nu}{c^3}$.

Now the black body radiations travel with velocity of light ~~c and~~ are transverse in character unlike sound waves in the string which are longitudinal.

As there are two possible polarisations for each transverse wave, the modes of vibrations of transvere waves is double as for longitudinal waves. Therefore for black body radiation or electromagnetic waves, the number of modes of vibrations per unit volume within frequency range ν and ν + $d\nu$

$$=\frac{2\times 4\pi\nu^2 d\nu}{c^3}=\frac{8\pi\nu^2 d\nu}{c^3} \qquad \text{...(6)}$$

## 3.14. Rayleigh-Jean's law of Spectral Distribution of Energy :

Rayleigh's formula for the distribution of energy in the normal spectrum is based on the principle of equipartition of energy for all the possible modes of free vibration which might be assigned to radiation. Thus they considered average energy of an oscillator (*i.e.*, per mode of vibration) as

$$\bar{\varepsilon}=kT \qquad \text{(classical result).}$$

We have already seen (3·13) that the number of modes of vibration per unit volume in the frequeney range ν and ν + $d\nu$ is given by

$$N_\nu d\nu=\frac{8\pi\nu^2}{c^3}d\nu.$$

The energy density within frequency range ν and ν + $d\nu$ is, therefore, given by

$$E_\nu \, d_\nu = \frac{8\pi\nu^2}{c^3} \, d\nu \times kT.$$

This is Rayleigh-Jean's law *in terms of frequency.*

In *terms of wavelength,* Rayleigh-Jean's law may be written as

$$E_\lambda \, d\lambda = \frac{8\pi}{c^3}\left(\frac{c}{\lambda}\right)^2 \left|\frac{c}{\lambda^2} \, d\lambda\right| . kT.$$

$$= \frac{8\pi kT}{\lambda^4} \, d\lambda,$$

This law, like Wien's law was found not to accord with the experimental curves of Lummer and Pringsheim, whereas the Wien's law fitted the curves for shorter wavelengths at lower temperatures. Rayleigh-Jean's law explains the experimental measurement of the energy distribution at long wavelengths at higher temperatures and fails for short wavelengths.

## 3.15. Planck's Radiation Law ;

Planck found an empirical formula to explain the exprimentally observed distribution of energy in the spectrum of a black body. The formula may be deduced using following assumptions which may be called as *Planck's hypothesis.*

1. A radiation chamber is filled up with black radiation. The walls of chamber is formed of molecules which can vibrate with all possible frequencies and these molecules are called resonators and can exchange energy with radiation. The vibration of the resonator entails one degree of freedom only.

2. The oscillators or resonators can not radiate or absorb energy continuously; but an oscillator of frequency ν can only radiate or absorb energy in units or quanta of magnitude $h\nu$, where $h$ is a universal constant, called the *Planck's constant,* its value being equal to $6{\cdot}62 \times 10^{-34}$ joule second. This assumption is the most revolutionary in character, In other words, this states that the exchanges of energy between radiation and matter can not take place continuously, but are limited to discrete set of values 0, $h\nu$, $2h\nu$, $3h\nu$, ..., $nh\nu$, *i.e.,* in multiplies of some small unit, called the *quantum.*

**Average energy of Planck's oscillator.** If $N$ is the total number of Planck's rasonators and $E$ their total energy, then the average energy per Planck's oscillator is given by

$$\bar{\varepsilon} = \frac{E}{N} \qquad \text{...(1)}$$

According to Maxwell's law of molecular motion, if ε is the energy, the number of molecules having energies 0, ε, 2ε, ..., rε, ...are in the ratio

$$1 : e^{-\varepsilon/kT} : e^{-2\varepsilon/kT} : \text{.........} : e^{-r\varepsilon/kT} \text{.........etc.} \qquad \text{...(2)}$$

If $N_0$ is the number of resonators having energy zero, then the number of resonators $N_1$ having energy ε will he $N_0 \, e^{-\varepsilon/kT}$, the number of resonators $N_2$ having energy 2ε will be $N_0 \, e^{-2\varepsilon/kT}$ and in general, the number of resonators $N_r$ having energy $r\varepsilon$ will be $N_0 \, e^{-r\,\varepsilon/kT}$ and so on.

$$\therefore \qquad N = N_0 + N_1 + N_2 + \ldots + N_r \ldots$$

$$= N_0 + N_0 \, e^{-\varepsilon/kT} + N_0 \, e^{-2\varepsilon/kT} + \ldots + N_0 e^{-r\varepsilon/kT} + \ldots$$

$$= N_0 \, [1 + e^{-\varepsilon/kT} + e^{-2\varepsilon/kT} + \ldots + e^{-r\varepsilon/kT} + \ldots].$$

Putting $e^{-\varepsilon/kT} = y$.

$$N = N_0 \, [1 + y + y^2 + \ldots + y^r + ]$$

or

$$N = \frac{N_0}{1 - y} \qquad \text{...(3)}$$

The total energy of Planck's resonators will be

$$E = 0 \times N_0 + \varepsilon \times N_1 + 2\varepsilon \times N_2 + \ldots + r\varepsilon \times N_r + \ldots$$

$$= 0 + \varepsilon N_0 \, e^{-\varepsilon/kT} + 2\varepsilon N_0 \, e^{-2\varepsilon/kT} + .. + r\varepsilon \,.\, N_0 \, e^{-r\varepsilon/kT} + \ldots$$

[using equation (2)].

$$= N_0 \, \varepsilon \, [e^{-\varepsilon/kT} + 2e^{-2\varepsilon/kT} \ldots + re^{-r\varepsilon/kT} + \ldots]$$

$$= N_0 \, \varepsilon \, [y + 2y^2 + 3y^3 + \ldots + ry^4 + \ldots]$$

$$= N_0 \, \varepsilon \, S$$

where

$$S = y + 2y^2 + 3y^3 + \ldots + ry^r + \ldots$$

$$Sy = y^2 + 2y^3 + \ldots + (r-1) \, y^r + \ldots$$

$$S \, (1 - y) = y + y^2 + y^3 + \ldots + y^4 + \ldots$$

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

$$\therefore \qquad S = \frac{y}{(1 - y)^2}$$

$$\therefore \qquad E = N_0 \, \varepsilon \,.\, \frac{y}{(1 - y)^2} \qquad \text{...(4)}$$

Therefore the average energy of a resonator will be

$$\bar{E} = \frac{E}{N} = \frac{N_0 \,.\, \varepsilon \,.\, \dfrac{y}{(1 - y)^2}}{\dfrac{N_0}{1 - y}}$$

$$= \frac{\varepsilon y}{1 - y} = \frac{\varepsilon e^{-\varepsilon/kT}}{1 - e^{-\varepsilon/kT}}$$

or

$$\bar{\varepsilon} = \frac{\varepsilon}{\varepsilon^{\varepsilon/kT - 1}} \qquad \text{...(5)}$$

According to Planck's hypothesis of quantum theory $\varepsilon = h\nu$, therefore the average energy of Planck's oscillator is given by

$$\bar{\varepsilon} = \frac{h\nu}{e^{k\nu/kT} - 1}. \qquad \text{...(6)}$$

Number of resonators between frequency range ν and $\nu + d\nu$ is given by $N\,(\nu)\,d\nu = \dfrac{8\pi\nu^2}{c^3}$ ...(7)

Now the *energy density* belonging to the range $d\nu$ can be obtained by multiplying the average energy of Planck's oscillator by the number of oscillators per unit volume, in this frequency range $\nu$ and $\nu + d\nu$.

*i.e.,*
$$E_\nu d\nu = \left(\frac{8\pi\nu^2}{c^3}d\nu\right)\left(\frac{h\nu}{e^{h\nu/kT}-1}\right)$$

or
$$E_\nu d\nu = \frac{8\pi h\nu^3}{c^3}\cdot\frac{1}{e^{h\nu/kT}-1}d\nu \qquad ...(8)$$

where $E_\nu d\nu$ is energy density (*i.e.,* total energy per unit volume belonging to the range $d\nu$.

Equation (8) is called *Planck's radiation law.*

The energy density $E_\lambda d\lambda$ belonging to range $d\lambda$ can be obtained by using the relation $\nu = \frac{c}{\lambda}$ and hence $|d\nu| = \left|-\frac{c}{\lambda^2}d\lambda\right|$ we get

$$E_\lambda d\lambda = \frac{8\pi h}{c^3}\left(\frac{c^3}{\lambda^3}\right)\cdot\frac{1}{e^{hc/\lambda kT}-1}\left|-\frac{c}{\lambda^2}d\lambda\right|$$
$$= \frac{8\pi hc}{\lambda^5}\cdot\frac{d\lambda}{e^{hc/\lambda kT}-1} \qquad ...(9)$$

This is *Planck's radiation law in terms of wavelength.*

## SOLVED EXAMPLES

**Example. 2.** *Show that Planck's law reduces to Wein's law for shorter wavelenghts and Rayleigh-Jean's law for longer wavelenghs.*

**Solution.** Planck's radiation law is

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\cdot\frac{1}{e^{hc/\lambda kT}-1}d\lambda$$

For shorter wavelengths $e^{hc/\lambda kT}$ becomes large as compared to unity and hence Planck's law reduces to

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\cdot\frac{1}{e^{hc/\lambda kT}}d\lambda$$
$$= \frac{8\pi hc}{\lambda^5}e^{-hc/k\lambda T}d\lambda \qquad ...(15)$$

which is *Wien's law.*

For *longer wavelengths* $e^{hc/\lambda kT}$ may be approximated to $\left(1+\frac{hc}{\lambda kT}\right)$ and hence Planck's law reduces to

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{\left(1+\frac{hc}{\lambda kT}-1\right)}\cdot d\lambda$$
$$= \frac{8\pi hc}{\lambda^5}\cdot\frac{\lambda kT}{hc}d\lambda$$

or
$$E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4}d\lambda \qquad ...(16)$$

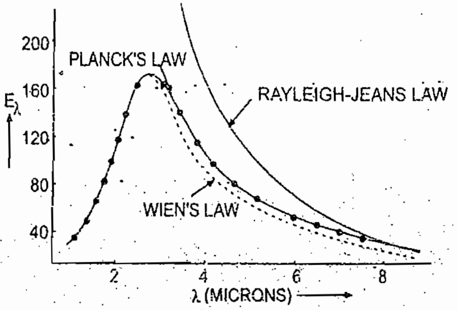
which is *Rayleigh-Jean's law,*

Thus we see that Wien's law holds for shorter wavelengths and Rayleigh-Jean's law for longer wavelengts. We can thus say *that both the Wien's and Rayleigh-Jean's law are incorporated in the Planck's law.*

### 3.16. Experimental Verification of Planck's radiation law and Comparison with other Formulae

The Planck's radiation law has been verified by numerous experiments. Here we shall discuss the experimental verification due to Lummer and Pringsheim. They used a special radiating chamber in which the conditions of *black body radiation or full radiation* were practically fulfilled.

The spectrum of the black-body radiation was produced by refraction through a fluorspar prism, fluorspar being very transparent to the infra-red radiations. It was very necessary to apply corrections in order to convert the prismatic spectrum to the normal one. This was done by means of the known dispersion curve of fluorspar.



**(Fig. 3.18)**

A concave mirror was used to obtain the image of the slit. This image was focussed on a Lummer-Kurlbaum linear spectrum bolometer which was used to measure the radiant energy or distribution of energy. This bolometer was enclosed in an air-tight case in order to diminish the absorption effects due to water vapour and carbon dioxide. The distribution of energy in the spectrum for various temperatures between 621 K and 1646 K was obtained and the curves were plotted. It was found that distribution of energy in the spectrum of a black-body as found by Planck's radiation law was in perfect agreement with the experiments.

The actual form of the distribution curve which has been derived by Planck from theoretical considerations represents the experimental results accurately. Planck's formula is consistent with Wien's law hence an experimental verification of Planck's formula is the same thing as an experimental verification of Wien's law. The curves shown in fig. 3·18 for a temperature of 1600 K, in accordance with the three laws, bring out clearly the close agreement between Wien's and Planck's formulae and their wide deviation from that of Rayleigh's. The circles show the actual observations on the energy distribution in the spectrum of a black-body at 1600K. The thick full line show the distribution predicted by Planck's formula indicating that the Planck's law is in perfect agreement with the experiments. The lower dotted line, which coincides with the thick full line upto about $\lambda = 2{\cdot}2$ microns, corresponds to Wien's formula, while the upper thin solid line is from the Rayleigh-Jean's formula. It is evident that the curve obtained by Planck approximated to that of Wien for small wavelengths and to that of Rayleigh for long wavelengths.

It is desirable at this stage to have a comparison between the three radiation formulae in an analytical way. Putting $\frac{h\nu}{kT} = \frac{hc}{\lambda kT} = x$, the three radiation formula may be written an

Rayleigh,
$$E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4}d\lambda$$

Wien. $$E_\lambda\, d\lambda = \frac{8\pi kT}{\lambda^4}\cdot\frac{x}{e^x}\,d\lambda$$

Planck. $$E_\lambda\, d\lambda = \frac{8\pi kT}{\lambda^4}\cdot\frac{x}{e^x-1}\,d\lambda.$$

Thus the Wien's and Planck's formulae differ from that of Rayleigh through the presence of the additional factors $\frac{x}{e^x}$ and $\frac{x}{e^x-1}$ respectively. As shown in example 2, both Wien's and Rayleigh's formulae are the special cases of Planck's formula which seems to be the correct formula for thermal radiation and is applicable for all wavelengths.

## 3.17. Impacts and Utility of Planck's Law :

The failure of both Wien's and Rayleigh-Jean's laws to fit the experimentally observed facts led Planck to work to find an improved formula. He succeeded in doing so only after making a new assumption that was completely at variance with classical ideas. He did not accept the principle of equipartition of energy and also discarded the idea of radiation being a continuous one. Instead, he introduced the quantum concept which led to the conclusion that electromagnetic radiation is not emitted in continuous amounts but in discrete, integral multiples of a minute elementary unit of energy (bundles of energy) each equal to $h\nu$. Thus bundles or packets or radiant energy are called *quanta* or *photons.* This was the beginning of the atomic theory of radiation which later *gave birth to quantum theory.*

In order to arrive at his new radiation formula, Planck imagined that a black-body enclosure is filled up not only with radiation but also with resonators or linear dipole oscillators of molecular dimensions, vibrating simple harmonically. He assumed that these resonators do not emit radiations continuously but only when the energy absorbed by them reaches a certain minimum value $E = h\nu$ or its multiple, $\nu$ being the frequency of radiation. Thus the energy of an oscillator can not vary continuously but must take on one of the discrete set of values 0, $h\nu$, .. $nh\nu$. Energies intermediate between these allowen values never occur *i.e.,* not a single oscillator can be found which possess energy, say, 1·56 $h\nu$,

It should be emphasized that Planck's revolutionary assumption of discrete energy levels for an oscillator was quite contrary to the then prevalent ideas and broke drastically with classical principles, the emission and absorption of radiation are associated with transitions (or jumps between two of these levels, the balance of energy of magnitude $h\nu$. It thus seems that radiation must join now matter and energy in having a basically atomic character. Planck was thus responsible for introducing the idea of 'atomicity of energy' but unlike an atom of matter the 'atom' of energy does not possess any fixed amount of energy because $h\nu$ depends obviously on the frequency of the oscillator. Thus quanta of radiation of different frequencies have different sizes (energies) and they are atomic only in the sense that they are discrete.

The fact that radiant energy is quantized is a radical departure from classical physics but has survived the tests of a variety of experiments The ideas embodied in Planck's quantum theory had led to the explanation of many a diverse physical phenomenon. Thus Einstein, in 1905 applied it to explain the phenomenon of *photoelectric effect.* Whereas Planck had proposed that radiation was composed of energy packets only in the neighbourhood of the emitter. Einstein proposed that these energy packets preserve their identity thoughout their life. Using these ideas and the Planck's expression for average energy of an oscillator, Einstein, in 1907, could succeed in explaining the variation of specific heat of solids with temperature. Bohr, in 1913, utilized this quantum idea to explain the spectral emission. As a matter of fact, it has led to the development of a new branch of physics which as a whole may be called the atomic mechanics.

## SOLVED EXAMPLES

**Example. 3.** *Show that the number of photons in black body radiation at a temperature T is equal to*

$$N = \frac{V}{\pi^2}\left(\frac{kT}{\hbar c}\right)^3 \int_0^\infty \frac{x^2dx}{e^x-1}$$

**Solution.** Number of resonators per unit volume in the frequency range $\nu$ and $\nu + d\nu$ in an enclosure $= \frac{8\pi\nu^2 d\nu}{c^3}$

Energy of each resonator $= \frac{h\nu}{e^{h\nu/kT}-1}$

∴ Total energy of resonators per unit volume in the enclosure

$$= \left(\frac{8\pi\nu^2\, d\nu}{c^3}\right)\left(\frac{h\nu}{e^{h\nu/kT}-1}\right)$$

Energy of each photon $= h\nu$.

Therefore, number of photons in the enclosure per unit volume in the frequency range $\nu$ and $\nu + d\nu$.

$$= \frac{8\pi\nu^2\, d\nu}{c^3}\cdot\frac{1}{e^{h\nu/kT}-1}.$$

If $V$ is the volume of the enclosure, then number of photons in the enclosure in frequency range $\nu + d\nu$.

$$n = \frac{8\pi V\,\nu^2\, d\nu}{c^3}\cdot\frac{1}{e^{h\nu/kT}-1}.$$

Total number of photons in enclosure

$$n = \frac{8\pi V}{c^3}\int_0^\infty \frac{\nu^2\, d\nu}{c^{h\nu/kT}-1}$$

Putting $\frac{h\nu}{kT} = x$ *i.e.,* $\nu = \frac{xkT}{h}$; $d\nu = \frac{kT}{h}dx,$

we get

$$n = \frac{V}{\pi^2}\left(\frac{2\pi kT}{hc}\right)^3 \int_0^\infty \frac{x^2dx}{e^x-1}$$

$$= \frac{V}{\pi^2}\left(\frac{kT}{\hbar c}\right)^3 \int_0^\infty \frac{x^2dx}{e^x-1}$$

when $\hbar = \frac{h}{2\pi}.$

**Example. 4.** *Obtain an expression for the wavelength corresponding to maximum energy of emission according to formula of Planck.*

**Solution.** Planck's formula is given by

$$E_\lambda\, d\lambda = \frac{8\pi hc}{\lambda^5}\,\frac{1}{e^{hc/\lambda kT}-1}\,d\lambda$$

Differentiating it partially with respect to λ, we get

$$\frac{\partial E_\lambda}{d\lambda} = \frac{1}{e^{hc/\lambda kT}-1} \times \frac{-5\,(8\pi hc)}{\lambda^6} + \frac{8\pi hc}{\lambda^5} \times \frac{\frac{hc}{\lambda^2 kT}\; e^{hc}/\lambda kT}{(e^{hc/\lambda kT}-1)^2}$$

$$= \frac{40\pi hc}{\lambda^6} \cdot \frac{1}{e^{hc/\lambda kT}-1} + \frac{8\pi hc}{\lambda^5} \times \frac{hc}{\lambda^2 kT}\; \frac{e^{hc/kT}}{(e^{hc/kT}-1)^2}$$

For maximum energy of emission *i.e.*, for maximum value of $E_\lambda$. $\frac{\partial E_\lambda}{\partial \lambda}$ must be equal to zero *i.e.*

$$\frac{40\pi hc}{\lambda^6} \cdot \frac{1}{e^{hc/\lambda kT}-1} + \frac{8\pi hc}{\lambda^5} \times \frac{hc}{\lambda^2 kT} \times \frac{e^{hc/\lambda kT}}{(e^{hc/\lambda kT}-1)^2} = 0$$

or
$$\frac{8\pi hc}{(e^{hc/\lambda kT}-1)\,\lambda^6}\left[-5 + \frac{hc}{\lambda kT} \times \frac{e^{kc/\lambda kT}}{(e^{hc/\lambda kT}-1)}\right] = 0$$

*i.e.*
$$-5 + \frac{hc}{\lambda kT} \times \frac{e^{hc/\lambda kT}}{(e^{hc/\lambda kT}-1)} = 0.$$

Putting $\frac{hc}{\lambda kT} = x$, the above expression becomes

$$-5 + \frac{xe^x}{e^x - 1} = 0$$

or
$$\frac{xe^x}{e^x - 1} = 5.$$

It is obvious from this equation that there must be a root in the neighbourhood of 5. Applying the method of approximation, the exact value of $x$ is found to be equal to 4·965 *i.e.*,

$$x = \frac{hc}{\lambda kT} = 4{\cdot}965.$$

Thus the wavelength corresponding to maximum energy of emission is given by

$$\lambda_m = \frac{hc}{4{\cdot}965kT}$$

Thus the wavelength $\lambda_m$ at which the energy per unit range of wavelength $E_\lambda$ has its maximum varies as $\frac{1}{T}$.

**Example. 5.** *Use Planck's formula to obtain expressions for (a) Stefan's constant and (b) Wien's constant in terms of Planck's constant and Boltzman's constant.* **(Rohilkhand 1992)**

**Solution. Stefan's constant.**

Using Planck's formula, the total radiant energy in unit volume of an isothermal enclosure is given by

$$U = \int_0^\infty E_\lambda\, d\lambda = 8\pi hc \int_0^\infty \frac{d\lambda}{\lambda^5\,(e^{hc/\lambda kT}-1)} \qquad \ldots(1)$$

But the total radiant energy in unit volume of an isothermal enclosure is also given by

$$U = AT^4 \qquad \ldots(2)$$

where $A$ is constant and $T$ is the absolute temperature of the enclosure.

Comparing eqn. (1) and (2) we have

$$AT^4 = 8\pi hc \int_0^\infty \frac{d\lambda}{\lambda^5\,(e^{hc/\lambda kT}-1)} \qquad \ldots(3)$$

Putting $x = \frac{hc}{\lambda kT}$ or $\lambda = \frac{hc}{xkT}$ *i.e.*, $d\lambda = -\frac{hc}{x^2\,kT}\,dx$, we have

$$AT^4 = 8\pi hc \int_\infty \frac{-\frac{hc\,dx}{x^2\,kT}}{\left(\frac{hc}{xkT}\right)^2 (e^x - 1)}$$

$$= \frac{8\pi\, k^4 T^4}{h^3 c^3}\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{8\pi k^4 T^4}{h^3 c^3} \cdot \left(\frac{\pi^4}{15}\right) \left[\because \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}\right]$$

⇒
$$A = \frac{8\pi^5 k^4}{15h^3 c^3}.$$

Since Stefan's constant (σ) is given by

$$\sigma = \frac{Ac}{4}.$$

∴
$$\sigma = \left(\frac{8\pi^5 k^4}{15h^3 c^3}\right) \times \frac{c}{4} = \frac{2}{15} \cdot \frac{\pi^5 k^4}{h^3 c^2}. \qquad \ldots(4)$$

which is the required expression for Stefan's constant.

**Wien's constant.** According to Wien's law, Wien's constant is given by

$$b = \lambda_m \,.\, T$$

where $\lambda_m$ is the wavelength for which the emitted energy is maximum and the expression for it, as derived in example 4, is given as

$$\lambda_m = \frac{hc}{4{\cdot}965\; kT}$$

or
$$\lambda_m \,.\, T = \frac{hc}{4{\cdot}965\; k}$$

Thus the Wien's constant $b\ (= \lambda_m T)$ is given by

$$b = \frac{hc}{4{\cdot}965\; k}$$

## EXERCISES

### SHORT ANSWER QUESTIONS

1. What do you mean by radiation ?
2. What do you mean by radiant energy.
3. Explain why does radiation exert pressure ?
4. What do you mean by diffuse radiation ? Write an expression for it.
5. What do you mean by a black body ? How can it be realised in practice ?

6. What are in characteristics of black body radiation.
7. Define emission and absorptive powers.
8. State and explain Kirchhoff's law of radiation.
9. State Stefan's law of radiation.
10. State Wien's displacement law.
11. State Wien's distribution law.
12. State Rayleigh Jean's law.
13. State Planck's radiation law.

## LONG ANSWER QUESTIONS

1. Show that the radiation in an isothermal enclosure depends only on the temperature and not on the nature of the walls of the enclosure or on the bodies present inside it.
2. State the prove Kirchhoff's lawof radiation and discuss its importance.
3. Explain the terms emissive and absorptive powers.
4. Deduce Kirchhoff's law of radiation and describe an experiment for its varification. *(Patna 2004)*
5. What is black body radiation ? Deduce expression for energy density and pressure of diffuse radiation. *(Ranchi Univ. 2005)*
6. Deduce that at any temperature, the ratio of emissive power to absorptive power of a substance is constant and is equal to the emissive power of a perfectly black-body.
7. Show that the diffuse radiation exerts on the wall of the cavity, in which it is contained, a pressure equal to the one third of its energy density.
8. State Stefan's law of radiation and explain how is it used to estimate the temperature of sun's surface. How is Stefan's constant determined ?
9. Prove that if the volume of black-body radiation is increased adiabatically by a factor 8, the radiation will be capable of existing in equilibrium with matter at a temperature one-half of the original temperature. *(Kanpur 2005)*
10. Discuss the distribution of energy in the spectrum of a black-body on the basis of experiments performed by Lummer and Pringsheim.

    What are the salient features of black-body radiation ?
11. Draw graphs showing the distribution of energy of a black-body at different temperatures, Discuss briefly the different laws which try to explain the above energy spectrum. *(Mumbai 2004)*
12. What is Wien's distribution law ? Deduce it from thermodynamical considerations.
13. Deduce Wien's displacement law for the distribution of energy in black-body spectrum. Examine its validity in terms of the experimental results and mention the basic concepts on which Planck's theory was based *(Rohilkhand 2006)*
14. State briefly the importance of theoretical and experimental investigations of black-body radiation. How far did the efforts of Jean and Wein succeeded in explaining the experimental results.

15. From pure thermodynamical considerations, deduce with the Wein's law $U_\lambda = AT^5 F(\lambda T)$ and show that it corresponds with the form
$$U_\nu = BT^3 \phi\left(\frac{\nu}{T}\right)$$
Draw a typical curve showing $U_\lambda$ against $\lambda$ for a given temperature, say $T_1 = 800$K. How does Wien's law enables you to deduce the curve for another temperature, say $T_2 = 1000$K from the curve for $T_1$ ?
16. Show how thermodynamic considerations alone lead to Wien's displacement law for the distribution of energy in the spectrum of a black-boay. Discuss its limitations.
17. What are the basic assumptions of Planck's theory of black-body radiation distribution formula and mention some of its uses. *(Rohilkhand 2006; Agra 2005)*
18. Deduce Planck's law of radiation. *(Patna Univ. 2004)*
19. Show that the average energy of a Planck oscillator of frequency $\nu$ in thermal equilibrium with heat reservoir at temperature $T$ is given by
$$<\epsilon> = \frac{h\nu}{e^{h\nu/kT} - 1}$$
Discuss the variations of $<\epsilon>$ with (i) temperature and (ii) frequency.
20. Derive an expression for the number of resonators per unit volume lying in the wavelength range $\lambda$ to $\lambda + d\lambda$.
21. What is quantum theory of radiation ? Derive Planck's formula for the distribution of energy in the spectrum of a black-body. Deduce from it Wien's displacement law and Rayleigh Jeans law.
22. (a) What is quantum theory of radiation ? Derive Planck's formula for distribution of energy in the spectrum of a black body. *(Ranchi 2004)*

    (b) Show that Wien's law and Rayleigh-Jeans Law are special cases of Planck's law. *(Ranchi 2004)*
23. Derive Planck's radiation formula and hence obtain an expression for Stefans contant. *(Delhi 2004)*
24. Show that Stefan's constant ($\sigma$) is related to Planck's constant ($h$) by the formula.
$$\sigma = \frac{2\pi^2 k^4}{15 \,.\, c^2 h^3}$$
25. Write short explanatory notes on the following :
    (i) Black-body radiation.
    (ii) Pressure of radiation
    (iii) Kirchhoff's law of heat radiation.
    (iv) Wien's displacement law.
    (v) Impact of Planck's law on the development of physics.

## NUMERICAL QUESTIONS

1. For a particular temperature the emissivity and absorption coefficient at wavelength 1000 Å, for a body is 8 and 0·5 units respectively. Deduce the emissivity for a black-body at the same temperature and wavelength.

   $\left[\text{Hint: } \frac{e_\lambda}{a_\lambda} = E_\lambda \text{ ; Ans. 16}\right]$

2. A black-body is placed in an evacuated enclosure whose walls are blackened and kept at 300K. Compare the net amount of heat gained or lost by the body (i) when its temperature is 600K and (ii) when its temperature is 100 K. [Ans. 243 : 16]

3. A black-body is placed in an evacuated enclosure whose walls are blackened and kept at 27°C. Compare the net amount of heat lost by the body (i) when its temperature is 527°C (ii) when its temperature is 127°C. [Ans. 23 : 1]

4. A black-body at 500°C has a surface area of 0·5 $m^2$ and radiates heat at the rate of $1{\cdot}02 \times 10^4$ J/s. Calculate Stefan's constant.

5. An iron furnace radiates $1{\cdot}53 \times 10^6$ calories per hour through an opening of cross-section $10^{-4}$ eq. meters. If the relative emittance of the fumace is 0·8. Calculate the temperature of furnance. [Ans. 2500 K]

[Hint : $E = Ae\sigma T^4 t$]

6. Calculate the radiant emittance of a black-body at a temperature of (i) 4,000 K, (ii) 400 K, $\sigma = 5{\cdot}672 \times 10^{-8}$ M.K.S. units. [Ans. 14,520 kilo-watt/$m^2$, 1,452 watt/$m^2$]

7. An iron-ball having surface area 100 $cm^2$ and temperature 527°C is placed in an enclosure at 27°C. If the surface emissivity of iron be 0·3, at what rate is heat being lost by radiation by the wall. [Ans. 16·68 cal./sec.]

8. Estimate the value of Stefan's constant if temperature of the filament of a 40 watt tungsten lamp is 2,170°C and the emissive surface area of the filament is 0·66 sq. cm. You are to assume that the energy radiated ~~is 0·31 of~~ that from a black-body in similar conditions and that any effect due to radiation from the glass envelope is negligible.

[Ans. $5{\cdot}49 \times 10^{-8}$ watt/$m^2K^4$]

9. Deduce the temperature at which a black body loses thermal energy at a rate of 1 watt/$cm^2$. Given $\sigma = 5{\cdot}6 \times 10^{-8}$ watt/$m^2K^4$. [Ans. 650 K]

10. A solid copper sphere cools at the rate of 2·8°C per minute when it temperature is 127°C. At what rate will a solid copper sphere of twice the radius cool when its temperature is 227°C, if in both cases, the surroundings are maintained at 27°C and the condtions are such that Stefan's law may be applied ? [Ans. 4·35°/min]

11. In an atomic explosion, the maximum temperature reached was of the order of $10^7$ K. Calculate the wave-length of maximum energy. Given Wien's constant = 0·2898 cm. K. [Ans. 2·986 Å]

12. Using Wien's displacement law, estimate the temperature of the sun. ($\lambda_m$ = 4,900 Å) [Ans. 5,898 K]

13. Find the quantity of energy radiated from 1 $cm^2$ of a surface in 1 second by a black-body if the maximum energy density corresponds to a wavelength of 4,840 Å. Given Wien's constant $b = 2{\cdot}9 \times 10^{-3}$ m-K and Stefan's constant $\sigma = 5{\cdot}67 \times 10^{-8}$ $W\,m^{-2}\,K^{-4}$.

[Ans. $7{\cdot}3 \times 10^{10}$ ergs. $cm.^{-2}$ $sec^{-1}$]

14. Calculate the energy radiated per minute from the filament of an incandescent lamp at 3000 K, if the surface area is 1·0 $cm^2$ and its emissivity is 0·425. Given : Stefan's constant $\sigma = 5{\cdot}672 \times 10^{-8}$ joule/(metre$^2$-sec-$K^4$). [Ans. $1{\cdot}17 \times 10^4$ joule/min.]

## MULTIPLE CHOICE QUESTIONS : SELECT THE RIGHT CHOICE

1. "Good absorbers are good emitters." This statement is called : *(Rohilkhand 2003)*
   (a) Prevost law (b) Kirchhoff's law
   (c) Stefan's law (d) Wien's law

2. For a perfectly block body, the absorptive power is : *(Rohilkhand 2003)*
   (a) 0 (b) 0·5 (c) 1 (d) ∞

3. Two stars $A$ and $B$ radiate maximum energy at 360 nm and 480 nm respectively. The ratio of their absolute temperatures is : *(Rohilkhand 2003)*
   (a) 3 : 4 (b) 4 : 3 (c) 256 : 81 (d) 81 : 256

4. For a non-conducting isothermal enclosure the quality and quantity of radiations inside it depends on enclosure's : *(Rohilkhand 2003)*
   (a) Temperature (b) Nature of walls
   (c) Nature of material (d) All of these

5. The temperature of a piece of metal is raised from 27°C to 51·2°C. The rate at which metal radiates energy increases nearly : *(Rohilkhand 2003)*
   (a) 1·36 times (b) 2 times (c) 4 times (d) 8 times

6. Wien's displacement law is : *(Rohilkhand 2006)*
   (a) $\lambda_m T = b$ (b) $E = \sigma T^4$
   (c) $\frac{\lambda_m}{T^5} = \text{constant}$ (d) $E = \sigma (T^4 - T_0^4)$

7. With what rate should energy be supplied to the filament of a bulb to maintain its temperaure at 3600 K of a hulb to maintain its temperature at 3600 K if it emits energy at the rate of 16 W at temperature of 1800 K ? *(Rohilkhand 2006)*
   (a) 4 W (b) 64 W (c) 128 W. (d) 256 W

8. The absolute temperature of a perfectly black body is increased to twice its value. The rate of emission of energy per unit area will become : *(Kanpur 2002)*
   (a) 2-times (b) 4-times (c) 8 times (d) 16 times

9. If $E$ is the total energy emitted by a body at a temperature $T$ kelvin and $E_{max}$ is the maximum energy emitted by it at the same temperature, then :
   (a) $E \propto T^4$, $E_{max} \propto T^5$ (b) $E \propto T^4$, $E_{max} \propto T^{-5}$
   (c) $E \propto T^{-4}$, $E_{max} \propto T^4$ (d) $E \propto T^4$, $E_{max} \propto T^4$

10. The intensity of radiation emitted by the sun has its maximum value at wavelength 510 nm and that emitted by north star has the maximum value at 350 nm. If these stars behave as black bodies, then the ratio of surface temperatures of the sun and north star is :
    (a) 1·46 (b) 0·69 (c) 1·21 (d) 0·83

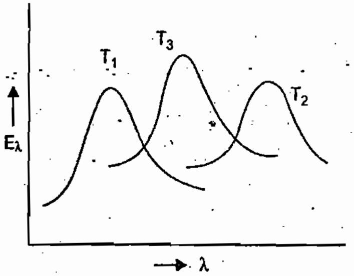
11. A black body is at temperature of 2880 K. The energy of radiation emitted by this body with wavelength between 499 nm and 500 nm is $U_1$, between 999 nm and 1000 nm is $U_2$ and between wavelength 1499 nm and 1500 nm is $U_3$. The Wien's construct $b = 2{\cdot}88 \times 10^6$ nm K, then :
    (a) $U_1 = 0$ (b) $U_3 = 0$ (c) $U_1 > U_2$ (d) $U_2 > U_1$

[Hint : $\lambda_m = \frac{b}{T} = \frac{2.88 \times 10^6}{2880} = 1000$ nm; maximum energy is radiated at 1000 nm *i.e.* $U_2$ is maximum]

12. The distribution of energy in the black body spectrum is best represented by :
(a) Wien's law (b) Stefan's law
(c) Planck's law (d) Kirchhoff's law

13. Electromagnate radiation is emitted by :
(a) all bodies at all temperatures (b) all bodies at 100°C
(c) all bodies at absolute zero (d) only a few bodies at all temperatures

14. The plots of intensity versus wavelengths for three black bodies at temperature $T_1$, $T_2$ and $T_3$ respectively are shown in fig. Their temperatures are such that :
(a) $T_1 > T_2 > T_3$ (b) $T_1 > T_3 > T_2$
(c) $T_2 > T_3 > T_1$ (d) $T_3 > T_2 > T_1$

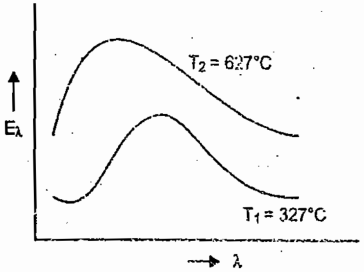


15. A radiation of energy $E$ falls normally on a perfectly reflecting surface. The momentum transferred to the surface is :
(a) $\frac{E}{c}$ (b) $\frac{E}{c^2}$ (c) $Ec$ (d) $\frac{2E}{c}$

16. A spherical black body with a radius 12 cm radiates 450 W power at 500 K. If the radius were halved and temperature doubled, the power radiated in watt would be :
(a) 225 (b) 450 (c) 900 (d) 1800

17. The energy spectrum of a black body exhibits a maximum around a wavelength $\lambda_0$. The temperature of the black body is now changed such that to energy is maximum around a wavelength $\frac{3\lambda_0}{4}$. The power radiated by the black body will now increase by a factor of :
(a) $\frac{4}{3}$ (b) $\frac{16}{9}$ (c) $\frac{64}{27}$ (d) $\frac{256}{81}$

18. The spectra of a black body at temperatures $T_1 = 327°C$ and $T_2 = 627°C$ are shown in fig. If $A_1$ and $A_2$ are areas under the two curves respectively, then the value of $\frac{A_2}{A_1}$ is :
(a) $\frac{9}{4}$ (b) $\frac{27}{8}$
(c) $\frac{81}{16}$ (d) $\frac{16}{81}$



19. A piece of red glass when heated to red hot will appear to be :
(a) White (b) red (c) green (d) invisible

ANSWERS

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. (b) | 2. (c) | 3. (b) | 4. (a) | 5. (a) | 6. (a) | 7. (d) | 8. (d) |
| 9. (a) | 10. (b) | 11. (d) | 12. (c) | 13. (a) | 14. (b) | 15. (a) | 16. (d) |
| 17. (d) | 18. (c) | 19. (d) | | | | | |

# 4

# CONCEPTS OF HEAT CONDUCTION

## 4.1. Heat Conduction

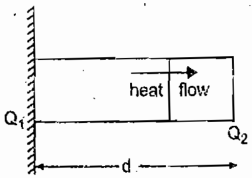
Whenever two parts of a body are at different temperatures, a spontaneous flow of heat takes place from the region of higher temperature to that of lower temperature. This process is known as 'conduction' of heat. It can be explained on a microscopic basis. Microscopically, heat is mechanical energy of individual atoms and molecules. When the molecules in one region have, on the average, more kinetic energy than those in a neighbouring region, they transfer energy to their neighbours by colliding with them. This transfer of energy takes place from a region of higher temperature, and hence greater molecular motion, to one of lower temperature.

In metals, the conduction of heat takes place by a different agency also. Metals have some "free" electrons which are able to move throughout the material, rather than being bound tightly to individual atoms. These electrons carry energy readily from the hotter to the colder region. In fact, this is the chief mechanism of heat conduction in metals. It is for this reason that materials which are good conductors of electricity are generally also good conductors of heat.

**Heat Conduction and Wave Propagation :** In heat conduction, energy is transferred from one part of a medium to the other by virtue of a temperature-difference between them, and the direction of energy flow is always from points of higher to points of lower temperature. In wave propagation, the energy is transferred from one part of a material medium to the other by virtue of the elasticity and inertia of the medium, and flows *in all directions*.

## 4.2. Fundamental Equation Of Heat Flow

**Steady State :** Let us take a bar of uniform cross-section and heat it at one end. Each cross-section of the bar receives heat by conduction from the adjacent cross-section towards the heated end. This heat is spent in three ways ; a part is absorbed by the cross-section to increase its temperature, another part escapes out from the sides of the cross-section, and the third is conducted to the next cross-section. The same happens at the next cross-section, and so on. Thus the temperature of each part of the bar rises, and the bar is said to be in a "variable state". After some time, however, *a state is reached when temperature at each point of the bar becomes stationary*. This is called the 'steady state'. In this state *no* heat is absorbed by the bar. The heat that reaches any section is transferred to the next, except that some heat may escape out from the sides. (The steady state is not the same as thermal equilibrium, in which all parts of the bar must have the *same* temperature).



(Fig. 4.1)

Let the faces of the bar be maintained at steady temperatures $\theta_1$ and $\theta_2$; the length of bar be $l$. The rate of temperature variation with length, along the length of bar is called the temperature gradient.

Temperature gradient $= \frac{\theta_1 - \theta_2}{l}$. Heat will flow through the slab from the face at higher temperature to that at the lower temperature. In steady state it is assumed that no heat escapes out from the sides of the slab, the lines of flow will be at all points normal to the faces of the slab. In steady state, the quantity of heat $Q$ entering one face in a given time is same as the heat leaving the other face in the same time. Experiment shows that $Q$ is proportional to (i) the area $A$, (ii) temperature gradient $\frac{\theta_1 - \theta_2}{l}$ (iii) time of flow $t$, and that is

$$Q \propto A\left(\frac{\theta_1 - \theta_2}{l}\right)t$$

or

$$Q = KA\frac{\theta_1 - \theta_2}{l}t, \qquad \text{...(i)}$$

where $K$ is a constant depending on the *material* of the slab. It is called the "coefficient of thermal conductivity" of the material of the slab. This equation is called the fundamental equation of heat flow.

If $A = 1$, $\frac{\theta_1 - \theta_2}{l} = 1$ and $t = 1$, then $K = Q$. Therefore, *the coefficient of thermal conductivity of a material is defined as the amount of heat that flows in unit time through unit area of the material perpendicular to the flow under unit temperature-gradient, when the steady state has been reached*. Its units are cal-$\text{cm}^{-1}$-$\text{sec}^{-1}$-$°\text{C}^{-1}$, and dimensions $[MLT^{-3}\Theta^{-1}]$.

A material for which $K$ is large is a good heat conductor, while if $K$ is small, the material is a poor conductor or a good insulator.

In case when the heat escapes out from the sides of the slab, the temperature-gradient is not uniform across the slab. In such a case, if $\theta$ and $\theta + \delta\theta$ be the temperatures at planes distant $x$ and $x + \delta x$ along the direction of heat-flow, then the temperature-gradient will be $\frac{\theta - (\theta + \delta\theta)}{\delta x} = -\frac{\delta\theta}{\delta x}$. In the limit $\delta x \to 0$; this becomes $-d\theta/dx$ which is the temperature-gradient *at the plane* $x$. (The negative sign expresses the fact that the temperature always decreases in the direction of heat-flow.) Then, the heat $dQ$ flowing across the plane $x$ in time $dt$ will be given by

$$dQ = -KA\frac{d\theta}{dx}dt.$$

The rate of heat-flow is

$$\boxed{H = \frac{dQ}{dt} = -KA\frac{d\theta}{dx}.}$$

## 4.3. Thermoelectric Conductivity (or Diffusivity)

*It is defined as the ratio of the coefficient of thermal conductivity to the thermal capacity per unit volume of the material*. It $\rho$ be the density of the material and $c$ its specific heat, then thermal capacity per unit volume is $\rho c$. Hence, if $K$ be the thermal conductivity, the thermometric conductivity will be given by

$$h = \frac{K}{\rho c}.$$

When one end of a bar is heated, the thermoelectric conductivity determines the rate at which the temperature of any part of the bar rises, before the steady state is reached.

The rate at which the temperature of a body rises (or falls) when heated (or cooled) depends upon the thermal capacity of the body, and is smaller when the thermal capacity is higher. But once a body attains a certain temperature then the sensation of hotness or coldness which it produces when touched depends only on the thermal conductivity of the body.

## 4.4. Thermal Resistance

Just as charge flows in an electrical circuit due to a potential difference between two points of the circuit, in the same way heat flows in a conductor due to a temperature difference between two points of the conductor. Hence, like electrical resistance, there is also a thermal resistance in a material.

Let $l$ be the length and $A$ the area of cross-section of a rod. Let $\theta_1$ and $\theta_2$ be the temperatures of the hot and the cold ends of the rod in the steady state. Then, the rate of flow of heat in the rod is given by

$$H = \frac{Q}{t} = KA\,\frac{\theta_1 - \theta_2}{l}$$

or

$$\frac{\theta_1 - \theta_2}{H} = \frac{l}{KA}.$$

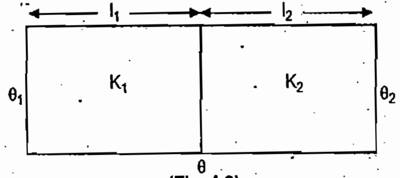
$(\theta_1 - \theta_2)$ is the temperature-difference between the ends of the conductor and $H$ is the rate of flow of heat. $(\theta_1 - \theta_2)/H$ is called the 'thermal resistance' $R$ of the conductor. Thus

$$R = \frac{\theta_1 - \theta_2}{H} = \frac{l}{KA}.$$

Thus, *greater the coefficient of thermal conductivity of a material, smaller is the thermal resistance of a rod of that material*. The unit of thermal resistance is 'second-°C/calorie'.

## 4.5. Temperature of Interface and Net Flow of Heat When Bars Are Connected In Series

Let us consider two slabs of thicknesses $l_1, l_2$ and conductivities $K_1, K_2$. Let $\theta_1$ and $\theta_2$ be the temperatures of the end faces and $\theta$ the temperature of the interface (Fig. 4.2). The rates of flow of heat through the thicknessess $l_1$ and $l_2$ are given by



(Fig. 4.2)

$$H_1 = \left(\frac{dQ_1}{dt}\right) = K_1 A\,\frac{\theta_1 - \theta}{l_1} \qquad \text{...(i)}$$

and

$$H_2 = \frac{dQ_2}{dt} = K_2 A\,\frac{\theta - \theta_2}{l_2} \qquad \text{...(ii)}$$

In the *steady* state, the rate of flow of heat throughout the compound slab will be the same *i.e.* $H_1 = H_2$, so that

$$K_1 A\,\frac{\theta_1 - \theta}{l_1} = K_2 A\,\frac{\theta - \theta_2}{l_2}$$

or

$$\frac{K_1\theta_1}{l_1} + \frac{K_2\theta_2}{l_2} = \left(\frac{K_1}{l_1} + \frac{K_2}{l_2}\right)\theta$$

$$\therefore \qquad \theta = \frac{\dfrac{K_1\theta_1}{l_1} + \dfrac{K_2\theta_2}{l_2}}{\dfrac{K_1}{l_1} + \dfrac{K_2}{l_2}}.$$

This is the expression for the temperature of the interface.

Let $H$ be the rate of heat-flow through the compound slab. Then, substituting the above value of $\theta$ in eq. (i), we get

$$H = \frac{K_1 A}{l_1}\left[\theta_1 - \frac{\dfrac{K_1\theta_1}{l_1} + \dfrac{K_2\theta_2}{l_2}}{\dfrac{K_1}{l_1} + \dfrac{K_2}{l_2}}\right]$$

$$= \frac{K_1 A}{l_1}\left[\frac{\dfrac{K_1\theta_1}{l_1} + \dfrac{K_2\theta_1}{l_2} - \dfrac{K_1\theta_1}{l_1} - \dfrac{K_2\theta_2}{l_2}}{\dfrac{K_1}{l_1} + \dfrac{K_2}{l_2}}\right]$$

$$= \frac{K_1 A}{l_1}\left[\frac{\dfrac{K_2}{l_2}(\theta_1 - \theta_2)}{\dfrac{K_1}{l_1} + \dfrac{K_2}{l_2}}\right]$$

$$= \frac{K_1 K_2}{l_1 l_2}\left[\frac{A(\theta_1 - \theta_2)}{\dfrac{K_1}{l_1} + \dfrac{K_2}{l_2}}\right]$$

$$= \frac{A(\theta_1 - \theta_2)}{\dfrac{l_1}{K_1} + \dfrac{l_2}{K_2}}.$$

For $n$ slabs in series, the expression would be

$$H = \frac{A(\theta_1 - \theta_n)}{\Sigma(l/K)}.$$

## 4.6. Equivalent Thermal Conductivity

For two bars : Let $A$ be the cross-sectional area and $l$ the thickness of each plate. Let $\theta_1, \theta_2$ and $\theta$ be the steady temperatures at the first face, second face and at the interface respectively. When the heat flows through the composite plate, its rate will be the same in each plate. Thus

$$H = K_1 A\,\frac{(\theta_1 - \theta)}{l} = K_2 A\,\frac{(\theta - \theta_2)}{l} \qquad \text{...(i)}$$

or

$$K_1\theta_1 - K_1\theta = K_2\theta - K_2\theta_2$$

or

$$K_1\theta_1 + K_2\theta_2 = K_1\theta + K_2\theta$$

$$\therefore \qquad \theta = \frac{K_1\theta_1 + K_2\theta_2}{K_1 + K_2}. \qquad \text{...(ii)}$$

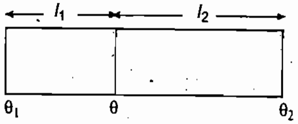
If $K$ be the equivalent thermal conductivity, then we have

$$H = KA\frac{\theta_1 - \theta_2}{2l}.$$

Equating it to (i), we get

$$KA\frac{\theta_1 - \theta_2}{2l} = K_1 A\frac{\theta_1 - \theta}{l}$$

or
$$K = 2K_1\frac{\theta_1 - \theta}{\theta_1 - \theta_2}.$$



**(Fig. 4.4)**

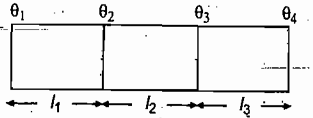
Substituting the value of $\theta$ from eq. (ii), we get

$$K = \frac{2K_1}{\theta_1 - \theta_2}\left[\theta_1 - \frac{K_1\theta_1 + K_2\theta_2}{K_1 + K_2}\right]$$
$$= \frac{2K_1}{\theta_1 - \theta_2}\left[\frac{K_1\theta_1 + K_2\theta_1 - K_1\theta_1 - K_2\theta_2}{K_1 + K_2}\right]$$
$$= \frac{2K_1}{\theta_1 - \theta_2}\frac{K_2(\theta_1 - \theta_2)}{K_1 + K_2}$$
$$= \frac{2K_1 K_2}{K_1 + K_2}.$$

This is the required expression.

The thermal conductivity of a perfect heat conductor is infinite.

**For Three bars :** Let $A$ be the cross-sectional area of each slab. Let $\theta_1, \theta_2, \theta_3, \theta_4$ be the steady temperatures at the first face, 1-2 interface, 2-3 interface and the third face respectively. The rate of heat flow would be the same throughout. Thus



**(Fig. 4.5)**

$$H = K_1 A\frac{\theta_1 - \theta_2}{l_1} = K_2 A\frac{\theta_2 - \theta_3}{l_2} = K_3 A\frac{\theta_3 - \theta_4}{l_3} = \text{constant}.$$

This gives

$$\theta_1 - \theta_2 = \frac{H}{A}\frac{l_1}{K_1}$$

$$\theta_2 - \theta_3 = \frac{H}{A}\frac{l_2}{K_2}$$

$$\theta_3 - \theta_4 = \frac{H}{A}\frac{l_3}{K_3}.$$

Adding :
$$\theta_1 - \theta_4 = \frac{H}{A}\left[\frac{l_1}{K_1} + \frac{l_2}{K_2} + \frac{l_3}{K_3}\right]. \qquad \text{...(iii)}$$

If $K$ be the equivalent conductivity for the combination, we may write

$$KA\frac{\theta_1 - \theta_4}{l_1 + l_2 + l_3} = H.$$

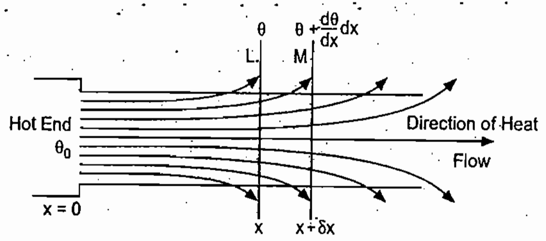
or
$$\theta_1 - \theta_4 = \frac{H}{A}\frac{l_1 + l_2 + l_3}{K}. \qquad \text{...(iv)}$$

Comparing eq. (iii) and (iv), we get

$$\frac{l_1 + l_2 + l_3}{K} = \frac{l_1}{K_1} + \frac{l_2}{K_2} + \frac{l_3}{K_3}.$$

## 4.7. Rectilinear Flow of Heat Along A Metal Bar : Fourier's Equation Of Heat Flow

Let us consider a long metal bar, one end of which is maintained at a steady *excess* temperature of $\theta_0$ above the surroundings. In the beginning, the temperatures at various points along the bar gradually rise but finally a steady state is reached at which these temperatures become stationary. A steady flow of heat now takes place along the bar. If the bar is exposed to the surroundings, a portion of the heat passing across any cross-section of the bar escapes out from the sides. Hence smaller and smaller amounts of heat pass across successive sections. The lines of flow are shown in Fig. 4.6.



**(Fig. 4.6)**

Let us consider two cross-sections of the bar, $L$ and $M$, distant $x$ and $x + \delta x$ from the hot end. Now, *before the steady state is reached*, the temperature at any section of the bar is rising. Let $\theta$ be the excess of temperature at the section $L$ at any instant $t$. Then, if $-\frac{d\theta}{dx}$ be the temperature-gradient at $L$, the excess temperature at $M$ will be $\theta + \frac{d\theta}{dx}\delta x$. If $A$ is the area of cross-section of the bar (assumed uniform) and $K$ the thermal conductivity of its material, the rate of heat-flow across the section $L$ will be

$$-KA\frac{d\theta}{dx}.$$

Similarly, the rate of heat-flow across the section $M$ will be

$$-KA\frac{d}{dx}\left\{\theta + \frac{d\theta}{dx}\delta x\right\}.$$

Therefore, the excess of heat flowing per second across $L$ over that flowing across $M$ is

$$-KA\frac{d\theta}{dx} - \left[-KA\frac{d}{dx}\left\{\theta + \frac{d\theta}{dx}\delta x\right\}\right]$$
$$= KA\frac{d^2\theta}{dx^2}\delta x. \qquad \text{...(i)}$$

This amount of heat is partly absorbed by the element of the bar between $L$ and $M$, and partly lost from the sides of the element to the surroundings. If $\rho$ be the density, $c$ the specific heat of the material of the bar, and $\frac{d\theta}{dt}$ the rate of rise in temperature, then the heat absorbed per second by the element will be equal to mass of the element × sp. heat × rise in temp. per sec, that is,

$$A\,\delta x\,\rho \times c \times \frac{d\theta}{dt}. \qquad \text{...(ii)}$$

Now, if $E$ be the emissivity* of the surface of the bar and $p$ the perimeter of its cross-section, then the heat escaped out per second from the sides of the element between $L$ and $M$ will be **

$$E \times p\,\delta x \times \theta. \qquad \text{...(iii)}$$

Eq. (i), (ii) and (iii) give

$$KA\frac{d^2\theta}{dx^2}\delta x = A\,\delta x\,\rho \times c \times \frac{d\theta}{dt} + E \times p\,\delta x \times \theta$$

or
$$\frac{K}{\rho c}\left\{\frac{d^2\theta}{dx^2}\right\} = \frac{d\theta}{dt} + \frac{Ep}{A\rho c}\theta$$

or
$$\frac{d\theta}{dt} = \frac{K}{\rho c}\left\{\frac{d^2\theta}{dx^2}\right\} - \frac{Ep}{A\rho c}\theta. \qquad \text{...(iv)}$$

This is the *Fourier's differential equation* for one-dimensional flow of heat.

**Temperature Distribution along the Bar when Exposed :** After the steady state is reached, the temperature at every point of the bar becomes *stationary i.e.* $\frac{d\theta}{dt} = 0$. Eq. (iv) then becomes

$$\frac{K}{\rho c}\left\{\frac{d^2\theta}{dx^2}\right\} - \frac{Ep}{A\rho c}\theta = 0$$

or
$$\frac{d^2\theta}{dx^2} = \frac{Ep}{KA}\theta = \mu^2\theta, \qquad \text{...(v)}$$

where $\mu^2 = Ep/KA$.

Let us now solve this differential equation. Let a solution be

$$\theta = a e^{\alpha x}, \qquad \text{...(vi)}$$

where $a$ and $\alpha$ are constants. Differentiating it twice, we obtain

$$\frac{d^2\theta}{dx^2} = \alpha^2 a e^{\alpha x}.$$

Putting these values of $\frac{d^2\theta}{dx^2}$ and $\theta$ in eq. (v), we get

$$\alpha^2 a e^{\alpha x} = \mu^2 a e^{\alpha x}$$

or
$$\alpha^2 = \mu^2$$

or
$$\alpha = \pm\mu.$$

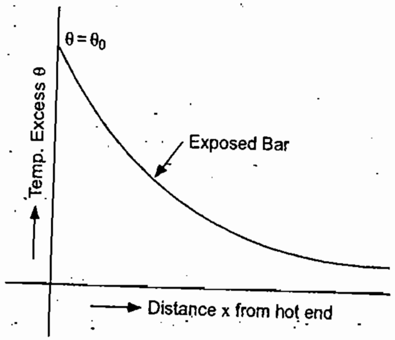
Thus, the solution of eq. (v) will be obained by putting $\alpha = \pm\mu$ in eq. (vi). That is, the solution is

$$\theta = a e^{\pm\mu x},$$

or the most general solution is

$$\theta = a_1 e^{+\mu x} + a_2 e^{-\mu x}, \qquad \text{...(vii)}$$

where $a_1$ and $a_2$ are arbitrary constants, the values of which can be determined by the experimental conditions.



(Fig. 4.7)

If the bar is considered to be infinitely long, its cold end will be nearly at the temperature of the surroundings, *i.e.*

as $x \to \infty$; $\theta \to 0$.

Applying this condition in eq. (vii), we have

$$0 = a_1 e^{\mu\infty} + a_2 e^{-\mu\infty}$$

or
$$0 = a_1 e^{\mu\infty} \qquad [\because e^{-\mu\infty} = 0]$$

$\therefore$
$$a_1 = 0.$$

Again, $\theta_0$ is the excess-temperature above the surroundings at the hot end ($x = 0$) of the bar, *i.e.*

$$\text{at } x = 0, \theta = \theta_0.$$

Appying this condition and also putting $a_1 = 0$ in eq. (vii), we get

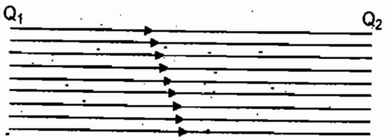
$$\theta_0 = 0 + a_2 e^0$$

$$\therefore a_2 = \theta_0.$$

Putting the values of $a_1$ and $a_2$ in eq. (vii), we get

$$\boxed{\theta = \theta_0 e^{-\mu x}.}$$

This equation shows that, for an exposed bar, the temperature falls off exponentially from the heated and as shown in Fig. 4.7.



(Fig. 4.8)

**Temperature-Distribution along the Bar when Covered :** If the bar is covered with some non-conducting material to prevent losses of heat from its surface, then its emissivity $E$ is zero. Now, in the steady state, the rate of flow of heat is same all along the bar because the heat reaching any section completely goes to the next section. This is represented in Fig. 4.8.

Now, as $E = 0$, $\mu^2\left(= \frac{Ep}{KA}\right) = 0$. Hence eq. (v) becomes

$$\frac{d^2\theta}{dx^2} = 0.$$

Integrating :
$$\frac{d\theta}{dx} = a_1 \text{ (constant)}.$$

Integrating again :
$$\theta = a_1 x + a_2, \qquad \text{...(viii)}$$

where $a_1$ and $a_2$ are constants.

Let $l$ be the length of the bar. Suppose its cold end is very nearly at the same temperature as the surroundings. Then the experimental conditions are

at $x = l$, $\theta = 0$,

at $x = 0$, $\theta = \theta_0$.

Applying these conditions in eq. (viii), we get

$$0 = a_1 l + a_2$$

and $\theta_0 = a_2$.

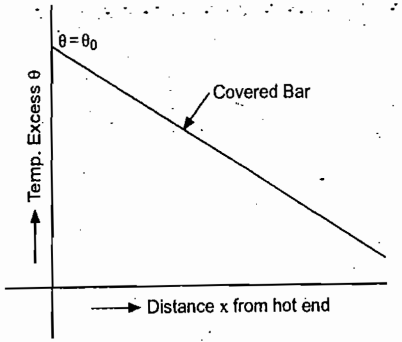
$\therefore$ $a_1 = -\frac{\theta_0}{l}$

and $a_2 = \theta_0$.

Putting these values in eq. (viii), we get

$$\boxed{\theta = -\frac{\theta_0}{l} x + \theta_0}.$$

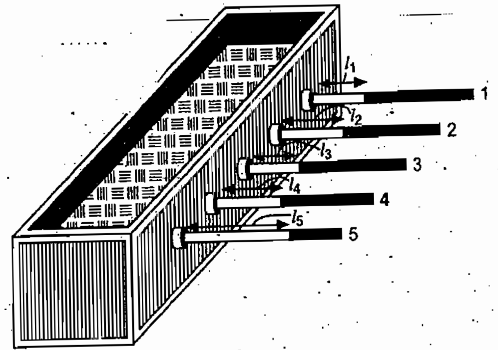
This equation shows that, for a covered bar, the temperature falls off linearly from the heated end as shown in Fig. 4.9.



(Fig. 4.9)

## 4.8. Ingen-hausz's Experiment Comparisons Of Electrical Conductivities

An approximate method of comparing the thermal conductivities of materials in the form of long thin rods was devised by Ingen-Hausz. The rods are taken identical in size and shape and similarly polished. They are then thinly coated with wax and placed with one end inserted in an oil-bath (Fig. 4.10). The oil in the bath is maintained at its boiling point. When the steady state is reached, the wax is found to be melted off upto different lengths along the different bars.



(Fig. 4.10)

Let $l_1, l_2, l_3, \ldots\ldots$ be the lengths upto which the wax is melted along the bars 1, 2, 3, ... Then, if $K_1, K_2, K_3 \ldots$ be their thermal conductivities, we can prove that

$$K_1 : K_2 : K_3 \ldots\ldots = l_1^2 : l_2^2 : l_3^2 \ldots\ldots$$

**Proof :** Let the rods be sufficiently long sothat their free ends be taken at the temperature of the surroundings. Let $\theta_0$ be the excess temperature of the heated ends, then the equation representing the temperature distribution along each bar in the experiment is $\theta = \theta_0 e^{-\mu x}$.

Let $\theta_m$ be the melting point of wax, then $\theta = \theta_m$, at $x = l_1$ for bar 1, at $x = l_2$ for bar, 2, at $x = l_3$ for bar 3.

$\therefore$ For bar 1, $\theta_m = \theta_0 e^{-\mu_1 l_1}$,

For bar 2, $\theta_m = \theta_0 e^{-\mu_2 l_2}$

and For bar 3, $\theta_m = \theta_0 e^{-\mu_3 l_3}$.

Hence $\mu_1 l_1 = \mu_2 l_2 = \mu_3 l_3$

or $\mu_1^2 = \frac{Ep}{K_1 A}, \mu_2^2 = \frac{Ep}{K_2 A}$ and $\mu_3^2 = \frac{Ep}{K_3 A}$;

because E, p and A for all the rods are the same, as they are identical in size, shape etc.

$$\therefore \quad \frac{Ep}{K_1 A} l_1^2 = \frac{Ep}{K_2 A} l_2^2 = \frac{Ep}{K_3 A} l_3^2$$

$$\text{or} \quad \frac{l_1^2}{K_1} = \frac{l_2^2}{K_2} = \frac{l_3^2}{K_3}$$

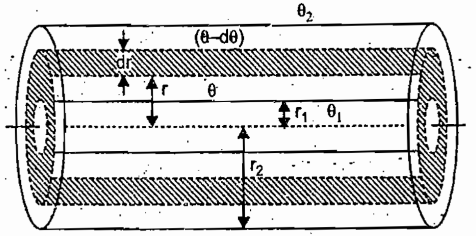
$$\text{or} \quad K_1 : K_2 : K_3 = l_1^2 : l_2^2 : l_2^2 : l_3^2$$

*i.e.*, the conductivities of the different rods vary as the square of the lengths upto which wax has melted on them.

## 4.9. Temperature Distribution in a Cylinder Heated Along the Axis (Cylindrical Flow of Heat)

Let us consider a cylindrical tube of length $l$, inner radius $r_1$ and outer radius $r_2$. Let the tube be heated along its axis by placing an electrically heated wire. Heat will flow radially from the inner side towards the outer side across the walls of the tube. When the steady state is reached, let the constant temperatures of the inner and outer surfaces of the tube be $\theta_1$ and $\theta_2$ respectively $(\theta_1 > \theta_2)$.

Consider a thin cylindrical shell of thickness $dr$ at a distance $r$ from the axis (fig. 4.11). Let $\theta$ and $(\theta - d\theta)$ be the temperature at $r$ and $(r + dr)$. The fall in temperature on travelling outwards by $dr$ is $d\theta$, hence the temperature gradient is $-\frac{d\theta}{dr}$. The amount of heat flowing per second through the shell of radius $r$ (and hence surface area $2\pi rl$) is given by



(Fig. 4.11)

$$Q = -K\, 2\pi rl \frac{d\theta}{dr} \qquad \ldots(1)$$

where $K$ is the thermal conductivity. The negative sign expresses the fact that $\theta$ diminishes with an increase in $r$.

$$Q \frac{dr}{r} = -2\pi K\, l\, d\theta. \qquad \ldots(2)$$

After a steady state is reached. $Q$ becomes constant. Integrating both sides of eqn. (2) between their respective limits, we get

$$Q \int_{r_1}^{r_2} \frac{dr}{r} = -2\pi K\, l \int_{\theta_1}^{\theta_2} d\theta$$

or

$$Q \log_e \frac{r_2}{r_1} = 2\pi K l\,(\theta_1 - \theta_2) \qquad \text{...(3)}$$

∴

$$K = \frac{Q \log_e \dfrac{r_2}{r_1}}{2\pi l\,(\theta_1 - \theta_2)} \qquad \text{...(4)}$$

This expression is used to find the thermal conductivity of poor conductors given in the form of cylindrical tubes.

Now, in order to find the temperature θ of the cylindrical shell at a distance $r$, equating the values of $Q$ from equation (1) and (3) :

$$Q = -K \,.\, 2\pi r l \frac{d\theta}{dr} = \frac{2\pi K l\,(\theta_1 - \theta_2)}{\log_e \dfrac{r_2}{r_1}}$$

or

$$d\theta = -\frac{(\theta_1 - \theta_2)}{\log_e \dfrac{r_2}{r_1}} \cdot \frac{dr}{r}$$

Integrating it, we get

$$\theta = -\frac{(\theta_1 - \theta_2)}{\log_e \dfrac{r_2}{r_1}} \log_e r + C \text{ (constant)}. \qquad \text{...(5)}$$

But when

$$r = r_1, \theta = \theta_1$$

$$\theta_1 = -\frac{(\theta_1 - \theta_2)}{\log_e \dfrac{r_2}{r_1}} \log_e r_1 + C$$

or

$$C = \theta_1 + \frac{\theta_1 - \theta_2}{\log_e \dfrac{r_2}{r_1}} \log_e r_1 \,.$$

Substituting the value of C in eqn. (5), we get

$$\theta = -\frac{\theta_1 - \theta_2}{\log_e \dfrac{r_2}{r_1}} \log_e r + \theta_1 + \frac{\theta_1 - \theta_2}{\log_e \dfrac{r_2}{r_1}} \log_e r_1$$

$$= \frac{1}{\log_e \dfrac{r_2}{r_1}} \left[ -(\theta_1 - \theta_2) \log_e r + \theta_1 \log_e \frac{r_2}{r_1} + (\theta_1 - \theta_2) \log_e r_1 \right]$$

$$= \frac{1}{\log_e \dfrac{r_2}{r_1}} [-(\theta_1 - \theta_2) \log_e r + \theta_1 \log_e r_2 - \theta_1 \log_e r_1 + \theta_1 \log_e r_1 - \theta_2 \log_e r_1]$$

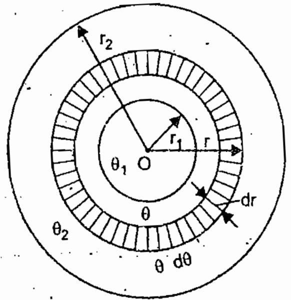
$$= \frac{1}{\log_e \dfrac{r_2}{r_1}} [(\theta_1 \log_e r_2 - \theta_2 \log_e r_1) - (\theta_1 - \theta_2) \log_e r] \qquad \text{...(6)}$$

This equation represents the temperature distribution in a cylindrical tube heated along the axis in steady state.

## 4.10. Temperature Distribution in a spherical Shell Heated at the Centre (Radial Flow of Heat)

Consider a spherical shell of internal and external radii $r_1$ and $r_2$ respectively. Let a source of heat, e.g., an electric heating element, be placed at the centre $O$ of the shell. The heat is conducted radially through the shell and lost subsequently to the surroundings from the other surface. Let $\theta_1$ and $\theta_2$ be the constant temperatures of the inside and outside of the shell in steady state (Fig. 4.12).

Consider an elementary shell of radius $r$ and thickness $dr$ having temperature θ and $(\theta - d\theta)$ on its inner and the outer surfaces respectively.



(Fig. 4.12)

The amount of heat flowing per second through this shell

$$Q = -KA \frac{d\theta}{dr} = -K\, 4\pi r^2 \cdot \frac{d\theta}{dr} \qquad \text{...(i) } (\because A = 4\pi r^2)$$

$$\frac{dr}{r^2} = -\frac{4\pi K}{Q} \cdot d\theta.$$

Integrating both sides between their respective limits and remembering that $Q$ is independent of $r$, we get

$$\int_{r_1}^{r_2} \frac{dr}{r^2} = -\frac{4\pi K}{Q} \int_{\theta_1}^{\theta_2} d\theta$$

or

$$\frac{1}{r_1} - \frac{1}{r_2} = \frac{4\pi K\,(\theta_1 - \theta_2)}{Q}$$

or

$$K = \frac{Q\,(r_1 - r_1)}{4\pi r_1 r_2\,(\theta_1 - \theta_2)} \qquad \text{...(ii)}$$

From it the value of conductivity $K$ can be calculated. It may be employed to find the conductivity of substances which are available in powder form, such as sand, clay, charoal etc.

Now the temperature distribution in the spherical shell may be obtained. Equating the values of $Q$ from equations (i) and (ii), we get

$$-K \,.\, 4\pi r^2 \frac{d\theta}{dt} = \frac{4\pi K\,(\theta_1 - \theta_2)\, r_1 r_2}{r_2 - r_1}$$

or

$$d\theta = -\frac{(\theta_1 - \theta_2)\, r_1 r_2}{r_2 - r_1} \cdot \frac{dr}{r^2}$$

Integrating,

$$\theta = -\frac{(\theta_1 - \theta_2)\, r_1 r_2}{r_2 - r_1} \left( -\frac{1}{r} \right) + C. \qquad \text{...(iii)}$$

Now in order to obtain the value of constant C, we have

at

$$r = r_1, \theta = \theta_1,$$

∴

$$\theta_1 = \frac{(\theta_1 - \theta_2)\, r_1 r_2}{r_2 - r_1} \cdot \frac{1}{r_1} + C.$$

or
$$C=\theta_1-(\theta_1-\theta_2)\frac{r_2}{r_2-r_1}.$$

Substituting it in equation (iii), we get

$$\theta=\frac{(\theta_1-\theta_2)\,r_1 r_2}{r\,(r_2-r_1)}+\theta_1-(\theta_1-\theta_2)\frac{r_2}{r_2-r_1}$$

$$\theta=\frac{1}{r_2-r_1}\left\{\frac{r_1 r_2(\theta_1-\theta_2)}{r}+r_2\theta_1-r_1\theta_1+r_2\theta_2-r_2\theta_1\right\}$$

$$=\frac{1}{r_2-r_1}\left\{\frac{r_1 r_2(\theta_1-\theta_2)}{r}+(r_2\theta_2-r_1\theta_1)\right\}$$

This gives the temperature of spherical surface of radius $r$.

## 4.11. Periodic Flow Of Heat

When one end of a bar is alternately heated and cooled, the heat flows through the bar periodically. Then, the temperature at any given point on the bar also varies periodically.

Let us assume that the temperature at the hot end of a bar, insulated from surroundings, varies simple harmonically, and is given by

$$\theta=\theta_0\cos\omega t, \qquad \text{...(i)}$$

where $\theta_0$ is the temperature-amplitude. Let the direction of heat-flow be along the $x$-axis. Then the Fourier's differential equation will be*

$$\frac{d\theta}{dt}=k\frac{d^2\theta}{dx^2}, \qquad \text{...(ii)}$$

where $k$ is the diffusivity ($k=\frac{K}{\rho c}$ where $K$ is conductivity, $\rho$ density and $c$ is sp. heat).

To solve this equation, let us try a solution

$$\theta=A\,e^{\alpha x+i\beta t}, \qquad \text{...(iii)}$$

where $A,\alpha,\beta$ are constants and $i=\sqrt{-1}$. This gives

$$\frac{d\theta}{dt}=A\,e^{\alpha x+i\beta t}(i\beta)\ \text{ and }\ \frac{d^2\theta}{dx^2}=A\,e^{\alpha x+i\beta t}(\alpha^2).$$

Substituting in eq. (ii), we get

$$i\beta=k\alpha^2$$

$$\therefore\ \alpha=\pm\sqrt{\frac{i\beta}{k}}.$$

Now, $(1+i)^2=2i$ and so $\sqrt{i}=\frac{1}{\sqrt{2}}(1+i)$. Hence

$$\alpha=\pm\sqrt{\frac{\beta}{2k}}\ (1+i).$$

---

* This will be obtained from eq. (iv) in 3.7 in which the term $\frac{Ep}{A\rho c}\theta$ will be omitted (since in the present case the loss of heat from the surface of the bar is not being considered).

Substituting this value in eq. (iii), we get

$$\theta=A\,e^{\pm\sqrt{\beta/2k}\,(1+i)\,x+i\beta t}.$$

When $x=\infty$ (at cold end), $\theta\neq\infty$. Hence only the negative sign is admissible.

Separating the real and imaginary parts, we get

$$\theta=A\,e^{-\sqrt{\beta/2k}\;x+i\,\{\beta t-\sqrt{\beta/2k}\,x\}}$$

$$=A\,e^{-\sqrt{\beta/2k}\,x}+\left[\cos\left\{\beta t-\sqrt{\frac{\beta}{2k}}\,x\right\}+i\sin\left\{\beta t-\sqrt{\frac{\beta}{2k}}\,x\right\}\right].$$

Rejecting the imaginary term, we have

$$\theta=A\,e^{-\sqrt{\beta/2k}\;x}\cos\left[\beta t-\sqrt{\frac{\beta}{2k}}\,x\right].$$

At $x=0$ (hot end), this gives $\theta=A\cos\beta t$. Comparing this with eq. (i), we have $A=\theta_0$ and $\beta=\omega$. Hence we have

$$\theta=\theta_0\,e^{-\sqrt{\omega/2k}\;x}\cos\left(\omega t-\sqrt{\frac{\omega}{2k}}\,x\right).$$

This represents a heat wave travelling with velocity $\sqrt{2\omega k}=\sqrt{\frac{4\pi k}{T}}$. It shows that at a particular point along the bar ($x$ = constant), the temperature $\theta$ varies harmonically with time, the period being that of the heat source. It further shows that the amplitude of temperature oscillations diminishes exponentially as the distance $x$ along the bar increases and becomes negligible at a sufficient distance.

**Angstrom's Method :** Angstrom used the method of periodic flow of heat to determine the thermal conductivity of a metal bar. He enclosed one end of the bar in a chamber through which steam and water could be alternately passed. The bar was heated for 12 minutes and cooled also for the same time. Thus the period of heat flow was $T=24$ minutes. Temperatures were observed every minute at two points on the bar by means of two thermocouples. The diffusivity was calculated from the formula

$$k=\frac{n\pi l^2}{T\,(\delta_n-\delta_n')\log_e(\beta_n/\beta_n')},$$

where $l$ is the distance between the two points and $\delta_n,\delta_n',\beta_n,\beta_n'$ are constants for the two points which were evaluated graphically from the observations.

**Conductivity of Earth's Crust :** The method of periodic heat flow is very suitable for finding the thermal conductivity of earth's crust. At any point the earth's surface is heated in the day and cooled in the night. This alternate heating and cooling travels into the interior of the earth in the form of a heat wave with a period $T=24$ hours. Again, at any point the earth receives larger heat in the summer than in winter, so that a second heat wave with a period $T=1$ year is propagated into the interior of the earth.

Forbes embedded a number of thermometers at different depths in the earth and investigated the progress of the heat wave inside the earth. The time $t$ in which a temperature at the surface reaches a point at a depth $d$ is

$$t=\frac{d}{v}=\sqrt{\frac{T}{4\pi k}}\ \ d.$$

By measuring $t$ for various values of $d$, he calculated the diffusivity of earth's crust at several places. Such investigations have also been used in determining the penetration of the daily and annual changes of temperature within the earth's crust. The information is very useful for geologists.

Kelvin calculated the time taken by the earth to cool from its initial molten fluid state to its present temperature, and estimated a value of 100 million years for the age of the earth. His estimate, however, falls short of the value given by geologists. This is due to the presence of radioactive substances inside the earth which continuously generate heat by spontaneous disintegration, and retard the cooling of the earth.

## 4.12. Rrelation Between Thermal and Electrical Conductivity : Wiedemann Franz Law

The outstanding properties of metals are their high electrical and thermal conductivities. Drude, in 1900, proposed that the distinctive character of a metal is due to some of the electrons being "free" that is, some electrons numbering one to three per atom, are loosely bound or not bound at all to any particular atom but are free to move about at random through the volume of the metal in a manner comparable with the kinetic motion of molecules in a gas.

Most of the metallic elements are crystalline involving a geometrical array of atoms in a space lattice. Within these atoms, the positive nuclei are surrounded by planetary electrons : the electrons in the outermost orbit are known as the valence electrons. In a sodium atom (atomic number $Z = 11$) there are two electrons in the filled $K$ shell, eight in the filled $L$ shell and a single outermost valence electron. In the metal, this electron is loosely bound to the nuclei and becomes the conduction electron, moving throughout the crystal. A monovalent crystal which contains $N$ atoms will have $N$ conduction electrons and $N$ positive ion cores (the central cores to the atoms). A metal may therefore be pictured as composed of positive metal ions whose valence electrons are free to roam among the three dimensional ionic array. As there are $10^{22}$ to $10^{23}$ atoms per cubic centimetre, a large number of *free electrons* is available moving in all directions inside the metal like the atoms or molecules of a perfect gas. This picture of a metal is known as the *electron gas model.*

### Electrical conductivity σ.

Drude applied the electron gas model to explain the fact of thermal and electrical conductivity. Using the assumption of electrons and applying the methods of kinetic theory of gases, he was able to deduce an expression for electrical conductivity. In the absence of an electric field these electrons are supposed to possess the velocity of thermal agitation appropriate to their mass and temperature. In general their motion is random and the mean velocity $\bar{v}$ is given by the kinetic theory of gases in conjunction with the law of equipartition of energy as

$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT, \qquad \ldots(1)$$

where $m$ is the mass of electron. $k$ is Boltzmann constant and $T$ the absolute temperature.

When an electrical field is established in the metal in a particular direction, these negatively charged free electrons stream in the positive field direction. These produce the electric current in a solid conductor. Let $X$ be the electric intensity, then an electron of charge $e$ will experience a force $Xe$ and undergo an aceleration $\frac{Xe}{m}$. However, it will not accelerate indefinitely but after short while collide with a positive ion in the metal. At each collision its velocity is reduced to zero and it is accelerated between two collisions. If $\lambda$ is the mean free path and $t$ the free time, the time taken between two successive collisions, then

$$t = \frac{\lambda}{v} = \lambda/\sqrt{(3kT/m)}. \qquad \ldots(2)$$

During this time $t$ the velocity imparted by the electric field will be the acceleration $\frac{Xe}{m}$ multiplied by this time *i.e.*, $\frac{Xe}{m}\cdot t$. Thus the velocity at the beginning of the path is zero and at its end is $\frac{Xet}{m}$. Hence the average drift velocity $u$ will be the mean of the two *i.e.*,

$$u = \frac{1}{2}\frac{Xet}{m} = \frac{Xe\lambda}{2mv} = \frac{Xe\lambda}{2m\sqrt{(3kT/m)}} = \frac{Xe\lambda}{\sqrt{(12kTm)}}$$

It $n$ is the number of free electrons per unit volume of the metal, there will be a flow of electrons at the rate of $mu$ per unit area per second. Hence the current density $J$ is given by,

$$J = neu = \frac{nXe^2\lambda}{2m\bar{v}} = \frac{nXe^2\lambda}{\sqrt{(12kTm)}} \qquad \ldots(3)$$

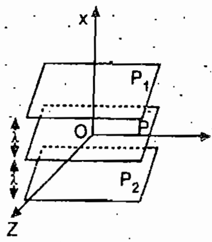
This the electrical conductivity $\sigma$ of unit length and unit cross-sectional area is

$$\sigma = \frac{J}{X} = \frac{ne^2\lambda}{\sqrt{12\,k\,T\,m}} \qquad \ldots(4)$$

This is Drude's formula for electrical conductivity.

### Thermal conductivity.

The free electrons also assist in the conduction of heat along the metals. As the free electrons behave like the molecules of a perfect gas, they will have a greater kinetic energy of thermal agitation at the hot end of a metal bar than those at the cold end. On account of their random motion, this energy will be passed on both by encounters and by the transfer for electrons from the hot to the cold end. If there are $n$ electrons moving randomly in all directions, their motion may be resolved parallel to the three axes $OX$, $OY$ and $OZ$ and we may say that $\frac{n}{6}$ electrons move in one particular direction parallel to one of the three axes. Hence if a plane $P$ of unit area be considered in the metal (Fig. 4.13), $\frac{n\bar{v}}{6}$ electrons will cross it upwards or downwards per second. Consider now a plane $P_1$ at temperature $T_1$ at a distance $\lambda$ (mean free path) from the plane $P$ and another plane $P_2$ at temperature $T_2$ at the same separation $\lambda$ on the other side of plane $P$. If $T_1 > T_2$, there is transfer of energy from $P_1$ to $P_2$. The number of electrons from $P_1 \rightarrow P_2$ per unit area per second is $\frac{n\bar{v}}{6}$ and each electron has energy $\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT_1$. Hence total energy transferred from $P_1$ to $P_2$ per unit area per second



(Fig. 4.13)

$$= \frac{n\bar{v}}{6}\cdot\frac{3}{2}kT_1.$$

Similarly, the energy transfered from $P_2$ to $P_1$ per unit area per second.

$$= \frac{n\bar{v}}{6} \cdot \frac{3}{2} kT_2.$$

Hence the net transfer of energy from $P_2$ to $P_1$ (through $P$) per unit area per second

$$Q = \frac{n\bar{v}}{6}\left(\frac{3kT_1}{2} - \frac{3kT_2}{2}\right) \qquad \text{...(5)}$$

But

$$Q = \frac{K(T_1 - T_2)}{2\lambda} \qquad \text{...(6)}$$

where $K$ is the thermal conductivity of the metal.

Equating equation (5) and (6), we get

$$\frac{K(T_1 - T_2)}{2\lambda} = \frac{n\bar{v}}{6}\left(\frac{3kT_1}{2} - \frac{3kT_2}{2}\right)$$

or

$$K = \frac{kn\bar{v}}{2}. \qquad \text{...(7)}$$

This is the expression for thermal conductivity of the solid. If the thermal conductivity $K$ for the electron gas is expressed in calories, then

$$K = \frac{1}{2} \cdot \frac{n\bar{v}\lambda}{J}. \qquad \text{...(8)}$$

## The Wiedemann-Franz Law

In 1854, Wiedemann and Franz performed a ~~number~~ of experiments on ~~the relative~~ thermal conductivities $K$ of different metals. As a result of these experiments and knowledge of electrical conductivities $\sigma$, they put forward an empirical law which bears their name and states that *the ratio of the thermal to the electrical conductivity of all metals is the same at a given temperature.* Lorentz, in 1872, extended this law and showed that the value of the ratio $\frac{K}{\sigma}$ is proportional to the absolute temperature $T$. Thus $\frac{K}{\sigma T}$ should have the same value at all temperatures for all metals.

The numerical value of $\frac{K}{\sigma}$ can be found from equation (4) and (8) to be

$$\frac{K}{\sigma} = \frac{kn\bar{v}\lambda}{2} \Big/ \frac{ne^2\lambda}{2m\bar{v}}$$

$$= \frac{km\bar{v}^2}{e^2}$$

$$= \frac{k \,.\, 3kT}{e^2} \qquad \left[\overset{\frac{1}{2}}{\wedge} m\overline{v^2} = \frac{3}{2}kT\right]$$

$$= 3\left(\frac{k}{e}\right)^2 T. \qquad \text{...(9)}$$

or

$$\frac{K}{\sigma T} = 3\left(\frac{k}{e}\right)^2$$

$$= \frac{3R^2}{N^2e^2}. \qquad \text{...(10)}$$

where $R$ is the gas constant, $N$ the Avogadro number and $e$ the value of the charge on an electron. Equation (10) expresses the law of both Wiedemann and Franz, of Lorentz and is related entirely to universal constants ($R$, $N$ and $e$).

The above equation has been tested experimentally by a large number of workers but specially by Jaegr and Diesselhorst and by Less. The experiments show that equation (10) is satistied at ordinary temperature for pure metals but there is a marked falling off in the value of the ratio $\frac{K}{\sigma T}$ at low temperatures which tends to approach zero at the absolute zero of temperature.

To compare the experimental values with the predictions of equation (10), attention must be paid to units. If $K$ is expressed in joule m$^{-1}$ K$^{-1}$ and $\sigma$ in mho/m, then

$$\frac{K}{\sigma T} = 3\left(\frac{k}{e}\right)^2 = 3\left(\frac{1{\cdot}38 \times 10^{-23}}{1{\cdot}6 \times 10^{-19}}\right)^2 = 2{\cdot}23 \times 10^{-8}$$

The values of $\frac{K}{\sigma T}$ obtained experimentally are shown in table . It is obvious that the law fits the facts very well at ordinary temperatures but definite deviations occur at low temperatures.

**Table.** *To illustrate Wiedemann and Franz's Law.*

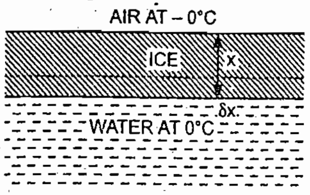
**Values of $\frac{K}{\sigma T} \times 10^8$**

| Metal | Results of Lee's direct Method | | | | | Jaeger and Diesselhorst | |
|---|---|---|---|---|---|---|---|
| | – 170°C | – 100°C | – 50°C | 0°C | 18°C | 18°C | 10°C |
| Aluminium | 1·50 | 1·81 | 1·98 | 2·09 | 2·13 | 2·19 | 2·27 |
| Copper | 1·85 | 2·17 | 2·26 | 2·30 | 2·32 | 2·20 | 2·32 |
| Silver | 2·04 | 2·29 | 2·36 | 2·33 | 2·33 | 2·36 | 2·37 |
| Zinc | 2·20 | 2·39 | 2·40 | 2·45 | 2·43 | 2·31 | 2·33 |
| Tin | 2·48 | 2·51 | 2·47 | 2·49 | 2·47 | 2·53 | 2·49 |
| Lead | 2·55 | 2·54 | 2·52 | 2·53 | 2·51 | 2·46 | 2·51 |
| Iron | 3·10 | 2·98 | 2·93 | 2·97 | 2·99 | 2·76 | 2·85 |
| Manganin | 5·94 | 4·16 | 3·58 | 3·41 | 3·34 | 3·14 | 2·97 |

This may be considered as fair agreement indicating that the simple electron-gas model of a metal is satisfactory. The falling off in the value of $\frac{K}{\sigma T}$ at low temperatures is also confirmed by the works of Meissner, Onnes and Holst. It is perhaps due to the increase in the values of thermal and electrical conductivities with a fall in temperature but the thermal conductivity does not increase so rapidly as does the electrical conductivity which appears to become infinite at the absolute zero.

## NUMERICAL EXAMPLES

**Ex. 1.** *The thickness of ice in a lake is 5 cm and the temperature of air is −10 °C. Calculate the time required for the thickness of ice to be doubled. Constants for ice are : conductivity* $= 0{\cdot}004$ cal–cm$^{-1}$–sec$^{-1}$–°C$^{-1}$, density $= 0{\cdot}92$ g / cm$^3$, *latent heat = 80 cal/g.*



(Fig. 4.14)

**Solution.** The cold air (below 0 °C) above the water in a lake takes in heat from the water. The water therefore begins to freeze into ice layer. Let us determine the rate of growth of this layer.

Let us consider a layer of ice $x$ cm thick already formed on a lake at 0°C, the temperature of air above it being $-\theta$ °C. Let $A$ be the area of the ice layer, $L$ the latent heat of fusion of ice and $\rho$ its density. Then the heat given up when the ice layer increases in thickness by an amount $dx$

$$= \text{mass} \times \text{latent heat}$$
$$= A\,dx\,\rho \times L \text{ calorie}.$$

If this quantity of heat is conducted upwards through the ice layer in $dt$ second, then we have

$$A\,dx\,\rho \times L = KA\frac{0-(-\theta)}{x}\,dt,$$

where $K$ is thermal conductivity of ice. This gives

$$\frac{dx}{dt} = \frac{K\theta}{\rho L x}.$$

$dx/dt$ is the rate at which the thickness of ice layer increases. Rearranging the above expression, we get

$$dt = \frac{\rho L x}{K\theta}\,dx.$$

Therefore, the time in which thickness of ice will increase from $x_1$ to $x_2$ will be given by

$$t = \frac{\rho L}{K\theta}\int_{x_1}^{x_2} x\,dx = \frac{\rho L}{K\theta}\left[\frac{x^2}{2}\right]_{x_1}^{x_2} = \frac{\rho L}{2K\theta}(x_2^2 - x_1^2).$$

In the given problem, we have $K = 0{\cdot}004$ cal–cm$^{-1}$–sec$^{-1}$–°C$^{-1}$, $\rho = 0{\cdot}92$ g / cm$^3$, $L = 80$ cal/g, $-\theta = -10$ °C, $x_1 = 5$ cm, $x_2 = 10$ cm (doubled).

$$\therefore \quad t = \frac{0{\cdot}92 \times 80}{2 \times 0{\cdot}004 \times 10}(10^2 - 5^2)$$
$$= 69000 \text{ seconds} = \mathbf{19{\cdot}1 \text{ hours}}.$$

**Ex. 2.** *How much time will it take for a layer of ice of thickness 20 cm to increase by 10 cm on the surface of a pond when the temperature of the surroundings is − 15 °C. Given :* $K = 0{\cdot}005$ cgs units, $L = 80$ cal/g, $\rho = 0{\cdot}90$ g/cm$^3$.

**Solution.** As in Ex 1

$$t = \frac{\rho L}{2K\theta}(x_2^2 - x_1^2)$$
$$= \frac{0{\cdot}90 \times 80}{2 \times 0{\cdot}005 \times 15}(30^2 - 20^2)$$
$$= \frac{0{\cdot}90 \times 80 \times 500}{2 \times 0{\cdot}005 \times 15} = 240000 \text{ sec} = \mathbf{66{\cdot}67 \text{ hours}}.$$

**Ex. 3.** *A lake is covered with ice 4 cm thick and the temperature of air above the ice is − 12 °C. At what rate, expressed in cm per hour, will the ice thicken ? Conductivity of ice* $= 0{\cdot}0052$ *cgs units, density of ice* $= 0{\cdot}92$ g/cm$^3$ *and latent heat of ice = 80 cal/g.*

**Solution.** As in Ex 1

$$\frac{dx}{dt} = \frac{K\theta}{\rho L x}$$
$$= \frac{0{\cdot}0052 \text{ cal/(cm–sec–°C)} \times (12 \text{ °C})}{0{\cdot}92 \text{ g/cm}^3 \times 80 \text{ cal/g} \times 4 \text{ cm}}$$
$$= 2{\cdot}12 \times 10^{-4} \text{ cm/sec}$$
$$= (2{\cdot}12 \times 10^{-4}) \times 3600 = \mathbf{0{\cdot}763 \text{ cm/hour}}.$$

**Ex. 4.** *The steady temperatures at the ends of a coper rod of length 25 cm and area of cross-section* 1·0 cm$^2$ *are 125 °C and 0 °C respectively. Calculate the temperature-gradient, rate of heat-flow, and the temperature at a distance 10 cm from the hot end. K for copper* $= 9{\cdot}2 \times 10^{-2}$ kilo–cal/(sec–meter–°C).

**Solution.** The rate of linear, steady heat-flow is given by

$$\frac{\Delta Q}{\Delta t} = KA\frac{\theta_1 - \theta_2}{d}, \qquad \text{...(i)}$$

where the symbols have their usual meanings.

Here, temperature-gradient, $\dfrac{\theta_1 - \theta_2}{d} = \dfrac{125}{25} = 5$ °C/cm.

$$K = 9{\cdot}2 \times 10^{-2} \text{ kilo–cal/(sec–meter–°C)}$$
$$= 9{\cdot}2 \times 10^{-1} \text{ cal/(sec–cm–°C)},$$

and $\quad A = 1{\cdot}0 \text{ cm}^2.$

$$\therefore \quad \frac{\Delta Q}{\Delta t} = (9{\cdot}2 \times 10^{-1}) \times 1{\cdot}0 \times 5 = \mathbf{4{\cdot}6 \text{ cal/sec}}.$$

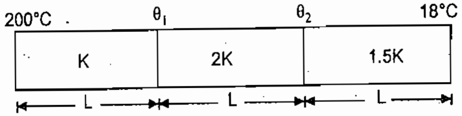
Now, in the steady state, the rate of heat-flow is same through all the sections of the bar. If the temperature at a distance of 10 cm from the hot end (*i.e.* $d = 10$ cm) be $\theta$ ; then from eq. (i), we have

$$\frac{\Delta Q}{\Delta t} = 4{\cdot}6 = 9{\cdot}2 \times 10^{-1} \times 1{\cdot}0 \times \frac{125 - \theta}{10}$$

or $\quad (125 - \theta) = \dfrac{4{\cdot}6 \times 10}{9{\cdot}2 \times 10^{-1}} = 50$

$$\therefore \theta = 125 - 50 = \mathbf{75 \text{ °C}}.$$

**Ex. 5.** *Three bars each of area of cross-section A and length L are connected in series. The thermal conductivities of their materials are K, 2K and 1·5 K. If the temperatures of the external ends of the first and the last bar are 200 °C and 18 °C, then calculate the temperatures of both the junctions. The loss of heat due to radiation is negligible.*



(Fig. 4.15)

**Solution.** Let the temperatures of the junctions (see Fig. 4.15) be $\theta_1$ and $\theta_2$ respectively. The loss of heat due to radiation is negligible. Therefore, in the steady state, the rate of flow of heat in the whole system will be same. Therefore

$$\frac{\Delta Q}{\Delta t}=KA\frac{(200-\theta_1)}{L}=(2\,K)\,A\frac{(\theta_1-\theta_2)}{L}=(1{\cdot}5\,K)\,A\frac{(\theta_2-18)}{L}$$

or $$200-\theta_1=2\,\theta_1-2\,\theta_2=1{\cdot}5\,\theta_2-27\,.$$

Solving : $\boldsymbol{\theta_1=116\ ^\circ\mathrm{C}\,,\ \theta_2=74\ ^\circ\mathrm{C}}$.

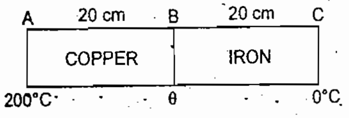
**Ex. 6.** *A bar of length 40 cm and uniform cross-section 5 cm$^2$ consists of two halves, AB of copper and CB of iron welded at B. The end A is maintained at 200 °C and C at 0 °C. The sides are thermally insulated. Find the rate of heat-flow along the bar in the steady state. K for Cu and Fe are* 0·9 and 0·1 *cal/(sec-cm-°C) respectively.*

**Solution.** Let $\theta$ be the temperature of the junction. In the steady state, the rate of heat-flow will be same throughout the bar. Therefore

$$\therefore\ \frac{\Delta Q}{\Delta t}=0{\cdot}9\times5\times\frac{200-\theta}{20}=0{\cdot}1\times5\times\frac{\theta-0}{20}.$$

Solving for $\theta$, we get

$$\theta=180^\circ.$$



(Fig. 4.16)

Now, putting the value of $\theta$ in the last eq., we get

$$\frac{\Delta Q}{\Delta t}=0{\cdot}1\times5\times\frac{180-0}{20}$$
$$=\mathbf{4{\cdot}5\ cal/sec}\,.$$

**Ex. 7.** *An electric hot plate of 100 cm$^2$ area has temperature of 820 °C on the heater side. A kettle of a perfect conductor with 250 cm$^3$ of water at a temperature of 20 °C is kept over it. Find how much time will be required for the water to just boil if the water equivalent of the kettle is 20 gm and thickness of the hot plate is 0·9 cm and thermal conductivity is 0·9 C.G.S. units.*

**Solution.** The mass of the water is 250 gm and the water equivalent of the kettle is 20 gm. The specific heat of water is 1 C. G. S. unit. Hence the heat required for the water to reach from 20 °C to 100 °C (boiling) is giving by

$$Q=(250\times1+20)\,(100-20)=21600\ \text{cal}\,.$$

Let $t$ be the time required for the heat $Q$ to flow through the hot plate. We know that, in usual notations,

$$Q=KA\frac{\theta_1-\theta_2}{d}\,t\,.$$

Here $Q=21600$ cal, $K=0{\cdot}9$ C. G. S. units, $A=100\ \text{cm}^2$, $(\theta_1-\theta_2)=\left\{820-\frac{20+100}{2}\right\}$ $=760\ ^\circ\mathrm{C}$ and $d=0{\cdot}9$ cm.

$$\therefore\ 21600=\frac{0{\cdot}9\times100\times760\times t}{0{\cdot}9}$$

or $$t=\frac{21600\times0{\cdot}9}{0{\cdot}9\times100\times760}=\mathbf{\frac{27}{95}\ sec}\,.$$

**Ex. 8.** *An insulating wall of area of 4 m$^2$ is made from cork, 16·5 cm thick, protected externally by 12·5 cm brick and lined on the inside with 10·0 cm wood. If the exposed surface of wood is maintained at $-5{\cdot}0$ °C and the outer surface of the brick at 20·0 °C, calculate (i) the rate of energy transfer through the wall and (ii) the interface temperatures. Given : thermal conductivity for brick $=2{\cdot}5\times10^{-3}$, for cork $=1{\cdot}1\times10^{-4}$ and for wood $=4{\cdot}0\times10^{-4}$ cal-sec$^{-1}$-cm$^{-1}$-°C$^{-1}$.*

**Solution.** Let $\theta_1$ be the temperature of the brick-cork interface and $\theta_2$ that of the cork-wood interface. The temperature of the outer surface of brick is 20·0 °C and that of the exposed surface of wood is – 5 °C. In the steady state, the heat flowing per second is same throughout. Therefore, equating the heat flowing per second through brick, cork and wood, we have

$$2{\cdot}5\times10^{-3}\times A\,\frac{20-\theta_1}{12{\cdot}5}=1{\cdot}1\times10^{-4}\times A\,\frac{\theta_1-\theta_2}{16{\cdot}5}$$
$$=4{\cdot}0\times10^{-4}\times A\,\frac{\theta_2-(-5)}{10}.$$

From this, we get two equations

$$25\times\frac{20-\theta_1}{12{\cdot}5}=1{\cdot}1\times\frac{\theta_1-\theta_2}{16{\cdot}5}$$

and $$25\times\frac{20-\theta_1}{12{\cdot}5}=4\times\frac{\theta_2+5}{10}.$$

Solving we get : $\boldsymbol{\theta_1=19{\cdot}3\ ^\circ\mathrm{C}}$ and $\boldsymbol{\theta_2=-1{\cdot}53\ ^\circ\mathrm{C}}$.

The rate of heat-flow through brick, say, is

$$\frac{\Delta Q}{\Delta t}=2{\cdot}5\times10^{-3}\times A\times\frac{20-\theta_1}{12{\cdot}5}$$
$$=2{\cdot}5\times10^{-3}\times(400\times400)\times\frac{20-19{\cdot}3}{12{\cdot}5}=\mathbf{22{\cdot}4\ cal/sec.}$$

**Ex. 9.** *Along the axis of a long uniform cylindrical shell of inner and outer radii 4 and 12 cm, there is a wire in which 7·0 watt of energy is developed per cm. length. If the conductivity of the material is* 0·003 *joule cm$^{-1}$ deg$^{-1}$ sec$^{-1}$ and the steady state temperature of outer surface is 20°C, deduce (i) the temperature at the inner face of the cylinder, (ii) the temperature at $r=8$ cm.*

**Solution.** (i) The energy developed in the wire = 7 watt/cm.

$$\frac{Q}{l}=7\ \text{joules/cm. sec.}$$
$$=\frac{7}{J}=\frac{7}{4{\cdot}2}=\frac{5}{3}\ \text{cals/cm sec.}$$

Also, the conductivity of material

$$K=0{\cdot}003\ \text{joule cm}^{-1}\,\text{deg}^{-1}\,\text{sec}^{-1}$$
$$=\frac{0{\cdot}003}{4{\cdot}2}=\frac{0{\cdot}01}{14}\ \text{cals. cm}^{-1}\,\text{sec}^{-1}$$

Now the conductivity of a cylindrical tube is given by

$$K=\frac{Q\log_e\frac{r_2}{r_1}}{2\pi l\,(\theta_1-\theta_2)}=\frac{Q\times2{\cdot}3\log_{10}\frac{r_2}{r_1}}{2\pi l\,(\theta_1-\theta_2)}\qquad(\because\ \log_e x=2{\cdot}3\log_{10}x)$$

Here, given $r_1=4$ cm, $r_2=12$ cm, $\theta_2=20$°C, $\theta=?$

$$K=\frac{0{\cdot}01}{14}=\frac{5\times2{\cdot}3\times10_{10}\frac{12}{4}}{3\times2\times3{\cdot}14\,(\theta_1-\theta_2)}\qquad\left[\because\ \frac{Q}{l}=\frac{5}{3}\right]$$

or $$(\theta_1-\theta_2)=\frac{5\times2{\cdot}3\times\log_{10}3\times14}{3\times2\times3{\cdot}14\times0{\cdot}01}.$$

$$= \frac{5 \times 2{\cdot}3 \times 0{\cdot}477 \times 14}{3 \times 2 \times 3{\cdot}14 \times 0{\cdot}01} = 407{\cdot}7$$

$$\therefore \quad \theta_1 = 407{\cdot}7 + \theta_2 = 407{\cdot}7 + 20 = \mathbf{427{\cdot}7^\circ C.}$$

(ii) Now the temperature of a cylindrical shell at a distance $r = 8$ cm from the axis

$$\theta = \frac{1}{\log_e \frac{r_2}{r_1}} [(\theta_1 \log_e r_2 - \theta_2 \log_e r_1) - (\theta_1 - \theta_2) \log_e r]$$

$$= \frac{1}{2{\cdot}3 \log_{10} \frac{12}{4}} [(427{\cdot}7 \times 2{\cdot}3 \log_{10} 12 - 20 \times 2{\cdot}3 \log_{10} 4) - 407{\cdot}7 \times 2{\cdot}3 \log_{10} 8]$$

$$= \frac{1}{\log_{10} 3} [(427{\cdot}7 \log_{10} 12 - 20 \log_{10} 4) - 407{\cdot}7 \log_{10} 8]$$

$$\theta = \frac{1}{0{\cdot}4771} [(427{\cdot}7 \times 1{\cdot}0792 - 20 \times 0{\cdot}6021) - 407{\cdot}7 \times 0{\cdot}9031].$$

$$= \frac{1}{0{\cdot}4771} [461{\cdot}4 - 12{\cdot}04 - 368{\cdot}1]$$

$$= \frac{81{\cdot}29}{0{\cdot}4771} = \mathbf{170{\cdot}3^\circ C.}$$

**Ex. 10.** *Two thin concentric spherical shells of radii 5 cm and 10 cm respectively have their annular cavity filled with charcoal powder. When energy is supplied at the rate of 10·5 watt to a heater at the centre, a temperature difference of 60°C is set up between the shells. Find the thermal conductivity of charcoal. ($J = 4{\cdot}2$ joule/cal).*

**Solution.** The thermal conductivity of charocal will be given by

$$K = \frac{Q\,(r_2 - r_1)}{4\pi r_1 r_2 (\theta_1 - \theta_2)}$$

Here, heat supplied per sec. $Q = 10{\cdot}5 \times$ Joule/sec.

$$= \frac{10{\cdot}5}{J} \text{ cal/sec.} = \frac{10{\cdot}5}{4{\cdot}2} \text{ cal/sec.}$$

Also given $r_2 = 10$ cm, $r_1 = 5$ cm, $(\theta_1 - \theta_2) = 60^\circ$C

$$K = \frac{\frac{10{\cdot}5}{4{\cdot}2}(10 - 5)}{3 \times 3{\cdot}14 \times 10 \times 5 \times 60}$$

$$= \mathbf{3{\cdot}3 \text{ timesd } 10^{-4} \text{ ca. cm}^{-1} \deg^{-1} \sec^{-1}.}$$

**Ex. 11.** *In a periodic flow of heat along an iron bar, the periodic time is 4 minutes. If the temperature maximum travels 6 cm in one minute, calculate the thermal conductivity of iron. Density of iron $= 7{\cdot}8$ g/cm$^3$, sp. heat of iron $= 0{\cdot}11$ cal/(g-°C).*

**Solution.** The velocity of heat-wave in the iron bar is given by

$$v = \sqrt{\frac{4\pi k}{T}},$$

where $k$ is the diffusivity of the bar and $T$ is the period of the wave. From this, we have

$$k = \frac{v^2 T}{4\pi}.$$

Further $k = \dfrac{K}{\rho c}$, where $K$ is conductivity, $\rho$ is density and $c$ is specific heat.

$$\therefore K = k \rho c = \frac{v^2 T \rho c}{4\pi}.$$

Here $v$ = 6 cm/minute = 0·1 cm/sec, $T$ = 4 min = 240 sec, $\rho$ = 7·8 g/cm$^3$ and $c$ = 0·11 cal/(g-°C).

$$\therefore K = \frac{(0{\cdot}1 \text{ cm/sec})^2 (240 \text{ sec})(7{\cdot}8 \text{ g/cm}^3)\left(0{\cdot}11 \frac{\text{cal}}{\text{g-}^\circ\text{C}}\right)}{4 \times 3{\cdot}14}$$

$$= \mathbf{0{\cdot}164 \text{ cal/(cm-sec-}^\circ\text{C)}}.$$

## EXERCISES

### SHORT ANSWER QUESTIONS

1. Explain the phenomenon of heat conduction.
2. What do you mean by steady state and temperature gradient in connection with heat conduction?
3. State fundamental equation of heat conduction. Hence define thermal conductivity.
4. What do you mean by the term diffusivity?
5. What do you mean by thermal resistance?
6. What is equivalent thermal conductivity of two metal rods connected in series?
7. In summer, a block of metal feels hotter than a block of wood while in winter it feels colder than wood, although both are at the same temperature. Explain its reason. Is there any temperature at which they both will feel equally hot or equally cold?
8. State what thermal properties a material should have to be suitable for constructing cooking utensils.
9. Distinguish between thermal conductivity and thermometric conductivity and temperature gradient.
10. State Fourier's equation of heat flow in a metal bar.
11. Draw graphs for temperature variation along the length of a rod in steady state when (i) bar is exposed and (ii) bar is covered.
12. How will you find the conductivity of earth's crust?
13. What is the relation between electrical and thermal conductivity of a metal?
14. State and explain Wiedemann Franz-law. Does it apply to gases?

### Long Answer Questions

1. (a) Explain the process of thermal conduction.
   (b) Explain clearly the terms : temperatue gradient, steady state and variable state.
2. How do you define the terms thermal conductivity for a material ? What do you understand by a thermal steady state and state the fundamental laws of heat conduction.
3. State fundamental equation of heat flow. Hence define coefficient of thermal conductivity. What are its dimensions ? On what factors does it depend ? Is it related to electrical conductivity ? If yes, why ?

4. Three slabs with thermal conductivity $K_1, K_2$ and $K_3$ and of thicknesses $d_1, d_2$ and $d_3$ respectively are placed in contact in the order 1, 2, 3. Prove that after the steady state is reached, the combination behaves as a single plate of conductivity $K$, given by

$$\frac{d_1+d_2+d_3}{K}=\frac{d_1}{K_1}+\frac{d_2}{K_2}+\frac{d_3}{K_3}.$$

5. Two slabs of thickness $d_1$ and $d_2$; thermal conductivities $K_1$ and $K_2$ are placed in contact with each other and heated at the junction. If the steady state temperature be $\theta_1$ and $\theta_2$ at the two free surfaces, show that the temperature at the interface between the slabs would be

$$\frac{\frac{K_1}{d_1}\cdot\theta_1+\frac{K_2}{d_2}\cdot\theta_2}{\frac{K_1}{d_1}+\frac{K_2}{d_2}}$$

6. A long metal bar is heated at one end. Derive and solve the Fourier's equation for rectilinear flow of heat along the bar. Discuss different cases.
7. Give the theory of periodic flow of heat along a long bar. Discuss its implications in connection with heat flow across the earth's crust.
8. Give an account of annual and dirunal waves of temperature into the earth and derive approximate expression for their wavelengths in terms of the appropriate thermal and other accounts.
9. Describe a method for determining the coefficient of thermal conductivity of a bad conductor having the shape of a disc.
10. Discuss, in detail, Forbe's method for finding the coefficient of thermal conductivity of a metal bar.
11. Describe Lee's method for the determination of thermal conductivity of good conductors.
12. Discuss Lee's method for finding the thermal conductivity of poor conductors.
13. What do you understand by periodic flow of heat ? Describe Angstrom's periodic flow method for determining the thermal conductivity. Discuss its applications to the heat flow in earth.
14. Describe Angstrom's experiment to measure the thermal conductivities. How can you determine the conductivity of earth's crust. *(Patna 2004)*
15. State and explain Wiedemann Franz Law. Discuss the law from experimental stand point. *(Patna 2004)*
16. Derive relation between electrical and thermal conductivity of a metal. How for the law is verified experimentally ?

## Numerical Questions

1. The temperature gradient in the earth's crust is 32°C per km and the mean conductivity of the rocks is 0·008 C.G.S. units. Taking the radius of the earth as 6,000 km., calculate the daily loss of heat by the earth. [Ans. $9{\cdot}95 \times 10^9$ cals.]

2. A block of two parallel plates, one of bras and the other of copper, has the copper face at 100°C and the brass face at 0°C. Find the temperature of the interface if the copper and brass plates have their thickness 4 cm. and 2 cm. and their conductivities are 0·92 and 0·26 C.G.S. units respectively. [Ans. 64°C]
3. A composite metal rod of uniform cross section 2 sq. cm. is made up of a 40 cm. rod of copper of thermal conductivity 0·92 C.G.S. units and a 25 cm. rod of aluminium of conductivity 0·50 units joined together. If the open face of copper is maintained at 100°C and that of aluminium at 0°C. Calculate (i) temperature of the junction of two rods, (ii) the heat flowing through each rod in 2 min. [Ans. (i) 53·5°C, (ii) 256·7 cal.]
4. The walls of a cold storage chamber are made of insulating bricks and are 10 cm. thick. On the inside the walls are lined with a cork layer 3 cm. thick. If the inside temperature is – 5°C and the outside temperatue is 25°C, find the temperature of the inner face and the heat flowing per sec. through every square meter of the wall surface. $K$ for brick = 0·005 and for cork = 0·0001 C.G.S. units. [Ans. 13°C, 6 cals.]
5. Calculate the rate at which ice layer 10 cm. thick, increases in thickness when its lower surface is in contact with water at 0°C and upper wth air at – 40°C. (For ice $K$ = ·005, $L$ = 80 and $\rho$ = 0·9 C.G.S. units) [Ans. $2{\cdot}7 \times 10^{-4}$ cm/s.]
6. The thickness of ice in a lake is 5 cm. and the temperature of air is – 20°C. Calculate the time required for the thickness of ice to be doubled ? Constants for ice are : conductivity = 0·004 cal. $\text{cm}^{-1}\,\text{sec}^{-1}\,{}^\circ\text{C}^{-1}$ density 0·92 gm/c.c., latent heat = 80 cal/gm. [Ans. 9·6 hours]
7. The temperature of the outer surface of earth may be treated as varying sinusoidally with period 24 hours and amplitude 0°C. Write down an expression for the ~~temperature at any~~ general depth $x$ at general time $t$ and discuss it.
8. For ordinary moist soil, the diffusivity $h$ is 0·0049. Calculate the wavelength and velocity for dirunal and annual waves of temperature. [Ans. 73 cm., $8{\cdot}4 \times 10^{-4}$ cm./sec., 14 meters; $4{\cdot}5 \times 10^{-5}$ cm./sec.]
9. A copper plate of radius 12·0 cm. and thickness 5·0 cm. conducts when the temperature difference between the circular end faces is 20·0°C. A spherical shell of aluminium radii 9·0 cm. and 4·0 cm. conducts heat radially under the same temperature difference. Compare the amounts of heat transferred per sec. in the two cases. Given thermal conductivity of Copper and Aluminium to be 0·92 and 0·5 C.G.S. units. [Ans. 46/25]
10. A uniform rod is heated at one end. In the steady state, the temperature of the rod at a distance 1·0 meter from he hot end is 30°C and at 2·0 meter is 20°C. Calculate the temperature of the hot end. [Ans. 40°C]
11. Thermal conductivity of copper is four times that of brass. Two rods of copper and brass of same length and cross-section are joined end to end. The free end of copper is at 0°C and that of brass rod is at 100°C. Calculate the temperature of junction. Neglect radiation losses. [Ans. 20°C]
12. An ice box is built of wood 1·75 cm. thick lined inside with cork 3 cm. thick. If the temperature of the inner surface of the cork is 0°C and that of the outer surface of wood is 12°C what is the temperature of the interface ? The thermal conductivities of wood and cork are 0·0006 and 0·00012 C.G.S. units respectively. [Ans. 10·75°C]

## MULTIPLE CHOICE QUESTIONS : SELECT THE RIGHT CHOICE

1. The rate of flow of heat through a metal bar of area of cross section 1 $m^2$ when temperature gradient is 1°C/m under steady state is called : *(Rohilkhand 2002)*
   (a) Thermal resistance (b) Thermal conductivity
   (c) diffusivity (d) resistivity
2. Under steady state, the temperature of a body : *(Rohilkhand 2002)*
   (a) increases with time
   (b) decreases with time
   (c) does not change with time and is same at all points of the body
   (d) does not change with time and can be different at different points of a body
3. Thermal conduction in metals takes place by : *(Rohilkhand 2002)*
   (a) Free electrons (b) Bound electrons
   (c) Vibrations of molecules (d) None of the above
4. A single plate of double thickness is made by joining two equal plates of thermal conductivities $K_1$ and $K_2$. The equivalent thermal conductivity of the composite plate will be : *(Rohilkhand 2002, 2003)*
   (a) $\frac{2K_1K_2}{K_1+K_2}$ (b) $\frac{K_1K_2}{K_1+K_2}$ (c) $\frac{K_1}{K_1+K_2}$ (d) $\frac{K_2}{K_1+K_2}$
5. If the density of material is $\rho$ and specific heat is $c$, then its thermal diffusivity is : (Rohilkhand 2002)
   (a) $h=\frac{c}{\rho K}$ (b) $h=\frac{K}{\rho c}$ (c) $h=\frac{K\rho}{c}$ (d) $h=\frac{\rho c}{K}$
6. Fourier equation for one dimensional flow of heat is of the form :
   (a) $\frac{\partial\theta}{\partial t}=h\frac{\partial\theta}{\partial x}-\mu\theta$ (b) $\frac{\partial\theta}{\partial t}=h\frac{\partial\theta}{\partial x}+\mu\theta$
   (c) $\frac{\partial\theta}{\partial t}=h\frac{\partial^2\theta}{\partial x^2}-\mu\theta$ (d) $\frac{\partial\theta}{\partial t}=h\frac{\partial^2\theta}{\partial x^2}+\mu\theta$
7. In the steady state of temperature, the flow of heat across the body depends :
   (a) only upon its thermal conductivity
   (b) upon its thermal conductivity and thermal capacity
   (c) upon its thermal capacity only
   (d) neither upon thermal conductivity nor upon thermal capacity
8. The S.I. unit of thermal conductivity is :
   (a) $JS\,m^{-1}\,{}^\circ C^{-1}$ (b) $JS^{-1}\,m^{-1}\,{}^\circ C^{-1}$
   (c) $JS^{-1}\,m^{-1}\,{}^\circ C$ (d) $JS^{-1}\,m\,{}^\circ C^{-1}$
9. If $l$ is the length and $A$ are of cross section of a rod and $K$ is thermal conductivity of material, then the thermal resistance is given by : *(Rohilkhand 2003)*
   (a) $\frac{Kl}{A}$ (b) $\frac{A}{Kl}$ (c) $\frac{KA}{l}$ (d) $\frac{l}{KA}$

10. Two rods of length $d_1$ and $d_2$ and coefficient of thermal conductivities $K_1$ and $K_2$ are kept touching each other. Both have the same area of cross section. The equivalent thermal conductivity is :
    (a) $K_1+K_2$ (b) $K_1d_1+K_2d_2$ (c) $\frac{K_2d_1+K_1d_2}{d_1+d_2}$ (d) $\frac{d_1+d_2}{\frac{d_1}{K_1}+\frac{d_2}{K_2}}$
11. Two walls of thickness $d_1$ and $d_2$, thermal conductivities $K_1$ and $K_2$ are in contact. In the steady state if the temperatures at the outer surfaces are $T_1$ and $T_2$, the temperature at the common wall will be :
    (a) $\frac{K_1T_1+K_2T_2}{d_1+d_2}$ (b) $\frac{K_1T_1d_2+K_2T_2d_1}{K_1d_2+K_2d_1}$
    (c) $\frac{(K_1d_1+K_2d_2)\,T_1T_2}{T_1+T_2}$ (d) $\frac{K_1d_1T_1+K_2d_2T_2}{K_1d_1+K_2d_2}$
12. The coefficient of thermal conductivity of a metal depends upon :
    (a) temperature difference between the two sides
    (b) thickness of the metal plate
    (c) area of the plate
    (d) none of the above
13. Four rods with different radii $r$ and length $l$ are used to connect two reservoirs of heat at different temperatures. Which one will conduct most heat ?
    (a) $r=1$ cm, $l=1$ m (b) $r=2$ cm, $l=2$ m
    (c) $r=1$ cm, $l=\frac{1}{2}$ m (d) $r=2$ cm, $l=\frac{1}{2}$ m
14. Heat is flowing through two cylindrical rods of same materials. The diameters of the rod are in the ratio 1 : 2 and theri lengths in the ratio 2 : 1. If the temperature difference between their ends is the same, then the ratio of amount of heat conducted throught them per unit time will be :
    (a) 1 : 1 (b) 2 : 1 (c) 1 : 4 (d) 1 : 8
15. A wall has two layers $A$ and $B$, each of different materials. Both the layers have the same thickness. The thermal conductivity of the material of $A$ is thrice that of $B$. Under thermal equilibrium, the temperature difference across the wall is 36°C. Then the temperature difference across the layer $A$ is :
    (a) 6°C (b) 9°C (c) 12°C (d) 27°C
16. Ice starts forming in a lake with water at 0°C, when the atmospheric temperature is –10°C. If the time taken for 1 cm of ice to be formed is 7 hours, the time taken for the thickness of ice to change from 1 cm to 2 cm is :
    (a) 7 hours (b) less than 7 hours
    (c) more than 7 hours but less than 14 hours (d) more than 14 hours
17. A metallic rod is heated at one end continuously. After some time steady state is reached. The flow of heat in the steady state does not depend upon :
    (a) the area of cros-section of the rod (b) the temperature gradient
    (c) the mass of the rod (d) the time of flow of heat

18. Two cylindrical rods of the same substance have diameters $d_1$ and $d_2$. The amounts of heat conducted by these two rods, for the same temperature difference between the two ends will be equal if their lengths are related by :

(a) $\frac{l_1}{l_2}=\frac{d_1}{d_2}$ (b) $\frac{l_1}{l_2}=\left(\frac{d_1}{d_2}\right)^2$ (c) $\frac{l_1}{l_2}=\frac{d_2}{d_1}$ (d) $\frac{l_1}{l_2}=\left(\frac{d_2}{d_1}\right)^2$

19. Quantity of heat flowing through a conductor in steady state is given by : *(Rohilkhand 2003)*

(a) $Q = KA\,(\theta_1 - \theta_2)\,t/d$ (b) $Q = At\,(\theta_1 - \theta_2)/Kd$

(c) $Q = At\,(\theta_1 - \theta_2)\,Kd$ (d) $Q = KA\,(\theta_1 - \theta_2)/td$

20. In Ingen-Hauz experiment the thermal conductivity $K$ and length $l$ of the rod upto which wax melts are related as :

(a) $\frac{K}{l}=$ constant (b) $\frac{K^2}{l}=$ constant (c) $\frac{K}{l^2}=$ constant (d) $Kl=$ constant

21. Two rods of length $l$ and $2l$, thermal conductivities $2K$ and $K$ are connected end of end. If cross sectional areas of two rods are equal, then equivalent thermal conductivity of the system is :

(a) $\left(\frac{5}{6}\right)K$ (b) $1{\cdot}5\,K$ (c) $1{\cdot}2\,K$ (d) $\left(\frac{8}{9}\right)K$

22. If the density of the material is $\rho$, specific that is $C_v$, diffusivity is $D$, then its thermal conductivity $K$ is : *(Rohilkhand 2003)*

(a) $K=\frac{C_v}{D\rho}$ (b) $K = C_v D\rho$ (c) $K=\frac{C_v D}{\rho}$ (d) $K=\frac{\rho C_v}{D}$

23. The ratio of thermal conductivity and electrical conductivity of a metal at a given temperature is constant. This law is called

(a) Ingen-Hauz law (b) Searle's law

(c) Planck's law (d) Wiedemann Franz law

24. The value of $\frac{K}{\sigma T}$ is

(a) a dimensionless constant (b) variable

(c) constant equal to $3\left(\frac{k}{e}\right)^2$ (d) constant equal to diffusivity ($D$)

**ANSWERS**

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

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# 5

# KINETIC THEORY OF GASES

## 5.1 Introduction

Of all states of matter the simplest is the gaseous state which is governed by simple and definite laws. A gas has certain properties, such as temperature, pressure, energy, etc. which are characteristic of the gas as a whole rather than of its individual molecules. When classical physical is applief to the mechanics of gases, the result is called the *kinetic theory of gases*. In the kinetic theory of gases, we tend to relate the microscopic behaviour of the individual gas molecules to the macroscopic properties of the gas as a whole.

The kinetic theory is a large and elegant subject and gives us the clearest and the most perfect illustration of the application of conception of molecules. It seeks to elucidate the behaviour of gases by theoretical means in terms of certain assumptions regarding its behaviour. The theory was developed by Bernoulli, in 1738, who for the first time, explained Boyle's law by molecular motions and is considered as the father of kinetic theory. The principal contributions that led to its establishment were made between 1850 and 1900 by Clausius, Maxwell, Boltzmann, Vander Waals, Jeans and Rayleigh which covered almost the entire field of different phenomena related with gases.

The kinetic theory is based on the following **fundamental assumptions.**

(i) A gas is composed for a large number of minute discrete particles *called molecules*, The molecules of a gas are thought to be rigid, perfectly elastic, solid speres, identical in all respects such as mass and size; but they differ in these from gas to gas.

(ii) The molecules within a container are in a state of *ceaseless chaotic motion* during which they move in all directions with all possible velocities.

(iii) The molecules in their motion *collide* with each other and with the walls of the container and thus their speeds and directions are changing continuously. It, however, does not affect the molecular density of the gas as the molecules do not accumulate at any place.

(iv) The bombardment of the container walls by the molecules gives rise to the phenomenon called *pressure* which is the rate of change of momentum per unit surface area of the walls.

(v) All collisions between molecules and with the walls are *perfectly elastic* so that there is no loss of kinetic energy in the collisions.

(vi) The molecules exert no forces on each other except when they collide which means that the energy of the gas is wholly *kinetic*.

(vii) The molecules traverse straight paths between collisions. The distance between any two consecutive collisions in called free *energy path* and the average distance travelled by a molecule between successive collisions is called the *mean free path*.

(viii) The time of collision is negligible as compared with the time taken to traverse the free path.

(ix) Since the molecules are small as compared with the distance between them, their volume may be considered to be negligible compared with the *total volume of the gas*.

(x) The *intermolecular* distance in a gas is much larger than that of a solid or liquid and the molecules of a gas are free to move in the entire space available to them.

## 5.2 Maxwell-Boltzmann's Law of Distribution of Velocities

If an individual molecule in its motion could be followed, many and large changes in its velocity would be observed as it moves about and collides with others. Thus, even if all molecules in a given sample of a pure gas had velocities exactly equal in absolute magnitude at any particular time, a few collisions would soon abolish their equality and a redistribution of both energy and velocity take place. Thus, a system of particles with uniform velocities would rapidly achieve a range of velocities from zero to infinity. It is necessary for many purposes to know the distribution of velocities in the final steady state of the gas when the distribution no longer changes by collisions.

The law of distribution of velocities was first guessed and partially established by Clark Maxwell, the proof of which by direct methods was given by Boltzmann. The law is known as the *Maxwell-Boltzmann's distribution law for the molecular velocities*. Maxwell and Boltmann, utilizing probability considerations, have in fact, shown that actual distribution of molecular velocities depends upon the temperature and molecular weight of a gas.

In order to derive the Maxwell-Boltzmann's law, let the gas molecules be assumed to obey the following conditions :

1. The number of gas molecules is large enough so that the number of molecules in any region in the same and that the molecules possess the same velocities in all directions.
2. The velocities along the three perpendicular co-ordinate axes are independent of each other.
3. The probability that any molecule selected at random has velocities lying between certain limits is purely a function of the velocity and of the limits considered.

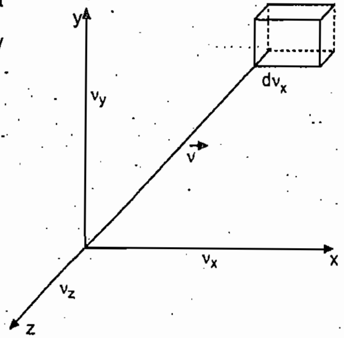
Let us now represent the molecules in a velocity diagram, with $O$ as the origin and $OX, OY, OZ$ as the co-ordinate axes (Fig. 5.1) Then any given velocity vector $\vec{v}$ can be decomposed into components $v_x, v_y$ and $v_z$ along $X$, $Y$ and $Z$ axes respectively. Thus the relation

$$v^2 = v_x^2 + v_y^2 + v_z^2 \qquad \ldots(1)$$

may be assumed to apply between the components of $\vec{v}$.

From assumption 3, it is obvious that the probability that a given molecule will have its velocity lying between $v_x$ and $v_a + dv_x$ is purely a function of the values of $v_x$ and $dv_x$ *i.e.*, it may be written $f(v_x)\,dv_x$ where $f(v_x)$ is a function of the velocity $v_x$. Further, since the velocities are similar and equivalent in all directions (assumption 1) the probability that the molecule will have velocity between $v_y$ and $v_y + dv_y$ is $f(v_y)\,dv_y$ and between $v_z$ and $v_z + dv_z$ is $f(v_z)\,dv_z$. Since the *probability of a composite event is equal to the product of the probabilities of individual events, provided that they are independent*, the probability that a molecule may have its velocity components lying between $v_x$ and $v_x + dv_x$, $v_y$ and $v_y + dv_y$, $v_z$ and $v_z + dv_z$ simultaneously, utilizing assumption 2, is given by

$$f(v_x)\,f(v_y)\,f(v_z)\,dv_x\,dv_y\,dv_z.$$



(Fig. 5.1)

The resultant velocity of the molecules is a single vector $\vec{v}$ as state above. According to assumption 3, the probability that this single velocity of value $v$ lies in the element of volume $dv_x\,dv_y\,dv_x$ is a function of $v$ and of $dv_x\,dv_y\,dv_z$ or more conveniently as $\phi(v^2)\,dv_x\,dv_y\,dv_z$ where $\phi$ denotes some function. On account of the isotropy of the gas, as regards the molecular velocity, we may write

$$f(v_x)\,f(v_y)\,f(v_z)\,dv_x\,dv_y\,dv_z = \phi(v^2)\,dv_x\,dv_y\,dv_z$$

or using eqn. (1)

$$f(v_x)\,f(v_y)\,f(v_z) = \phi(v_x^2 + v_y^2 + v_z^2). \qquad \ldots(2)$$

In order to solve this equation, we note that for a particular value of $v$ chosen, $\phi(v^2)$ is a constant *i.e.*, the differential of this quantity is equal to zero, hence $d[\phi(v^2)] = 0$, *i.e.*,

$$d[f(v_x)\,f(v_y)\,f(v_z)] = 0.$$

Differentiating it,

$$f'(v_x)\,dv_x f(v_y)\,f(v_z) + f'(v_y)\,dv_y f(v_x)\,f(v_z) + f'(v_z)\,dv_z f(v_x)\,f(v_y) = 0$$

Dividing by $f(v_x)\,f(v_y)\,f(v_z)$, we get

$$\frac{f'(v_x)}{f(v_x)}\,dv_x + \frac{f'(v_y)}{f(v_y)}\,dv_y + \frac{f'(v_z)}{f(v_z)}\,dv_z = 0. \qquad \ldots(3)$$

Now from eqn. (1), we have $v^2 = v_x^2 + v_y^2 + v_z^2$, which on differentiation for a fixed (constant) value of $v$ gives

$$v_x\,dv_x + v_y\,dv_y + v_z\,dv_z = 0.$$

Multiplying eqn. (3) by an arbitrary constant $\beta$ and adding the resultant to equation. (2)

$$\left(\frac{f'(v_x)}{f(v_x)} + \beta v_x\right)dv_x + \left(\frac{f'(v_y)}{f(v_y)} + \beta v_y\right)dv_y + \left(\frac{f'(v_z)}{f(v_z)} + \beta v_z\right)dv_z = 0. \qquad \ldots(4)$$

Now since by assumption 2 the velocity components are independent of each other, equation (4) can be satisfied only if each of the term is separately equal to zero. Therefore

$$\left.\begin{aligned} \frac{f'(v_x)}{f(v_x)}\,dv_x &= -\beta v_x\,dv_x \\ \frac{f'(v_y)}{f(v_y)}\,dv_y &= -\beta v_y\,dv_y \\ \frac{f'(v_z)}{f(v_z)}\,dv_z &= -\beta v_z\,dv_z \end{aligned}\right\} \qquad \ldots(5)$$

Integrating the first equation of equations (5) with respect to $v_x$ we get

$$\log f(v_x) = -\frac{\beta v_x^2}{2} + \log a$$

where $a$ is some constant

or $$\log \frac{f(v_x)}{a} = -\frac{\beta v_x^2}{2}$$

or $$f(v_x) = a e^{-(\beta v_x^2)/2} = a e^{-b v_x^2} \qquad \ldots(6)$$

where $b = \dfrac{\beta}{2}$ is a constant.

Similarly writing for other two components

$$f(v_y) = ae^{-b v_y^2} \qquad \ldots(7)$$

and

$$f(v_z) = a\, e^{-bv_z^2} \qquad \ldots(8)$$

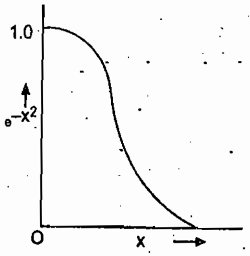
From eqn. (6), (7) and (8) we, therefore, have

$$f(v_x) f(v_y) f(v_z) = a^3 e^{-b(v_x^2+v_y^2+v_z^2)} \qquad \ldots(9)$$

Thus $f(v_x)\, dv_x$, the probability that a molecule has the velocity between $v_x$ and $v_x + dv_x$ is given by

$$f(v_x)\, dv_x = ae^{-bv_x^2} dv_x \qquad \ldots(10)$$

This distribution law expressed in eqn. (10) is represented graphically in fig. 5.2 where $e^{-x^2}$ is plotted against $x$. Thus $bv_x^2$ has been put equal to $x^2$. The maximum ordinate of the curve corresponds to $v_x = 0$ and has the value $a$ which has been put equal to 1 in fig. 5.2.



(Fig. 5.2)

**Evalution of constants 'a' and 'b'.** Let $n$ be the number of molecules per unit volume of the gas with all possible velocities from $-\infty$ to $+\infty$. Then the number of molecules per unit volume with velocity components between $v_x$ and $v_x + dv_x$, $v_y$ and $v_y + dv_y$, $v_z$ and $v_z + dv_z$ is $n\, f(v_x) f(v_y) f(v_z)\, dv_x\, dv_y\, dv_z$. Hence

$$\iiint_{-\infty}^{+\infty} n\, f(v_x) f(v_y) f(v_z)\, dv_x\, dv_y\, dv_z = n.$$

Substituting the values of the function from eqn. (9), we get

$$\iiint_{-\infty}^{+\infty} a^3 e^{-b(v_x^2+v_y^2+v_z^2)} dv_x\, dv_y\, dv_z = 1. \qquad \ldots(11)$$

The value of the definite integral of the form $\int_{-\infty}^{+\infty} e^{-bv_x^2} dv_x$ is $\sqrt{\left(\frac{\pi}{b}\right)}$. Substituting the values of such integrals in eqn., (11), we have

$$a^3 \left(\frac{\pi}{b}\right)^{3/2} = 1.$$

or

$$a^3 = \left(\frac{b}{\pi}\right)^{3/2}$$

or

$$a = \sqrt{\left(\frac{b}{\pi}\right)} \qquad \ldots(12)$$

To determine $b$ let us first calculate the pressure exerted by the gas on the walls of the enclosure. For it, let us consider a perfact gas enclosed in a vessel and take the $X$-axis to be perpendicular to one surface of the enclosure. Then a molecule moving with a velocity component $v_x$ will collide with this surface and will be reflected with a velocity $-v_x$ after collision. Hence the change in momentum suffered by the molecule during collision is $2mv_x$. The other two components viz. $v_y$ and $v_z$ suffer no change, hence they contribute nothing to the pressure and can be neglected. Now pressue is equal to the change in momentum suffered by the molecule striking per unit area of the wall per second and hence it is equal to $2mv_x$ multiplied by the number of collisions on the surface in unit time. If $n_{v_x}$ is the number of molecules per unit volume having the velocity $v_x$, the number of impacts on an area $\delta A$ in time $\delta t$ must be equal to $n_{v_x} v_x\, \delta t\, \delta A$. Hence the pessure $P$ on the wall, averaged through the time interval $\delta t$ is given by

$$P\, \delta A\, \delta t = \sum_{v_x=0}^{\infty} 2mv_x \times n_{v_x} v_x\, \delta t\, \delta A$$

or

$$P = 2m \sum_{0}^{\infty} n_{v_x} v_x^2. \qquad \ldots(13)$$

The sign of summation has been put because the pressure is caused by all molecules having a positive $X$-component of velocity which can have value ranging from 0 to $\infty$.

Now the number of molecules per unit volume having the velocity component lying between $v_x$ and $v_x + dv_x$ is given in accordance of eqn.(10) to be

$$n_{v_x} = f(v_x) = nae^{-bv_x^2}$$

or

$$n_{v_x} = n\sqrt{\left(\frac{b}{\pi}\right)}\, e^{-bv_x^2}$$

Substituting this value of $n_{v_x}$ in eqn. (13) and replacing the sign of summation by the sign of integration we get

$$P = 2m \int_0^{\infty} n \sqrt{\left(\frac{b}{\pi}\right)}\, e^{-bv_x^2} v_x^2\, dv_x$$

$$= 2mn \sqrt{\left(\frac{b}{\pi}\right)} \int_0^{\infty} e^{-bv_x^2} v_x^2\, dv_x$$

$$= 2mn \sqrt{\left(\frac{b}{\pi}\right)} \cdot \frac{1}{4} \sqrt{\left(\frac{\pi}{b^3}\right)} = \frac{mn}{2b}$$

because $\int_0^{\infty} e^{-bv_x^2} v_x^2\, dv_x = \frac{1}{4}\sqrt{\left(\frac{\pi}{b^3}\right)}$.

But $P$ is also equal to $nkT$ where $k$ is the Boltzmann constant. Therefore

$$nkT = \frac{mn}{2b}$$

or

$$b = \frac{m}{2kT} \qquad \ldots(14)$$

Substituting this value of $b$ in eqn. (12), we get

$$a = \sqrt{\left(\frac{b}{\pi}\right)} = \sqrt{\left(\frac{m}{2\pi kT}\right)}. \qquad \ldots(15)$$

Thus, the number $dn$ of molecules having velocity component lying between $v_x$ and $v_x + dv_x$, $v_y$ and $v_y + dv_y$, and $v_z$ and $v_z + dv_z$ is given by

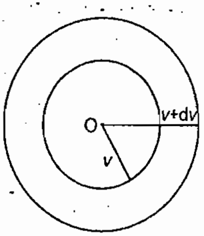
$$dn = nf(v_x) f(v_y) f(v_z)\, dv_x\, dv_y\, dv_z$$

$$= na^3 e^{-b(v_x^2+v_y^2+v_z^2)} dv_x\, dv_y\, dv_z \qquad \ldots(16)$$

$$= n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2}\left(\frac{v_x^2+v_y^2+v_z^2}{kT}\right)} dv_x\, dv_y\, dv_z \qquad \ldots(17)$$

This is *Maxwell's distribution law.*

**Number of molecules having velocity within $v$ and $v + dv$.**



(Fig. 5.3)

Expression (16) can be used to deduce the number of molecules having velocities lying between $v$ and $v + dv$. Let all such molecules lie between two concentric spheres of radii $v$ and $v + dv$ with 0 as the common centre, the starting point of all molecules (fig. 5.3). Then volume of annulus

$$= \frac{4}{3}\pi\left[(v+dv)^3 - v^3\right] = 4\pi v^2\, dv \qquad \text{(neglecting smaller terms).}$$

This is the same at the so called *velocity volume* $dv_x\, dv_y\, dv_z$ of equation (16).

Hence substituting $4\pi v^2\, dv$ for $dv_x\, dv_y\, dv_z$ and putting $v^2 = v_x^2 + v_y^2 + v_z^2$ in equation (16), we get

$$n\,(v)\, dv = 4\pi\, na^3\, e^{-dv^2}\, v^2\, dv \qquad \ldots(18)$$

or

$$\frac{n\,(v)\, dv}{n} = 4\pi\, a^3\, e^{-bv^2}\, v^2\, dv. \qquad \ldots(19)$$

This is the required *Maxwell-Bolzmann's distribution law for molecular velocities.* In this expression $n\,(v)\, dv$ is the number of molecules out of a total $n$ having velocities lying between $v$ and $v + dv$.

**Graphical representation :** If we put in equation (18) $bv^2 = x^2$, then

$$n\,(v)\, dv = 4\pi\, na^3\, e^{-x^2} \cdot \frac{x^2}{b} \cdot \frac{x\, dx}{bv}$$

$$= 4\pi n \left(\frac{b}{\pi}\right)^{3/2} e^{-x^2} \cdot \frac{x^3 dx}{b^2} \cdot \frac{\sqrt{b}}{x}$$

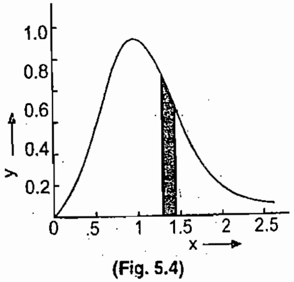
$$= 4n\pi^{-1/2} e^{-x^2}\, x^2\, dx, \qquad \ldots(20)$$

Which helps of represent the law graphically Fig. 4.4 given the plot of the function

$$y = 4\pi^{-1/2}\, e^{-x^2}\, x^2 \text{ against } x.$$

The number of molecules $n\,(v)\, dv$ having velocities lying between $x$ and $x + dx$ is proportional to the shaded area. The total area between the curve and the $x$-axis gives the total number of molecules having velocities between zero and infinity. Thus the molecular velocities range from zero to infinity.

From this plot it may be seen that the probability of a molecule being motionless an any instant is extremely small. It is zero when $x = 0$ or $x = \infty$. For velocities greater that zero, the probability increases which passes passes through the maximum and then falls away towards zero again for very high velocities. Thus, both, very high and very low, velocities are highly improbable. The probability corresponding to $x = 1$ is maximum while it is considerably small for $x = 2$ or $x = \frac{1}{2}$. The velocity for which the curve is maximum is the *most probable velocity.* If we were to pick molecules at random, this velocity would be found most often.



(Fig. 5.4)

## SOLVED EXAMPLES

**Ex. 1.** *Given the Maxwellian distribution function,*

$$n\,(v)\, dv = 4\pi n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, v^2\, dv.$$

*Show that the fraction of molecules having energy between E and E + dE is given by*

$$f\,(E)\, dE = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2} e^{-E/kT}\, E^{1/2}\, dE$$

**Solution.** Maxwell's distribution law is

$$n\,(v)\, d\,v = 4\pi n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, v^2\, dv.$$

We know $E = \frac{1}{2}mv^2$

or

$$v = \left(\frac{2E}{m}\right)^{1/2}.$$

∴

$$dv = \frac{1}{2}\left(\frac{2E}{m}\right)^{-1/2}\left(\frac{2dE}{m}\right).$$

Here $dv$ is the range in speed corresponding to the range in energy $dE$. Hence if $n\,(E)\, dE$ represents the number of molecules in the energy range $E$ and $E + dE$, we must have

$$n\,(v)\, dv = n\,(E)\, dE$$

$$n\,(E)\, dE = 4\pi n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m\,(2E/m)}{2kT}} \cdot \frac{2E}{m}\frac{1}{2}\left(\frac{2E}{m}\right)^{-1/2}\left(\frac{2dE}{m}\right)$$

$$= 2\pi n\left(\frac{1}{\pi kT}\right)^{3/2} e^{-E/kT} \cdot E^{1/2}\, dE$$

The fraction (or probability) of molecules having energy lying between $E$ and $E + dE$ is the given by

$$f\,(E)\, dE = \frac{n\,(E)\, dE}{n} = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2} e^{-E/kT} \cdot E^{1/2}\, dE.$$

**Ex. 2.** *Using Maxwell-Boltzmann law, show that the fraction of molecules within the momentum range p and d + dp is given by*

$$f\,(p)\, dp = 4\pi\left(\frac{1}{2\pi mkT}\right)^{3/2} \cdot e^{-p^2/2mkT} \cdot p^2\, dp.$$

**Solution.** According to Maxwell-Boltzmann law, the fraction of molecules in the velocity range $v$ and $v + dv$ is

$$\frac{n\,(v)\,.\,dv}{n} = f\,(v)\, dv = 4\pi a^3 e^{-bv^2}\, v^2\, dv.$$

Now since $p = mv$, so that $v = \frac{p}{m}$

and

$$dp = m\, dv.$$

∴

$$f\,(p)\, dp = 4\pi\, a^3\, e^{-b\,(p^2/m^2)} \cdot \left(\frac{p^2}{m^2}\right)\frac{dp}{m}$$

$$= \frac{4\pi a^3}{m^3} e^{-bp^2/m^2} \cdot p^2\, dp.$$

Substituting the values of constants,

$$a = \sqrt{\left(\frac{m}{2\pi k T}\right)} \text{ and } b = \frac{m}{2kT}$$

$$f(p)\, dp = \frac{4\pi}{m^3}\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mp^2}{2m^2kT}}\, p^2\, dp$$

$$= 4\pi\left(\frac{1}{2\pi mkT}\right)^{3/2} e^{-p^2/2mkT}\, p^2\, dp.$$

## 5.3 Experimental Test of Maxwell's Law

Maxwell-Boltzman law of distribution of molecular velocities was put to experimental test and found to be true. Till 1920, only the indirect evidence was available to establish the truth of the law while now several direct experimental proofs are at hand. We shall discuss here a few of them :

**1. From the finite width of spectral lines :** The Maxwell-Boltzman law can be *indirectly* verified by a study of the width of a spectral line. Theroetically every monochromatic beam of light should be represented by a line of no width (geometrical line) but the Doppler effect causes a broadening of otherwise narrow spectral lines. Thus, every spectral line has a finite width, because of the fact that no radiating atom is absolutely at rest but moving in all directions with all possible velocities. The light emitted by an atom would be represented by a single line only if the atom is at rest but according to kinetic theory they are moving to and fro, the distribution of velocities being given by Maxwell's law. Hence if the frequency of light emitted by an atom at rest is $\nu_0$, that emitted by an atom approaching the observer with a velocity $v$ would be changed by Doppler effect to $\nu_0\left(1+\frac{v}{c}\right)$, where $c$ is the velocity of light. Since $v$ varies from 0 to ∞, the spectral line should theoretically have all frequencies or be of infinite width. But according to Maxwell's law very high velocities are extremely rare and hence their contribution to intensity is extremely small. We can now find the distribution of intensity in the line.

According to Maxwell's law the number of molecule having their velocity lying between $v$ and $v + dv$ is given by

$$n(v)\, dv = n_0\, a e^{-mv^2/2kT}\, dv,$$

where $a$ is a constant.

These particles emit light of frequency $\nu_0\left(1+\frac{v}{c}\right)$ and the intensity of spectral line is proportional to the number of the particles. Therefore,

$$I = I_0\, e^{-mv^2/2kT}.$$

where $I_0$ is the intensity of the central line.

If $\lambda_0\left(=\frac{\nu}{c}\right)$ is the wave-length of the central line and $(\lambda_0 - x)$ of that corresponding to the frequency $\nu_0\left(1+\frac{v}{c}\right)$, then

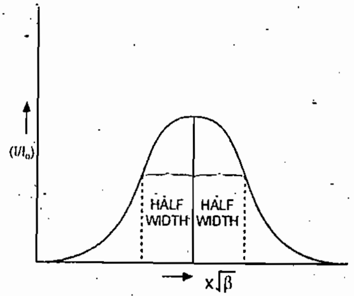
$$\lambda_0 - x = \frac{c}{\nu_0\left(1+\frac{v}{c}\right)} = \frac{c}{\nu_0}\left(1-\frac{v}{c}\right) = \lambda_0 - \frac{v}{\nu_0}$$

or $$x = \frac{v}{\nu_0} = \lambda_0 \cdot \frac{v}{c} \qquad \left[\because\ \lambda_0 = \frac{c}{\nu_0}\right]$$

If $I_x$ is the intensity at a distance $x$ (measured in wave-length units) from the central line, then

$$I_x = I_0\, e^{-\beta x^2}.$$

where $\beta = \frac{m\nu_0^2}{2kT}$



(Fig. 5.5)

The distribution of intensity in the line about the centre is shown in Fig. 5.5. The distance on the wavelength scale on either side, where $I_x = \frac{1}{2} I_0$ is known as *half width* and is denoted by ω. From the above equation we may write

$$\frac{I_0}{I_x} = e^{\beta\omega^2} = 2$$

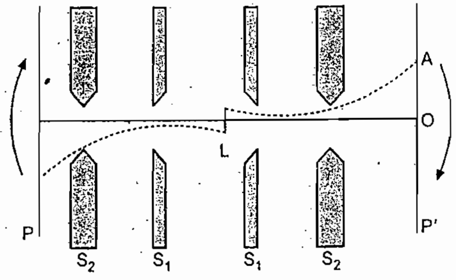
or $$\omega^2 = \frac{\log 2}{\beta} = \frac{\log 2}{m\nu_0^2/2kT} = \frac{(2\log 2)\, kT}{mc^2}\lambda_0^2$$

or $$\frac{\omega}{\lambda_0} = \frac{1}{c}\sqrt{\left(\frac{(2\log 2)\, kT}{m}\right)} = \frac{\sqrt{\{(2\log 2)\, R\}}}{c}\sqrt{\left(\frac{T}{A}\right)} \quad \text{(Since } R = Nk\text{)}$$

where $A$ is the atomic weight.

Thus, the half width is inversely proportional to atomic weight of the element *i.e.*, it is more for lighter elements. It has actually been found to be so. Hydrogen lines are always found to be very much broad and diffuse. On the other hand spectral lines due to heavy elements like Ag and Cd are found to be quite sharp thus, leading to an experiment verification of the Maxwell's law of distribution of velocities.

**2. Stern's Experiment :** The first *direct experimental proof of Maxwell's law* was given by Stern. Fig. 5.6 depicts the principle of his experiment, where $L$ is a platinum wire coated with silver and represented perpendicular to the plane of the paper. The wire is heated by an electric current and consequently it emits atomic silver in all directions. The slits $S_1$ and $S_2$ which are parallel to the platinum wire, define a stream of silver which condenses on the plates $P$ and $P'$. The whole apparatus is enclosed in a highly evacuated glass vessel so that the silver atoms may not suffer any collisions in space. The slits $S_1$, $S_2$ and the plates $P$, $P'$ are rotated together as a rigid system about the wire $L$ as axis in a clockwise direction as shown. Had the plates been at rest, the stream would have traversed along $LO$ forming a deposit at $O$ but when the system is rotating at a high speed, as shown, the deposit is formed at a point $A$ above $O$. Fast moving molecules or atoms will condense nearer to $O$, than the slower

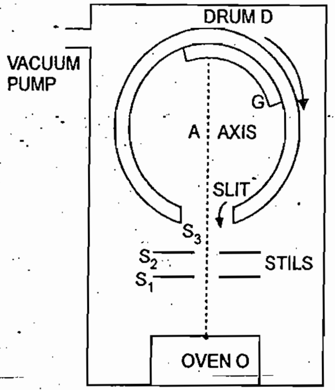


(Fig. 5.6)

ones. A velocity spectrum af silver will thus be obtained. The relative intensity of the deposit can be measured by means of a microphotometer and then the ratio of number of molecules with different velocities can be deduced and Maxwell-Boltzmann's law tested.

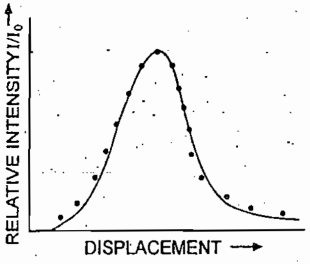
The results of Stern were however, not quite satisfactory because of the difficulty in retaining vacuum in the vessel as the spindle of the rotating system had to project outside the vessel for coupling it to the driving motor, As a result the Maxwellian law could be verified about 15%.

**3. Zartman and Ko's Experiment :** One of the most direct experimental verification of a Maxwelling law was obtained by Zartman & Ko, in 1930. It is a modification of the Stern's method and is as follows : As shown fig. 5.7, a beam of bismuth molecules emerging from a slit in the oven $O$ into an evacuated region is collimated by the slits $S_1$ and $S_2$. Above the slits is a cylindrical drum $D$ which is rotated in the vaccum about axis $A$ by a high speed motor housed in the same casing. A slit $S_3$ along one side of the drum has to be in a particular position to enable the beam of molecules to enter it. If the drum is stationary so that the beam can admit, it travels across a diameter of the drum and strikes the glass plates $G$ mounted on the inside surface of the drum opposite the slit $S_3$. But as the drum is rotated at a constant angular velocity, short bursts of molecules are admitted on each rotation. Since the speeds of the molecules vary, some cross the diameter quickly while some take much more time. The slower molecules reach $G$ later than the faster ones. Less in the speed of a molecule, the farther of the left is the point where $G$ is struck *i.e.*, the faster molecules hit $G$ more to the right. The bismuth molecules stick to the glass plate where they strike and thus a deposit whose density varies across $G$ according to the velocity distribution of the molecules in the oven, is obtained. In this way the distribution of velocities is translated by the apparatus into a distribution in space around the inside of the drum as indicated by the variation in the darkening of the glass when the bismuth is deposited. The thickness of the deposit *i.e.*, the density distribution is measured with a microphotometer.



(Fig. 5.7)

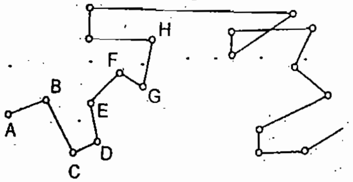
The result obtained by Zartman are shown in Fig. 5.8 where the ordinate represents the intensity of deposit and the abscissa the displacement from the zero mark or the velocity of the corresponding molecule. The points in the diagram are the observed densities of the deposit and the line as calculated on the assumption that the velocities of the molecules are distributed according to Maxwell's law. As is seen, the agrement between the theoretical curve and the observed points is excellent showing thereby that an accurate test of Maxwell's law is possible by this method.



(Fig. 5.8)

## 5.4 Mean Free Path

According to kinetic theory, the molecules of a gas are moving with very large velocities, even at ordinary temperatures. There is no force to restrain their motion and hence the gaseous mass contained in a vessel should disappear in no time. But it is contrary to actual observations as we are all aware that the top of a cloud of smoke holds together for hours. Thus there was a serious objection against the assumption that the molecules of a gas move with large rectilinear velocities; hence there must be some factor which prevents the free escape of particles. The difficulty was solved by Clausius by ascribing to the molecules a finite though very small size and by introducing the idea of collision between the molecules. If molecules were truely geometrical points, no collision would take place between them. Actual molecules are, however, of finite size, rigid, perfectly elastic spheres free from mutual force action. They make frequent collisions with each other and change the magnitude and direction of their velocities. As the molecules exert no force on one another except during collisions, they move in straight lines with uniform velocity between two successive collisions, this straight line path being called the *free path*. Thus the path of the centre of mass of a small field molecules must be an irregular zig-zag having at each corner a collision with another molecules and consisting of straight free paths between them as shown in Fig. 5.9. Thus, a molecule starting from $A$ moves along $AB$, suffers a collision at $B$ with another molecule when the direction as well as magnitude of its velocity is changed and it moves along $BC$. After travelling a distance $BC$, it again suffers a collision at $C$ and moves along $CD$ and so on. $AB, CD, DE$ etc., are all known as *free paths* and their individual lengths vary widely. If we follow a molecule until it has traversed a great many free paths, the average of their lengths will have a definite value which is called the *mean free path* and is denoted by $\lambda$.



(Fig. 5.9)

Thus, *the mean free path is the average distance through with a molecule can travel through a gas without colliding with another molecule.* It may be called the *average free-~~run between two collisions. It is~~* then a statistical quantity and the value to some extent, will depend upon the method employed in striking an average. Thus there is a certain arbitariness in our standard in defining a mean free path. However, if a reference is made to a group of molecules instead of a single one and a mean value of all the free paths that are executed in a given time by all the molecules in a given volume is taken we shall get a definite quantity provided the time and volume are not too small. Thus, if $\lambda_1, \lambda_2, \lambda_3, \ldots \lambda_N$ are the successive free paths traversed in the total time $t$, then

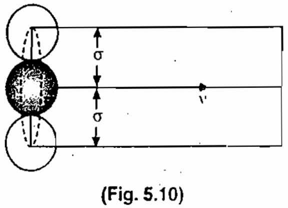
$$\lambda_1 + \lambda_2 + \lambda_3 + \ldots + \lambda_N = \bar{v}t,$$

where $\bar{v}$ is the average speed of molecule and $N$ the number of collisions suffered (*i.e.*, the free **path traversed**) in time $t$. If $\lambda$ is the mean free path, we must have

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \ldots \lambda_N}{N} = \frac{\bar{v}t}{N} = \frac{S}{N}$$

where $S$ is the total distance travelled in $N$ collisions.

**Expression for mean free path :** Let us consider a gas possessing $n$ molecules per unit volume. Let us assume only a *single molecule traversing the gas with velocity $v$ and suppose other molecules to be at rest.* The moving molecule will collide with all such molecules whose centres lie within a distance $\sigma$ from its centre, $\sigma$ being the molecular diameter as shown in fig. 5.10. The space thus traversed in a second is a cylinder of base $\pi\sigma^2$ and height $v$ and hence of volume $\pi\sigma^2 v$. The interior of the cylinder will enclose on the average $\pi\sigma^2 vn$ molecules suffering impact. This expression also represents the number of collisions $N$ made by the moving molecule per unit time *i.e.*,



(Fig. 5.10)

$$N = \pi\sigma^2 vn.$$

As the distance traversed by the molecule in one second is its velocity $v$, the mean free path is given by

$$\lambda = \frac{S}{N} = \frac{v}{\pi\sigma^2 vn} = \frac{1}{\pi\sigma^2 n}. \qquad \ldots(1)$$

This expression, however, does not represent the actual state of affairs and is generally in error numerically because it assumes that only one molecule under consideration is moving while all the other molecules standstill to await its coming. As matter of fact the molecules possess all posible velocities, the distribution of velocities amont them being given by Maxwell's distribution law. Hence, if a molecule moves with an absolute velocity $v$, in moving this distance $v$ it will collide with $\pi\sigma^2 r\, n$ other molecules where $r$ represents the mean relative velocity of the molecules with respect to the others. Therefore, the mean free path of that molecule is given by

$$\lambda = \frac{\text{Total distance traversed in one second}}{\text{No of collisions suffered by the mole. in one second}} = \frac{v}{\pi\sigma^2 r\, n} \qquad \ldots(2)$$

But according to Maxwell's law, the particular molecule under consideration may have all possible velocities and hence if $\bar{v}$ is the average velocity of the molecule and $r$ the mean relative velocity of all molecules with respect to all other, the mean free path averaged over molecules of all velocities is

$$\lambda = \frac{\bar{v}}{\pi\sigma^2 r\, n}. \qquad \ldots(3)$$

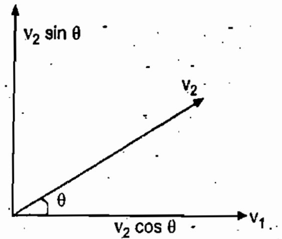
Let us now suppose that the particular molecule under consideration moves with velocity $v_1$. Its relative velocity with respect to another molecule of velocity $v_2$ making an angle θ with it (Referring to fig. 4.11) or the relative velocity of approach between two molecules, is given by

$$r_2 = (v_1 - v_2 \cos\theta)\,\mathbf{i} - (0 - v_2 \sin\theta)\,\mathbf{j}$$

or $$|\, r_2 \,| = \sqrt{(v_1 - v_2 \cos\theta)^2 + (v_2 \sin\theta)^2}$$

or $$r_2 = (v_1^2 + v_2^2 - 2v_1 v_2 \cos\theta)^{1/2} \qquad \ldots(4)$$

Now all the directions for velocity $v_2$ are equally probable. The probability that it lies within the solid angle lying between θ and $\theta + d\theta$ is $\frac{1}{2}\sin\theta\, d\theta$*. Hence the average relative velocity (*i.e.*, average value of $r_2$) is given by



(Fig. 5.11)

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* Surface area of ring lying between θ and $\theta + d\theta$

$$= 2\pi R \sin\theta\, R\, d\theta = 2\pi R^2 \sin\theta\, d\theta$$

Solid angle subtended at the centre O by this ring

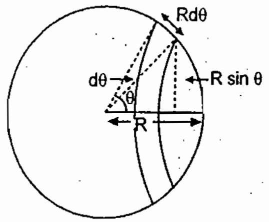
$$= \frac{\text{surface area}}{\text{Square of the distance}} = \frac{2\pi R^2 \sin\theta\, d\theta}{R^2}$$

$$= 2\pi \sin\theta\, d\theta.$$

Solid angle subtended at O by the entire sphere $= \frac{4\pi R^2}{R^2} = 4\pi$

Hence probability of lying between the solid angle lying between θ and $\theta + d\theta$

$$= \frac{2\pi \sin\theta\, d\theta}{4\pi} = \frac{1}{2}\sin\theta\, d\theta.$$



(Fig. 5.12)

$$\bar{r}_2 = \int_0^\pi r_2 \frac{1}{2} \sin\theta\, d\theta = \frac{1}{2}\int_0^\pi (v_1^2 + v_2^2 - 2v_1 v_2 \cos\theta)^{1/2} \sin\theta\, d\theta.$$

Putting $v_1^2 + v_2^2 - 2v_1 v_2 \cos\theta = x$ so that $2v_1 v_2 \sin\theta\, d\theta = dx$ or $\sin\theta\, d\theta = \frac{dx}{2v_1 v_2}$

Again substituting $x$ in terms of θ, we get

$$\bar{r}_2 = \frac{1}{2}\int_{x_1}^{x_2} \frac{x^{1/2}\, dx}{2\, v_1 v_2}$$

$$= \frac{1}{2\,(2\, v_1\, v_2)} \left[ \frac{x^{3/2}}{3/2} \right]_{x_1}^{x_2}$$

$$\bar{r}_2 = \frac{1}{2 \times 2v_2\, v_2 \times \frac{3}{2}} \times \left[ (v_1^2 + v_2^2 - 2v_1 v_2 \cos\theta)^{3/2} \right]_0^\pi$$

$$= \frac{1}{6v_1 v_2} [v_1^2 + v_2^2 + 2v_1 v_2]^{3/2} - (v_1^2 + v_2^2 - 2v_1 v_2)^{3/2}]$$

$$= \frac{1}{6v_1 v_2} [(v_1 + v_2)^3 - (v_1 - v_2)^3]. \qquad \ldots(5)$$

The value of $\bar{r}_2$ depends on whether $v_1 > v_2$ or $v_2 > v_1$, for if $v_1 > v_2$, the solution gives a positive value for $(v_1 - v_2)$ and hence *when* $v_1 > v_2$

$$\bar{v}_2 = \frac{1}{6v_1 v_2} (v_1^3 + v_2^3 + 3v_1^2 v_2 + 3v_2^2 v_1) - (v_1^3 - v_2^3 + 3v_2^2 v_1 - 3v_1^2 v_2)$$

$$= \frac{1}{6v_1 v_2} [2v_2^3 + 6v_1^2 v_2]$$

$$= \frac{3v_1^2 + v_2^2}{3v_1} \qquad \ldots(5a)$$

If $v_2 > v_1$, $(v_1 - v_2)$ becomes negative, but the relative velocity given by (4) is always positive. Hence the signs are reversed and it is necessary to write $(v_2 - v_1)^3$ instead of $(v_1 - v_2)^3$. Thus

When $v_2 > v_1$

$$\bar{r}_2 = \frac{1}{6v_1 v_2} [(v_1^3 + v_2^3 + 3v_1^2 v_2 + 3v_2^2 v_1) - (v_2^3 - v_1^2 + 3v_1^2 v_2 - 3v_1 v_2^2)]$$

$$= \frac{3v_2^2 + v_1^2}{3v_2} \qquad \ldots(5b)$$

Now the probability that their exit molecules of velocity $v_2$ in the range $v_2$ and $v_2 + dv_2$ is

$$4\pi a^3 e^{-bv_2^2} \cdot v_2^2\, dv_2.$$

Therefore, the average relative velocity of the molecule with velocity $v_1$ with respect to all other is

$$r_1 = \int_0^\infty \bar{r}_2 \cdot 4\pi a^3 e^{-bv_2^2} \cdot v_2^2\, dv_2. \qquad \ldots(6)$$

But $\bar{r}_2$ has two different values given by (5*a*) and (5*b*). Hence

$$r_1 = \int_0^{v_1} \frac{3v_1^2 + v_2^2}{3v_1} \cdot 4\pi a^3 e^{-bv_2^2} \cdot v_2^2\, dv_2 + \int_{v_1}^\infty \frac{3v_2^2 + v_1^3}{3v_2} \cdot 4\pi a^3 \cdot e^{-bv_2^2} v_2^2\, dv_2.$$

The integration between 0 and $v_1$ of the $\frac{3v_1^2+v_2^2}{3v_1}$ term applies to values of $v_2 < v_1$ and the integration from $v_1$ to $\infty$ of the $\frac{3v_2^2+v_1^2}{3v_2}$ term applies to values of $v_2 > v_1$.

This value of $r_1$ must next be multiplied by the probability of existence of molecules having the velocity $v_1$ which is

$$4\pi a^3 e^{-bv_1^2} \cdot v_1^2\, dv_1$$

and integrated from 0 to $\infty$ to take account of the variations in the velocity $v_2$. Thus the average velocity $r$ of any molecule with respect to all others is space is

$$r = \int_0^\infty 4\pi a^3 e^{-bv_1^2} v_1^2\, dv_1 \cdot \int_0^{v_1} \frac{3v_1^2+v_2^2}{3v_1} \cdot 4\pi a^3 e^{-bv_2^2} v_2^2\, dv_2$$
$$+ \int_0^\infty 4\pi a^3 e^{-bv_1^2} v_1^2\, dv_1 \int_{v_1}^\infty \frac{3v_2^2+v_1^2}{3v_2} \cdot 4\pi a^3 e^{-bv_2^2} v_2^2\, dv_2$$

or
$$r = 16\pi a^6 (I_1 + I_2)$$

where
$$I_1 = \int_0^\infty v_1^2 e^{-bv^2}\, dv_1 \int_0^{v_1} \frac{3v_1^2+v_2^2}{3v_1} \cdot v_2^2 e^{-bv_2^2}\, dv_2$$

and
$$I_2 = \int_0^\infty v_1^2 e^{-bv_1^2}\, dv_1 \int_{v_1}^\infty \frac{3v_2^2+v_1^2}{3v_2} \cdot v_2^2 e^{-bv_2^2}\, dv_2.$$

On integration it will be seen that $I_2$ is of the same form as $I_1$ and

$$I_1 = I_2 = \frac{1}{8\sqrt{2}}\left(\frac{\pi}{b^7}\right)^{1/2}$$

Hence,
$$r = 16\pi^2 a^6 \times \frac{2}{8\sqrt{2}}\left(\frac{\pi}{b^7}\right)^{1/2}$$
$$= 16\pi^2 \sqrt{\left(\frac{b}{\pi}\right)^6} \times \frac{1}{4\sqrt{2}}\left(\frac{\pi}{b^7}\right)^{1/2} \qquad \left[\therefore\ a = \sqrt{\frac{b}{\pi}}\right]$$
$$= \frac{4}{\sqrt{(2b\pi)}} = \frac{3}{\sqrt{\left(2\pi \cdot \frac{m}{2kT}\right)}} = 4\sqrt{\left(\frac{kT}{m\pi}\right)} \qquad \left[\because\ b = \frac{m}{2kT}\right]$$
$$= \sqrt{\left(2 \times \frac{8kT}{m\pi}\right)} = \bar{v}\sqrt{2}, \qquad \left[\because\ \bar{v} = \sqrt{\left(\frac{8kT}{m\pi}\right)}\right]$$

Substituting the value of $r$ in eqn. (3), we get the expression for mean free path

$$\lambda = \frac{\bar{v}}{\pi\sigma^2 n\bar{v}\sqrt{2}} = \frac{1}{\sqrt{2}\,\pi\sigma^2 n} \qquad \ldots(7)$$

## 5.5 Order and Variation of Mean Free Path

In order to calculate the *order of magnitude of mean free path* λ, let us introduce a reference length $l$ defined by the condition that a cube of side $l$ contains on the average just one molecule. Then the number of molecules per unit volume $n = \frac{1}{l^3}$ and the approximate expression of mean free path

$$\lambda = \frac{1}{n\pi\sigma^2} = \frac{1}{\frac{1}{l^3}\pi\sigma^2}$$

or
$$\frac{\lambda}{l} = \frac{8}{\pi}\left(\frac{l}{\sigma}\right)^2 \qquad \ldots(1)$$

Now the radius of hydrogen atom *i.e.*, first Bohr orbit is of the order of $0{\cdot}5 \times 10^{-8}$ cm. Estimating that the radius of a hydrogen molecules is double that of an atom, we find that the molecular diameter is given by

$$\sigma = 2\,(2 \times 0{\cdot}5 \times 10^{-8}) = 2 \times 10^{-8}\ \text{cm.} \qquad \ldots(2)$$

The number of molecules per unit volume can be found from Avogardo number. At 0°C and 1 atmosphere pressure it is $2{\cdot}8 \times 10^{19}/\text{cm}^3$. Thus

$$l^3 = \frac{1}{n} = \frac{1}{2{\cdot}8 \times 10^{19}} = \frac{1}{28} \times 10^{-18}\ \text{cm}^2$$

or
$$l \approx \frac{1}{3} \times 10^{-6}\ \text{cm.} \qquad \ldots(3)$$

Combining eqns. (2) and (3) we have

$$\frac{l}{\sigma} = \frac{\frac{1}{3} \times 10^{-6}}{2 \times 10^{-8}} = \frac{50}{3} \qquad \ldots(4)$$

Putting this value of $l/\sigma$ in eqn. (1), we get

$$\frac{\lambda}{l} = \frac{8}{\pi}\left(\frac{50}{3}\right)^2 = \frac{10^4}{36\pi} \approx 100. \qquad \ldots(5)$$

From a survey of equation (4) and (5), the following proportion can be set by

$$\lambda : l : \sigma = 10^4 : 10^2 : 6.$$

Thus, under present assumptions, *the mean free path λ is 100 times larger than the mean distance $l$ between molecules which in turn is much larger than the molecular diameter.*

Although the above proportion has been set up for hydrogen, it is also equally valid for $O_2$ and $N_2$ etc. because according to Avogardo's law the length $l$ is the same for all perfect gases and the molecular diameter do not differ materially from each other.

A rough estimate of the absolute value of λ may now be made by taking $\sigma = 2 \times 10^{-8}$ cm. and $n = 2{\cdot}8 \times 10^{19}/\text{cm}^3$ approximately as shown above. Thus,

$$\lambda = \frac{1}{\pi n\sigma^2} = \frac{1}{3{\cdot}14 \times 2{\cdot}8 \times 10^{19} \times (2 \times 10^{-8})^2}$$
$$\approx 3 \times 10^{-5}\ \text{cm.}$$

Thus, the mean *free path is less than the wave-length of light in the visible spectrum. For air it is only about* $10^{-5}$ cm *i.e.*, 0·1μ.

**Variation of λ :** It may be noted from the expression for mean free path

$$\lambda = \frac{1}{\pi n \sigma^2} \qquad \ldots(6)$$

That *the free path varies inversely with the square of the molecular diameter.* Thus, smaller the size of the molecules, the larger will be the mean free path.

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

$$\lambda = \frac{m}{\pi \sigma^2 \rho} \qquad \ldots(7)$$

Thus the *mean free path is inversely proportional to the density of the gas.*

From perfect gas equation $PV = nkT$ for $V = 1$, we have

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

$$\therefore \qquad \lambda = \frac{kT}{\pi \sigma^2 p} \qquad \ldots(8)$$

Obviously *the mean free path is inversely proportinal to the pressure of the gas and directly proportional to the absolute temperature of the gas.*

## 5.6 Mean Free Path and Collision Probability

Although a molecule suffers collisions quite irregularly but still there will be a certain average rate of collisions if considered over a long period of time. The *average rate of collisions* per second is called *collision rate* and is denoted by the latter $P$. Thus the number of collisions suffered by the molecule in time $t$ is $Pt$. Also if the mean velocity of the molecule is $v$, the total distance described by it in time $t$ is $vt$. Then the average distance travelled by the molecule between two successive collisions, *i.e.* the mean free path λ is given by

$$\lambda = \frac{\text{Total distance traversed in time } t}{\text{Number of collisions suffered in this time}} = \frac{vt}{Pt} = \frac{v}{P}. \qquad \ldots(1)$$

If we confine ourselves to those free paths only where the molecule possesses velocity $v$ and denoted by $\lambda_v$ the mean free path and by $P_v$, the collision rate for the molecule of velocity $v$ only, then equation (1) can be written as

$$\lambda_v = \frac{v}{P_v} \qquad \ldots(2)$$

As $P_v\, t$ is the change or probability that the molecule of velocity $v$ suffers collision in time $t$, we may now call the quantity $P_v$ as *collision probability.*

## 5.7 Law of Distribution of Free Path (or the Probobility of a Free Path of Given Length)

Let us calculate the probability that a molecule moving with velocity $v$ travels a length $x$ without suffering collision. It will obviously be a function of $x$, say $f(x)$. The probability that will suffer a collision after traversing the distance $dx$ in time $dt$ is

$$P_v\, dt = P_v \frac{dx}{v} = \frac{dx}{\lambda v} \text{ (using equation 2 of section 5.6).}$$

The probability that it will traverse the distance $dx$ without making a collision is therefore $\left(1 - \frac{dx}{\lambda_v}\right)$. Hence the probability the a molecule will traverse a distance $x$ and then a further distance $dx$ (*i.e.* a total distance $x + dx$) without making a collision is, since the two probabilities are independent, given by the product

$$f(x) \times \left(1 - \frac{dx}{\lambda_v}\right) \qquad \ldots(1)$$

This must be equal to $f(x + dx)$, since $f(x + dx)$ is the probability that the molecule describes the distance $x + dx$ without making a collision. Thus,

$$f(x + dx) = f(x)\left(1 - \frac{dx}{\lambda_v}\right)$$

or
$$f(x) + \frac{df(x)}{dx} dx = f(x) - f(x)\frac{dx}{\lambda_v}$$

or
$$\frac{f'(x)}{f(x)} = -\frac{dx}{\lambda_v}$$

Integrating, we have

$$\log f(x) = -\frac{x}{\lambda_v} + \log A$$

or
$$f(x) = Ae^{-x/\lambda_v} \qquad \ldots(2)$$

where log $A$ is an arbitrary constant of integration.

If $x = 0$, $f(x)$ is obviously equal to unity, which snows that $A = 1$. We have therefore

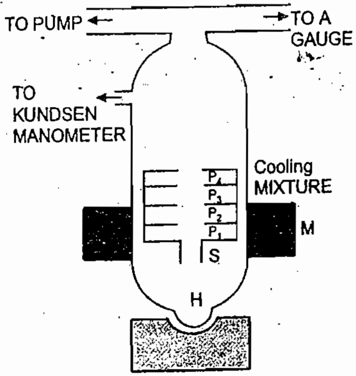
$$f(x) = e^{-x/\lambda_v} \qquad \ldots(3)$$

This is the *law of distribution of free paths* and shows that if $N_0$ molecules of velocity $v$ are incident on the gas, then only a fraction $N_0 e^{-x/\lambda_v}$ will be able to describe a distance $x$ without making collision.

## 5.8 Experimental Determination of Mean Free Path λ

Till 1920, there was no direct experimental method to determine the mean free path λ, when Max Born employed the apparatus sketched in fig. 5.13. $T$ is a tube made of quartz. At the point $H$ silver is heated which evaporates and passes through the narrow slit $S$ and then through a circular hole in each of the four brass discs $P_1, P_2, P_3$ and $P_4$ placed one above the other and at a distance of 1 cm from each other. Each of the brass discs carries a glass quadrant on which silver atoms get deposited due to the cooling effect of cooling mixture $M$. The arrangement of the quadrants is made such that each quadrant receives one fourth of the incident beam.

The procedure adopted to determine λ is that the density $d_{10}$ of deposit on a quadrant is measured with a microphotometer, all the gas from the tube is pumped out and the free path is equal to the length of the chamber. Then the gas is again introduced producing a free path λ and the



(Fig. 5.13)

density $d_1$ on the same quadrant is again measured. Then from the law of distribution of free paths, we have

$$d_1 = d_{10}\, e^{-x_1/\lambda} \quad \text{...(i)}$$

where $x_1$ is the distance of the quadrant from the slit $S$.

Similarly, the density $d_2$ and $d_{20}$ on the next quadrant at a distance $x_2$ from the slit $S$ is measured, whence

$$d_2 = d_{20}\, e^{-x_2/\lambda}. \quad \text{...(ii)}$$

Combining equations (i) and (ii), we get for mean free path

$$\lambda = (x_2 - x_1) \log_e \frac{d_2\, d_{10}}{d_1\, d_{20}} \quad \text{...(iii)}$$

Experimentally it was found that $\lambda = 1{\cdot}7$ cm. when the pressure, measured with Macleod Gauge or Kundsen manometer, $p = 5{\cdot}8 \times 10^{-3}$ mm. and $\lambda = 2{\cdot}5$ cm. when $p = 4{\cdot}5 \times 10^{-3}$ mm. Thus, the product $p\lambda =$ constant as predicted by theory. This excellent agreement between theory and particles. verifies the law of distribution of free paths and provides an accurate methods for determining $\lambda$.

## SOLVED EXAMPLES

**Ex. 3.** *The molecular diameter of a gas is $3 \times 10^{-8}$ cm. Calculate the mean free path at temperature 27°C and pressure 1 atmosphere.* **(Rohilkhand 2005)**

**Solution.** The mean free path

$$\lambda = \frac{1}{\sqrt{2}\,(\pi\sigma^2 n)}.$$

If $m$ is the mass of the molecule, then $mn = \rho$, where $\rho$ is the density of the gas

$$\therefore \qquad \lambda = \frac{m}{\sqrt{2}\,(\pi\sigma^2 \rho)}.$$

Since the pressure excited by the gas is given by

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

where $\bar{v}^2$, the mean square speed is given by

$$\bar{v}^2 = \frac{3kT}{m}.$$

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

or

$$\frac{m}{\rho} = \frac{kT}{P}$$

Hence mean free path at temperature $T$ and pressure $P$ is given by

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

Given $T = 27°\text{C} = 300\text{K}$, $P = 1$ atmos $= 1{\cdot}01 \times 10^5\ \text{N/m}^2$.

$\sigma = 3 \times 10^{-8}$ cm $= 3 \times 10^{-10}$ m and $k = 1{\cdot}38 \times 10^{-23}$ J/K

$$\therefore \qquad \lambda = \frac{1{\cdot}38 \times 10^{-23} \times 300}{1{\cdot}414 \times 3{\cdot}14 \times (3 \times 10^{-10})^2 \times 1{\cdot}01 \times 10^5}$$

$$= \frac{4{\cdot}14 \times 10^{-21}}{1{\cdot}414 \times 3{\cdot}14 \times 9 \times 1{\cdot}01 \times 10^{-15}}$$

$$= 1{\cdot}02 \times 10^{-7}\ \text{m}$$

## 5.9 Transport Phenomena

The equilibrium state of a gas is the most probable state; but if the gas is not in a state of equilibrium, we may have any of the following three cases :

1. The different parts of the gas may have different velocities. If so, then there will be a relative motion of the layers of the gas with respect to one another. In such a case the layers moving faster impart momentum to the slower moving layers through a long chain of collisions to bring the equilibrium state. This gives rise to the phenomenon of *viscosity*.

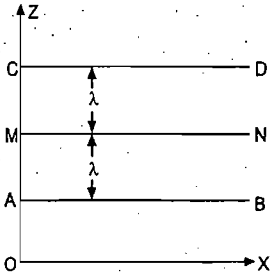
2. The different parts of the gas may have different temperatures. If so, the molecules of the gas will carry kinetic energy from regions of higher temperature to the regions of lower temperature to bring the equilibrium state. This gives rise to the phenomenon of *conduction*.

3. The different parts of the gas may have different molecular concentrations, *i.e.*, the number of molecules per unit volume. If so, the molecules of the gas will carry the mass from regions of higher concentrations to those of lower concentrations to bring the equilibrium state. This gives rise to the phenomenon of *diffusions*.

Thus, we see that viscosity, conduction and diffusion represent the transport of momentum, energy and mass respectively. These phenomena, *i.e.* viscocity, conduction and diffusion are therefore called the *transport phenomena*.

## 5.10 Viscosity

The phenomenon of viscosity occurs in a gas when different layers of it move with different speeds. Suppose a gas is moving in parallel layers between two horizontal planes $AB$ and $CD$ which are parallel to the $XY$-plane (fig. 5.14). Suppose that motion takes place parallel to the axis of $X$ and that the velocity of the layer just in contact with the plane $AB$ is zero and increases towards the plane $CD$. Thus, there is a relative motion between the layers and a velocity gradient in the $z$-direction. Consider an imaginary intermediate plane $MN$. The layers of the gas above the plane $MN$ are moving faster than those below it. The faster moving layers exert a tangential force on the plane $MN$ tending to increase its velocity while the layers below $MN$ exert an equal force in opposite direction. Thus, the different layers of the gas tend to destroy the relative motion between them. This property of the gas is called *viscosity*.



**(Fig. 5.14)**

The molecules of the gas possess forward momentum in the $X$-direction due to the flow of gas. The layers of the gas above the plane $MN$ have greater velocity and hence the greater momentum in a horizontal direction than the layers below $MN$. Then, because of thermal motions, some of the molecules from a faster moving layer cross the plane $MN$ downwards and drift into an adjacent layer where the forward velocity is less, transporting forward momentum to the slower moving layer.

Conversely, some molecules of the slower moving layer cross the plane *MN* upwards and drift into the faster moving layer decreasing the momentum of the latter. This transfer of momentum, which is equivalent to internal friction, can be computed from kinetic theory consideration as follows :

Let *G* be the momentum of each molecule in the plane *MN* and $(dG/dz)$ the momentum gradient (rate of change of momentum with distance) in an upward direction perpendicular to *MN*. Let each of the planes *AB* and *CD* be at a distance λ from *MN*, where λ is the mean free path. Then,

The momentum of each molecule at the plane *CD*

$$= G + \lambda\frac{dG}{dz} \qquad \ldots(1)$$

and the momentum of each molecule at the plane *AB*

$$= G - \lambda\frac{dG}{dz} \qquad \ldots(2)$$

Thus a molecule crossing the plane *MN* in the downward direction, transports a momentum given by (1) and one going upwards transports the momentum given by (2). Hence the net transfer of momentum across the plane *MN* in the downward direction due the transfer of the above pair obtained by substracting eqn. (2) from (1) which is

$$\left(G+\lambda\frac{dG}{dz}\right)-\left(G-\lambda\frac{dG}{dz}\right)=2\lambda\frac{dG}{dz} \qquad \ldots(3)$$

The number of molecules crossing the plane *MN* in the downwards direction can now be calculated. Let *n* be the number of molecules per unit volume and $\bar{v}$ their average speed. Then since molecules are moving due to thermal agitation in all possible directions, it may be supposed that one-third of these molecules are moving along each of the three directions *X*, *Y* and *Z*. Therefore, on an average, one-sixth of the molecules move parallel to any one axis in one particular direction. Thus, the number of molecules crossing the plane *MN* upwards or downwards per unit area per second,

$$= \frac{1}{6} n\bar{v}. \qquad \ldots(4)$$

Making use of equ. (3) we get for the total momentum transported downwards per unit area of the plane *MN* per second to be

$$= \frac{1}{6} n\bar{v} \times 2\lambda\frac{dG}{dz}$$

$$= \frac{1}{3} n\bar{v}\,\lambda\frac{dG}{dz} = \frac{1}{3} n\,\bar{v}\,\lambda\frac{d}{dz}(mv_x) = \frac{1}{3} mn\bar{v}\lambda\frac{dv_x}{dz} \qquad \ldots(5)$$

where momentum $G = mv_x$, $v_x$ being the velocity of molecules at the plane *MN*.

But according to Newton's law, force is the rate of change of momentum. Hence expression (5) is a measure of the force exerted on the plane *MN* by the upper layers. As we are considering unit area, this force is the same as tangential stress.

Now *coefficient of velocity* η *is defined as the tangential force per unit area between two layers required to maintain a unit velocity gradient in it, i.e.*

$$\eta = \frac{\text{Tangential stress}}{\text{Velocity gradient}} = \frac{\frac{1}{3} mn\bar{v}\lambda\,(dv_x/dz)}{(dv_x/dz)} = \frac{1}{3} mn\bar{v}\lambda \qquad \ldots(6)$$

But we know that mean free path

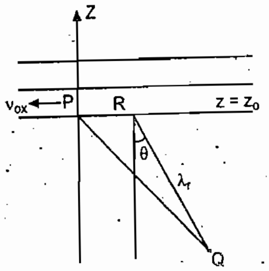
$$\lambda = \frac{1}{\sqrt{2}\,\pi n\sigma^2}$$

$$\therefore \qquad \eta = \frac{1}{3} mn\bar{v} \times \frac{1}{\sqrt{2}\,\pi\, n\, \sigma^2} = \frac{1}{3}\frac{m\bar{v}}{\sqrt{2}\,\pi\sigma^2} \qquad \ldots(7)$$

**More exact analysis :** In the above derivation of η, we have adopted a very rough method and hence it needs innumerable adjustment. We had assumed there that all the gas molecules traversed the mean free path λ and brough the same average momentum. In reality, the molecules crossing the plane *MN* have their collision anywhere between the region *ABCD* because they may travel in any inclined direction. As a result the plane *AB* and *CD* should not be drawn at distance equal to λ but at the average of projections of the free path of the various molecules on z-axis. Similarly, the projections of velocities on z-axis should be used while calculating the number of molecules crossing the plane *MN*.

Let us consider a gas uniform in temperature and density moving parallel to the horizontal *XY*-plane and thus having no mass motion along the z-axis. If we denoted the mass velocity by $v_0$, then as before the assumption is that the mass velocity $v_{0x}$ in the direction of the x-axis increases upward as z increases *i.e.*, a velocity gradient $\frac{dv_{0x}}{dz}$ exists along the z-axis.

Let us consider a mole which meets the plane $z = z_0$ at *P*, having come after suffering a collision at *Q* (fig 5.15). Then *QP* represents the path of the molecule since its last collision. Owing to its mass velocity $v_{0x}$, the gaseous layer as a whole moves say from *R* to *P* in the same interval of time in which molecule moves from *Q* to *P*. Thus the velocity components $(v_x, v_y, v_z)$ of the molcule relative the gaseous layer become $v_{0x} - v_x, v_y, v_z$ and the path described by the molecule relative to the mass motion of the surrounding gas is *QR*. Let the length *QR* be denoted by $\lambda_r$ and the angle it makes with the Z-axis be θ.



(Fig. 5.15)

Let us denote $mv_x$ the *x*-momentum of any molecule by μ and let $\bar{\mu}$ denote the mean value of μ at any point of the gas. Then $\bar{\mu} = mv_{0x}$ increases with z and is a function of z only. Let $\bar{\mu}$ for the Z-plane be denoted by $\bar{\mu}(z)$. Then $\bar{\mu}$ for the place of *Q*, whose z co-ordinate is $z_0 - \lambda_r \cos\theta$ may be denoted by $\bar{\mu}(z_0 - \lambda_r\cos\theta)$ and is less than that of *P* by an amount $\lambda_r \cos\theta \frac{d\bar{\mu}}{dz}$

*i.e.*

$$\bar{\mu}(z_0 - \lambda_r\cos\theta) = \bar{\mu}(z_0) - \lambda_r\cos\theta\frac{d\bar{\mu}}{dz}.$$

Hence the group of molecules under discussion carry, on the average, an amount of momentum appropriate to the point *Q viz.*

$$\bar{\mu}(z_0) - \lambda_r\cos\theta\,\frac{d\bar{\mu}}{dZ}. \qquad \ldots(1)$$

Now since all directions of molecular velocity may be regarded as equally probable, the probability of it lying within the solid angle between θ and θ + dθ is equal to $\frac{1}{2}\sin\theta\, d\theta$*. If *n* is the molecular density, then the number of molecules coming from unit volume near *Q* having relative

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* Refer to foot note of section 5.4.

molecular velocities lying within specified small ranged $dv$ (*i.e.*, between $v$ and $v+dv$) and $d\theta$ (*i.e.*, between $\theta$ and $\theta+d\theta$) is given by

$$\frac{1}{2} nf(v) \sin\theta \, d\theta \, dv. \qquad \ldots(9)$$

where $\int_0^\infty f(v)\, dv = 1$ in order that the total number may be equal to $n$.

Now the number of molecules having a velocity satisfying these conditions, which cross unit area of the plane $z = z_0$ near $R$, per second are only those which at any instant occupy a cylinder of base unity in the plane $z = z_0$ and of height $v \cos\theta$. Hence the total number of molecules having velocity between $v$ and $v + dv$ which in one second cross unit area of the particular plane in a direction making an angle $\theta$ with the axis of $Z$ is

$$\frac{1}{2} n \sin\theta \, d\theta f(v) \, dv \cdot v\cos\theta. \qquad \ldots(10)$$

The amount of momentum carried across the plane by them in the direction of $Z$ increasing is, therefore, [ Using equations (8) and (10)]

$$\frac{1}{2} n \sin\theta \, d\theta \cdot f(v) \cdot dv \, v \cos\theta \left\{ \bar{\mu}(z_0) - \lambda_v \cos\theta \frac{d\bar{\mu}}{dz} \right\}$$

where $\lambda_v = \bar{\lambda}_r$ is the *mean free path* for a molecule moving with velocity $v$ and has replaced $\lambda_r$ because the molecules might have suffered their last collision in any of the plane and hence a mean value $\bar{\lambda}_r = \lambda_v$ has been used.

On integrating the expression just found for all values of $\theta$ from 0 to $\pi$, we obtain the total transfer of momentum by all molecules with velocities between $v$ and $v + dv$, whatever their direction. On further integrating from $v = 0$ to $v = \infty$, we obtain for the total amount of momentum carried across unit area of the plane by all the molecules per second which is equal to

$$\int_0^\infty vf(v)\, dv \cdot \frac{n}{2} \int_0^\pi \sin\theta \cos\theta \left\{ \bar{\mu}(z_0) - \lambda_v \cos\theta \frac{d\bar{\mu}}{dz} \right\}$$

$$= \int_0^\infty v f(v)\, dv \left[ -\frac{n}{2} \lambda_v \frac{d\bar{\mu}}{dz} \right]$$

$$= -\frac{1}{2} n \left( \frac{d\bar{\mu}}{dz} \right) \bar{v} \lambda_r, \qquad \ldots(11)$$

where $\bar{v}\lambda_r$, denotes the mean value of $v\lambda_v$ average over all the molecules of the gas. If we put $v\lambda_v = \bar{v}\lambda$, where $\lambda$ is the mean free path of a molecule defined in another way and $v$ the mean molecular velocity, then equation (11) becomes equal to

$$-\frac{1}{2} n\bar{v}\lambda \frac{d\bar{\mu}}{dz}$$

a negative indicating that the transfer of momentum is from above to below. Putting $\bar{\mu} = mv_{0x}$ we find that the downward transfer of momentum per unit area per second is equal to

$$\frac{1}{2} mn\bar{v}\lambda \frac{dv_{0x}}{dz} \qquad \ldots(12)$$

This transfer of momentum results in a viscous drag of equal amount across the plane $z = z_0$. A viscous fluid moving with the same velocity as the gas would exert a viscous drag per unit area crossing the plane in question, equal to

$$\eta \frac{dv_{0x}}{dz} \qquad \ldots(13)$$

Equating the expression (12) and (13), we get

$$\eta \frac{dv_{0x}}{dz} = \frac{1}{2} m \, n\bar{v} \, \lambda \frac{dv_{0x}}{dz}$$

or

$$\eta = \frac{1}{3} mn\bar{v}\lambda = \frac{1}{3} \rho\bar{v}\lambda, \qquad \ldots(14)$$

where $\rho = mn$ is the density of the gas.

This expression for coefficient of viscosity is the same as was obtained earlier in equation (6). This derivation, although undoubtedly better than the previous one, still requires certain modifications. Firstly we have not described what this new mean free path is and in what way has it been taken. Secondly, The assumption that the velocity distribution $f(v)$ is Maxwellian is not justified because the gas is endowed with mass motion. A more serious error has been introduced by neglecting the persistence of velocities which has been investigated by Jeans and showed that

$$\lambda = \frac{1 \cdot 382}{\sqrt{2} \, \pi n \sigma^2}$$

So that the viscosity coefficient is given by

$$\eta = \frac{1}{3} mn\bar{v}\lambda = 0 \cdot 461 \frac{m\bar{v}}{\sqrt{2} \, \pi\sigma^2} \qquad \ldots(15)$$

Chapman and Enskog have further modified the Maxwell's formula for viscosity and arrived at the exact formula.

$$\eta = 0 \cdot 499 \frac{m\bar{v}}{\sqrt{2} \, \pi\sigma^2}. \qquad \ldots(16)$$

## 5.11 Agreement between Theory and Observations for the Coefficient of Viscosity :

If we substitute $\lambda = \frac{1}{\sqrt{2} \, \pi n\sigma^2}$ is equation (14) of §5.10, we get

$$\eta = \frac{1}{3\sqrt{2}} \cdot \frac{m\bar{v}}{\pi\sigma^2} \qquad \ldots(1)$$

1. It is seen at once from this equation since $\bar{v}$ varies as $\frac{1}{\sqrt{m}}$, $\eta$ **for different gases should vary** as $\sqrt{m}$. As a matter of fact molecular diameter $\sigma$ also varies from gas to gas and if account he taken of this variation of $\sigma$, which is comparatively small for most gases this result is found to hold quite accurately.

2. Variation of viscosity with pressure (or density) : Equation (1) is independent of pressure, for neither $m$, $\bar{v}$, nor $\sigma$ is a function of pressure. *Thus, coefficient of viscosity of a gas is independent of the pressure or the density of the gas.* This has been conformed experimentally for pressures from a few mm. of mercury upto several atmospheres. This fact formed one of the most brilliant successes of the kinetic theory of gases. In order to test the validity of the law, Maxwell fixed three parallel and coaxial circular discs on a common axis and suspended them by a torison thread inside a vessel containing air. These movable discs were made to oscillate between four parallel fixed discs when it was found that the oscillations die away at the same rate whether the air was dense or rare, showing that $\eta$ is independent of density or pressure.

At very low pressures, hawever, this law breaks down. This is due to the fact that at these low pressures, the gas becomes rarefied and the molecular collisions become very rare. Thus with decrease in pressure, the mean free path $\lambda$ gradually increases till it becomes comparable with the dimensions of the vessel in which the experiment is conducted. Then $\lambda$ can not increase further by reduction of pressure and remains constant. Any further decrease of pressure reduces the density $\rho$, but $\lambda$ remains constant and hence $\eta$ *decreases with decrease in pressure at excessively small pressure* in accordance of equation (14) of § 5.10

At very much high pressure, where attractive forces between the molecules become appreciable. Maxwell's law fails altogether. At such high pressures, the mean free path becomes comparative with molecular diameter $\sigma$ and the transport of momentum is not through a distance $\lambda$ but through a distance $\lambda + \sigma \cos \theta$. Because of this the value $\frac{\eta}{\rho}$ will not be constant but according to Enskog, will vary as

$$\frac{\eta}{\rho} = \frac{1}{2{\cdot}545}\left[\frac{V}{b} + 0{\cdot}8 + 0{\cdot}7614\,\frac{b}{V}\right]\left(\frac{\eta}{\rho}\right)_{min}$$

where $V$ is the gaseous volume and $b$ the Vander Waall's constant. This formula is found to represent the observed variations of $(\eta/\rho)$ fairly well as verified by Michels and Gibson. For nitrogen $(N_2)$, $\eta/\rho$ passes through a minimum $V = 0{\cdot}87266b$ at 580 atmospheres as predicted by theory. For $CO_2$ this minimum value occurs at 77·2 atmosphere as observed by Warburg and Babo, and verified by Enskog.

**3. Variation of viscosity with temperature** : If we replace $\bar{v}$ in equation (1) above by $\sqrt{\left(\frac{8kT}{m\pi}\right)}$, we get

$$\eta = \frac{2}{3\pi^{3/2}\sigma^2}\sqrt{(mkT)}. \qquad \ldots(2)$$

The predicts that $\eta$ should vary as $\sqrt{T}$. It is a fact that the viscosity of gases does rise in all cases with a rise of temperature but the increases in much more rapid than the square root of $T$. It is due to erroneous assumption that the molecules are rigid elastic spheres devoid of mutually interacting forces and that $\sigma$ is independent of $T$. Actually the molecules are surrounded by repulsive fields of force and increasing the temperature means increasing the molecular velocities which increases the degree to which molecules penetrate into each other fields of forces at collision which in turn had the effect of decreasing the effective sizes of molecules. Thus the effective size of the molecules is large at low temperature and small at high temperature. Thus $\eta$ from equation (1) depends on themperature both through the factor $\bar{v}$ in the numerator and factor $\sigma^2$ in the denominator. Consequently $\eta$ *does not vary simply as the square root of temperature but more rapidly than this.*

If we assume that the law of force between two molecules separated by a distance $r$ is of the from $(\mu / r^S)$, then it can be shown that $\frac{1}{\sigma^2}$ will vary as $\frac{2}{T^{s-1}}$ and $\eta$ will vary as $T^n$, where

$$n = \frac{1}{3} + \frac{2}{s-1}$$

Accordingly we may write for visocity

$$\eta = AT^n. \qquad \ldots(3)$$

where $A$ is a constant for the substance. The experimental data show good agreement with this equation for hydrogen, helium, neon but not fairly good for $N_2$ and $CO_2$.

For some gases, $\eta$ is found as a meter of experiment to vary in the form

$$\eta = \eta_0\left(\frac{T}{273}\right)^n \qquad \ldots(4)$$

where $\eta_0$ is the coefficient of viscosity at 0°C.

Sutherland in 1993, assumed that the effective, value of $\sigma$ at temperature $T$ is

$$\sigma^2 = \sigma_\infty^2\left(1 + \frac{c}{T}\right)$$

where $\sigma_\infty$ is the value of $\sigma$ when $T = \infty$ and $c$ is some constant. Accordingly he put forward the formula for viscosity at temperature $T$ to be

$$\eta = \eta_0\left(\frac{T}{273}\right)^{3/2}\frac{c+273}{c+T}$$

This formula meets with very considerable success in predicting the variation of viscosity with temperature for many gases. Lennard-Jones. Hasses and Cook further modified the formula with an improvement upon the law of force.

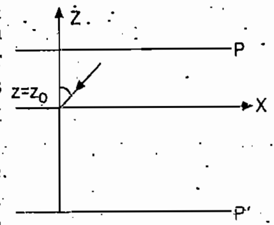
## 5.12 Thermal Conductivity

The conduction of heat through a gas is molecular process, the molecules in the hotter regions of the gas having greater average energies than those in a colder part, and losing this excess of energy by imparing it to the colder molecules with which they collide. Thus thermal conductivity is the transport of energy resulting from molecular motions.

The problem of thermal conductivity of gases can be treated in precisely the same manner as that viscosity except for the difference that in the present problem the molecules are to be considered as the carriers of heat energy instead of momentum. Hence the expression for the conductivity of a gas can be derived by proceeding exactly as in § 5.10 and replacting $\mu$ by $E$ where we get for the total transfer of energy per unit area to be given by

$$\frac{1}{2}n\bar{v}\lambda\frac{dE}{dz}. \qquad \ldots(1)$$

Expression (1) can also be derived in a slightly different manner. For it, consider two parallel plates $P$ and $P'$. Fig. 5.16, between which a steady temperature gradient is maintained keeping $P$ at a higher temperature. Let the plates lie in $XY$-plane and space between then is filled with gas. Let us consider a plane $z = z_0$ and let the mean energy (in joule) of a molecules in this plane be $\bar{E}$, so that $\bar{E}$ is a function of $z$. Consider now the molecules which cross a unit area of the plane. $z = z_0$. These molecules will, in general, come after traversing a distance $\lambda$ from their last collision in a direction making an angle 0 with the axis of $Z$. Thus these molecules on the average come from a plane whose z coordinate is



(Fig. 5.16)

$$z_0 + \lambda\cos\theta.$$

The mean energy of these molecules is therefore

$$\bar{E} + \lambda\cos\theta\,\frac{d\bar{E}}{dz} \qquad \ldots(2)$$

The number of molecules which in one second cross the unit area of this particular plane in a direction making an angle between $\theta$ and $\theta + d\theta$ wth the axis of $Z$ is

$$\frac{1}{2}n\bar{v}\cos\theta\sin\theta\,d\theta. \qquad \ldots(3)$$

The amount of energy carried across the plane by them in the direction of $Z$ increasing is

$$\left(\bar{E}+\lambda\cos\theta\frac{d\bar{E}}{dz}\right)\cdot\frac{1}{2}n\,\bar{v}\cos\theta\sin\theta\,d\theta. \qquad ...(4)$$

The total amount energy carried by the molecules in unit time across unit area of the plane in the direction of Z increasing will be

$$=\frac{1}{2}n\bar{v}\int_{\theta=0}^{\theta=\pi}\left(\bar{E}+\lambda\cos\theta\frac{d\bar{E}}{dz}\right)\cos\theta\sin\theta\,d\theta$$

$$=-\frac{1}{3}n\bar{v}\lambda\frac{d\bar{E}}{dz} \qquad ...(5)$$

If $K$ is the coefficient of thermal conductivity of the gas, the flow of heat across unit area of the plane is $-K\frac{dT}{dz}$ where $\frac{dT}{dz}$ is the temperature gradient and $K$ is in S.I unit. Equating this to expression (5), we have

$$K\frac{dT}{dz}=\frac{1}{3}n\bar{v}\lambda\frac{d\bar{E}}{dT}\frac{dT}{dz}$$

or

$$K=\frac{1}{3}n\,\bar{v}\,\lambda\frac{d\bar{E}}{dT} \qquad ...(6)$$

If now $m$ is the mass of one mole. the number of molecules per unit mass of the gas is $1/m$ and $C_V$, specific heat at constant volume is given by

$$C_V=\frac{1}{m}\frac{d\bar{E}}{dT}.$$

Substituting this value of $\frac{d\bar{E}}{dz}$ in eqn. (6) we get

$$K=\frac{1}{3}n\,\bar{v}\,\lambda\,.\,mC_V=\eta C_V. \qquad ...(7)$$

The above equation is not in agreement with experimental data. Calculation show that the relation between $K$ and $\eta$ should be

$$K=\varepsilon\eta C_V, \qquad ...(8)$$

where $\varepsilon$ is a factor which depends on the atomicity of the gas and varies from 1 to 2·5. Chapman and Enskog carried out a more accurate study applicable to monoatomic gases and obtained for molecules with translation energy only, and spherical symmetry, the value

$$K=2{\cdot}5\,\eta C_V \qquad ...(9)$$

in which the coefficient $\varepsilon$ has the value 2·5. The value $\varepsilon=2{\cdot}5$ for all monoatomic gases is found fairly accurate and satisfactory.

The evaluation of $\varepsilon$ for polyatomic molecules presents a problem of great complexity since the molecules of this kind may rotate or have internal motions in addition to translational motions. Obviously they will possess energy other then the translation energy. Let us suppose that on the average this energy (energy due to cause other than translation) is $\beta$ times the average translational energy. Then the average total energy of a molecule $E$ now becomes

$$\bar{E}=\frac{3}{2}RT+\beta\cdot\frac{3}{2}RT=\frac{3}{2}RT(1+\beta)$$

where $\frac{3}{2}RT$ is the kinetic energy of translational motion. Then $C_V$ is

$$C_V=\frac{1}{m}\cdot\frac{d\bar{E}}{dT}=\frac{3R}{2m}(1+\beta). \qquad ...(10)$$

But since

$$C_P-C_V=\frac{R}{m}$$

We have

$$C_P=C_V\,.\frac{R}{m}=\frac{R}{2m}(1+\beta)+\frac{R}{m}$$

Hence

$$\gamma=\frac{C_P}{C_V}=1+\frac{2}{3(1+\beta)}, \qquad ...(11)$$

or

$$1+\beta=\frac{2}{3(\gamma-1)} \qquad ...(12)$$

Now putting the value $C_V$ of from (10) in eqn. (7) we get for thermal conductivity

$$K=\eta\,C_V=\frac{3}{2}(1+\beta)\frac{R}{m}\eta.$$

But, as we have seen, when energy is wholly translational ($\beta=0$), this value of $K$ should be multiplied by $\frac{5}{2}$. Combining these two contributions to the transport of energy, we get

$$K=\frac{3}{2}\left(\frac{5}{2}+\beta\right)\frac{R}{m}\eta$$

But $\frac{3}{2}\cdot\frac{R}{m}=\frac{C_V}{1+\beta}$ from eqn. (10).

$$\therefore \qquad K=\frac{\frac{5}{2}+\beta}{1+\beta}\eta\,C_v.$$

Substituting the value of $\beta$ and $1+\beta$ from eqn. (12) we arrive at the formula

$$K=\frac{1}{4}(9\gamma-2)\,\eta\,C_V. \qquad ...(13)$$

Hence

$$\frac{K}{\eta\,C_V}=\varepsilon=\frac{1}{4}(9\gamma-5). \qquad ...(14)$$

Thus for monoatomic gases ($\gamma=1{\cdot}67$), $\varepsilon=2{\cdot}5$; for diatomic gases ($\gamma=1{\cdot}4$), $\varepsilon=1{\cdot}9$; while for rigid triatomic molecules ($\gamma=1{\cdot}33$; $\varepsilon=1{\cdot}75$ becoming still smaller for polyatomic molecules. These values of $\frac{K}{\eta\,C_V}$ agree fairly well with those experimentally determined.

## 5.13 Variation of Conductivity with Pressure and Temperature.

As regards the variation of thermal conductivity $K$ with pressure and temperature, let us focus our attention on the relation,

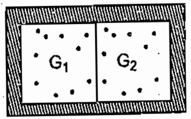
$$K=\varepsilon\eta C_V.$$

As the variation of $C_V$ is small, the variation of conductivity with pressure and temperature is, in general, the same as the variation of viscosity. Thus *conductivity like viscosity should be independent of pressure.* It was verified experimentally first by Stefan and later by others. The law, however, fails at extermely high and low pressures. At very low pressure $K$ become less.

Again, assuming $C_V$ constant, conductivity should, as in the case of viscosity, be theoretically proportional to the square root of absolute temperature. But $K$ varies in the same manner with temperature as $\eta$ does *i.e., it increases more rapidly than proportional to* $\sqrt{T}$. Experiments of Winklemann indicate it to be true, but later experiments show that $K$ increases less rapidly with $T$ than the value of $\eta$. As in the case of viscosity, below 0°C, a much *more rapid decrease in K with a decrease in T is noted in* accordance with Sutherland's theory for viscosity.

## 5.14. Diffusion

If a gas contains two or more different kinds of molecules whose relative densities vary from point to point, a process known as diffusion takes place until the concentration is uniform through out. For it, consider a vessel (Fig. 5.17) containing two different gases $G_1$ and $G_2$ separated by a partition. The gases are at the same pressue and temperature so that the number of molecules per unit volume is the same on both sides. When the partition is removed *i.e.*, the gases are made to communicate with each other, there is no mass motion of the gas in either direction but after some time both the gases are found to be distributed uniformly througout the entire volume. The phenomenon is known as *interdiffusion of two gases* and if we fix our attention only on one gas, we can say that it diffuses into other gas. *This phenomenon due to which each gas permeates the other is called diffusion.*



**(Fig. 5.17)**

The phenomenon of diffusion is not restricted to gases but occurs in liquids and solids also. *It may be described as the transport of mass resulting from random molecular motion and takes place whenever there is a concentration gradient i.e.*, when the number of molecules per unit volume on one side of a surface differs from that on the other side. In such a case a denser region will lose more molecules to regions of scarcity than it will gain. The density of a gas becomes uniform throughout its volume when the gas reaches the equilibrium state.

In order to derive an expression for coefficient of diffusion (ratio of the number of molecules across unit area in one second to the concentration gradient), let us consider a horizontal plane drawn in a gas and let the molecular concentration $n$ remain constant along it and vary in the vertical direction (z-axis). Experiments show that the number of molecules which cross unit area of the horizontal plane per unit area per second in the positive direction of the z-azis is given by

$$n = -D\frac{dn}{dz} \qquad \ldots(1)$$

where $D$ is called the coefficient of diffusion.

Imagine now two gases arranged in layers on above the other parallel to the axis of $z$ diffusing through one another. Let at any instant $n_1$ and $n_2$ be the concentrations of the two gases which vary along the axis of $z$ *i.e.*, $n_1$ and $n_2$ are functions of $z$ only. As temperature and pressure must be constant throughout the gas, we must have from Avogadro's law for perfect gases

$$n_1 + n_2 = n = \text{constant}.$$

Differentiating with respect to z.

$$\frac{dn_1}{dz} + \frac{dn_2}{dz} = 0,$$

or

$$-\frac{dn_1}{dz} = \frac{dn_2}{dz} = \alpha.$$

Therefore,

$$n_1 = A_1 - \alpha z,$$

and

$$n_2 = A_2 + \alpha z,$$

where $A_1$, $A_2$ and $\alpha$ are constants referring to the plane $z = z_0$ across which we will consider the molecular transfer.

We will now calculate the number of molecules crossing the plane $z = z_0$. It will be done exactly in the similar manner as for viscosity. Let $\bar{v}_1$ and $\lambda_1$ denote respectively the mean molecular velocity and the mean free path for molecules of the first kind in the gas whereas $\bar{v}_2$ and $\lambda_2$ denote corresponding quantities for the second kind. Molecular concentration pertaining at the point from which the molecules started their last collision will now be evaluated. Those molecules which move making an angle $\theta$ with the axis of $z$ might have suffered their last collision in a plane of which the $z$ co-ordinate is $z_0 - \lambda_1 \cos\theta$ and in this plane the concentration may be taken to be

$$A_1 - \alpha(z_0 - \lambda_1 \cos\theta).$$

Therefore, the number of molecules of the first kind which cross the plane $z = z_0$ per unit area per unit time in the direction of $z$ increasing, as in case of viscosity is given by

$$\nu_1 = \int_0^\infty \int_0^\pi [A_1 - \alpha(z_0 - \lambda_1 \cos\theta)] \cdot \frac{1}{2} \sin\theta \cos\theta \, d\theta \, . \, v f(v) \, dv$$

$$\Rightarrow \qquad \nu_1 = \frac{1}{3} \alpha \lambda_1 \bar{v}_1. \qquad \ldots(2)$$

Similarly, the number of molecules of the second kind in the direction of $z$ increasing *i.e.*, upwards is given by

$$\nu_2 = -\frac{1}{3} \alpha \lambda_2 \bar{v}_2 \qquad \ldots(3)$$

Generally $\nu_1 + \nu_2 \neq 0$ and hence a number of molecules $\nu_1 + \nu_2$ will tend to move in the upward direction tending to set a difference of pressure in the gas which should, however remain constant throughout. As a result, gas would adjust itselt against this tendency by a slow mass motion with a valocity $v_z$ parallel to the axis of z. Obviously the mass velocity $v_z$ will be a function of z and will be such that there is no net transfer of volume in either direction. Thus, the rate of increase of the number of molecules of the first kind on the passive side of plane $z = z_0$ per unit area actually becomes

$$\Gamma_1 = \nu_1 + v_z n_1. \qquad \ldots(4)$$

Similarly, the rate of increase of molecules of the second kind

$$\Gamma_2 = \nu_2 + v_z n_2. \qquad \ldots(5)$$

As the flow is to be steady, the total flow of molecules over every plane must be zero,

*i.e.*,

$$\Gamma_1 + \Gamma_2 = 0$$

or

$$\nu_1 + v_z n_1 + \nu_2 + v_z n_2 = 0$$

or

$$v_z = -\frac{\nu_1 + \nu_2}{n_1 + n_2} \qquad \ldots(6)$$

Substituting this value of $v_z$ in equation (4), we have the true transfer of molecules of the first kind per unit area per unit time *i.e.*, the diffusion current density given by

$$\Gamma_1 = \nu_1 - \frac{\nu_1 + \nu_2}{n_1 + n_2} n_1$$

$$= \frac{\nu_1 n_2 - \nu_2 n_1}{n_1 + n_2}$$

$$= \frac{\frac{1}{3} \alpha \lambda_1 \bar{v}_1 n_2 + \frac{1}{3} \alpha \lambda_2 \bar{v}_2 n_1}{n_1 + n_2}.$$

[Substituting for $\nu_1 + \nu_2$ from equation (2) and (3)]

As $\alpha = -\frac{dn_1}{dz} = \frac{dn_2}{dz}$, we have

$$\Gamma_1 = -\frac{dn_1}{dz} \cdot \frac{\lambda_1 \bar{v}_1 n_2 + \lambda_2 \bar{v}_2 n_1}{3(n_1 + n_2)} \qquad ...(7)$$

But if $D_{12}$ is the coefficient of diffusion of the two gases, then according to definition the diffusion current density.

$$\Gamma_1 = -D_{12} \frac{dn_1}{dz}$$

or

$$D_{12} = \frac{1}{3} \frac{\lambda_1 \bar{v}_1 n_2 + \lambda_2 \bar{v}_2 n_1}{n_1 + n_2} \qquad ...(8)$$

This is the well known equation of diffusion and is symmetrical for the two gases,

*i.e.,* $$D_{12} = D_{21}.$$

It is generally known as *Mayer's formula* for coefficient of diffusion.

Formula (8) becomes specially simple if the molecules of two gases are approximately of equal size and mass. Then we may take $\lambda$ and $\bar{v}$ to be the same for each gas and obtain.

$$D_{11} = \frac{1}{3} \lambda \bar{v}. \qquad ...(9)$$

Comparing it with the corresponding approximate formula for the coefficient of viscosity.

$$\eta = \frac{1}{3} \lambda \bar{v} \rho.$$

We get the following relation

$$D_{11} = D = \frac{\eta}{\rho}, \qquad ...(10)$$

where $D_{11}$ or $D$ may be called the *coefficient of self diffusion* or *diffusitivity* of a single gas.

Sir James Jean has modified the simple formula (10) in which we have neglected the dependence of *free path* upon velocity and the persistence of velocities. The modified form of equation (10) is

$$D = 1{\cdot}342 \frac{\eta}{\rho}. \qquad ...(11)$$

The calculations of Chapman and Enskog for elastic spheres predict the relation approximately.

$$D = 1{\cdot}2 \frac{\eta}{\rho} \qquad ...(12)$$

While Maxwell's theory for molecules repelling each other according to inverse fifth power of the distance yields for coefficient of self diffusion.

$$D = 1{\cdot}543 \frac{\eta}{\rho} \qquad ...(13)$$

**Variation of diffusion :** We shall now see how diffusivity should vary with temperature and pressure. It is obvious from equation (10) that it should vary with temperature and pressure in the same way as do the relation $\left(\frac{\eta}{\rho}\right)$ for the gases. Since $\eta$ varies as $\sqrt{T}$ and not at all with $P$ and also $\rho$ varies as $P$ and $T^{-1}$, it is obvious that the diffusivity should vary as $P^{-1}$ and as $T^{3/2}$,

*i.e.,* $$D \propto P^{-1}\, T^{3/2}.$$

Experimental observation lead to the result that $D$ varies inversely as the pressure $P$ but the power of $T$ lies between 1·750 and 2.

## 5.15 The Brownian Motion

In 1827, a botanist Robert Brown observed that pollen grains suspended in water and viewed under a powerful microscope show an irregular continuous dancing motion. Extending his observations to suspensions of a large number of inorganic substances the so-called colloidal solutions, he found it to be a general phenomenon. In fact, any kind of sufficiently small particles, no matter how non-vital, suspended in a liquid performed similar perpetual dances. The suspended particles under a high power microscope appear like stars of the light, dancing hither and thither without apparent rhyme or reason. Each particle spins, rises, sinks and rises again without ever coming to rest. The motion is perpetual and spontaneous and is one of the most interesting phenomenon in Physics. *This ceaseless rendom and swarming motion is called the Brownian motion*, after its discover.

The established facts regarding Brownian motion are as follows :

1. The motions are completely irregular and random. No two particles are found to execute the some motion. Thus it can not be due to convection or eddy currents.
2. The motions are continuous and eternal *i.e.,* the motions continue indefiniely without showing any signs of stopping or even abating.
3. ~~The smaller~~ the particles ~~the more~~ lively and noticeable are the motion.
4. It is independent of the nature of the suspended particles~~, two~~ particles of the same weight and size move equally fast at the same temperature.
5. The motion becomes more vigorous when the temperature is increased or the viscosity of the supporting fluid is decreased.
6. It is independent of the shaking of the vessel.

A large number of hypothesis as to the *cause of Brownian motion* have been put forward. It was at first attributed to surface tension irregularities in the temperature of the liquid vibrations, chemical or electrical action and so on. All these explanations were found insufficient and a very little real progress was made in our knowledge of the subject until the modern view ascribing it to molecular agitation was put forward by Delsaux in 1877 and again by Gouy in 1888. They showed that the particles were acting merely as indicators of the molecular motion of the liquid in which they were immersed. Thus Brownian motion is due to bombardment of the dispersed particles by molecules of the medium. If the particles are sufficiently large, the forces due to molecular impact will almost completely balance and hence the Brownian motion can not be observed with large sized particles. But if the size of the particle is very small, it will be acted upon by a resultant unbalanced force and will consequently move this way or that in response to the force. Thus the particles move to and fro in an entirely haphazard fashion corresponding to the haphazard movement of the molecules of the liquid.

French chemist Perrin made a through study of Brownian motion in colloidal suspension. He tested the hypothesis that the suspended particles which dance about in a stationary liquid in Brownian motion behave in the same way as a gas molecules. Although the molecules of a gas can not be seen, it can be supposed that the gas molecules are in continuous motion in all directions frequently colliding against one another. Thus from the point of view of thermal agitation there is no distinction between the molecules of an ordinary gas and the Brownian particles. We may indeed extend all the laws of kinetic theory of gases to a suspension which is composed of a larger number of small particles suspended in a liquid. The laws hold for light as well as heavy particles and are applicable to even visible particles such as the Brownian particles.

## 5.16. LANGEVIN'S THEORY

Langenin gave a simplified treatment of Brownian motion. The treatment is based on the hypothesis that the Brownian motion is entirely irregular and there is no effect of gravity on it. Every particle in the suspension suffers a very large number of collisions by molecules of the liquid; there are about $10^{21}$ collisions per second suffered by every Brownian particle in a liquid under normal condition and each collision is expected to produce a deflection in the path of particle; however small it may be. It is not possible to consider separate collision; the effect of these collisions to produce an average systematic force representing the viscous force experienced by the particle and a fluctuating part (X) of the force which is responsible for the Brownian motion. Assuming the particles to be spherical, the viscous force is given by Stokes law

$$F = -6\pi\eta rv.$$

where $v$ is velocity of particle, $r$ is radius and $\eta$ is coefficient of viscosity.

Negative sign shows that viscous force is opposite to velocity. If we assume that the motion is along $x$-axis, we have .

$$F_x = -6\pi\eta r\left(\frac{dx}{dt}\right) = -c\frac{dx}{dt}$$

where $c = 6\pi\eta r$ is a constant.

The equation of motion of the particle is given by

$$m\frac{d^2x}{dt^2} = -c\frac{dx}{dt} + X \qquad \text{...(1)}$$

where X is actual instantaneous force causing the Brownian motion. As motion of particle is irregular and changes in direction, so X changes irregularly. The phenomenon is of the nature of random walk and therefore in sufficiently long time $t$ (>> $10^{-21}$ sec) the particle suffers an average displacement $x$. For other particles $x$ will have other values therefore the average displacement in a sufficiently long time will be nearly zero. Therefore we consider the quantity ($x^2$) which does not change sign with change of sign of $x$. We have

$$\frac{d}{dt}(x^2) = \frac{d}{dx}(x^2)\frac{dx}{dt} = 2x\frac{dx}{dt}$$

$$\Rightarrow \qquad x\frac{dx}{dt} = \frac{1}{2}\frac{d}{dt}(x^2)$$

Also

$$\frac{d^2}{dt^2}(x^2) = \frac{d}{dt}\left(\frac{dx}{dt}\right) = \frac{d}{dt}\left(2x\frac{dx}{dt}\right)$$

$$= 2x\frac{d^2x}{dt^2} + 2\left(\frac{dx}{dt}\right)^2$$

$$\Rightarrow \qquad x\frac{d^2x}{dt^2} = \frac{1}{2}\frac{d^2}{dt^2}(x^2) - \left(\frac{dx}{dt}\right)^2$$

In view of these equations, equation (1) multiplied by $x$, gives

$$\frac{1}{2}m\frac{d^2}{dt^2}(x^2) - m\left(\frac{dx}{dt}\right)^2 = -\frac{1}{2}c\frac{d}{dt}(x^2) + Xx$$

Integrating with respect to time, we get

$$\frac{1}{2}m\left[2x\frac{dx}{dt}\right]_0^t - m\int_0^t\left(\frac{dx}{dt}\right)^2 dt = -\frac{1}{2}c\,[x^2] + \int_0^t Xx\,dt \qquad \text{...(2)}$$

The first term is negligible due to two factors : firstly it is proportional to $\sqrt{t}$ and secondly for some particle $x$ is positive and for other $x$ is negative. If we average over a large number of particles, the last term containing X will also vanish since it is positive for some particles and negative for the others. Further since the particles are in thermal equilibrium, the mean kinetic energy will be given by the law of equipartition of energy; accordingly the mean kinetic energy per degree of freedom.

$$\frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2}kT$$

In view of this second term becomes

$$m\int_0^t\left(\frac{dx}{dt}\right)dt = \int_0^t m\left(\frac{dx}{dt}\right)^2 dt = kT\int_0^t dt = kTt$$

The overbar denotes average value for a large number of particles therefore equation (2) gives

$$kT\,t = \frac{1}{2}c\,\overline{\Delta(x^2)}$$

where $\Delta(x^2)$ denotes change in $x^2$ in time $t$. If motion of particles starts from origin, then $\Delta(x^2) = x^2$

$$\overline{x^2} = \frac{2kT}{c}\tau \qquad \text{...(3)}$$

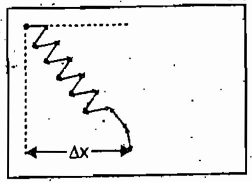
where $\tau$ is time interval which is sufficiently large to allow a large number of collisions.

If component of displacement along $x$-axis is denoted by $\Delta x$ instead of $x$, then, equation (3) gives

$$\overline{(\Delta x)^2} = \frac{2kT}{c}\tau$$

or

$$\overline{(\Delta x)^2} = \frac{kT}{3\pi\eta r}\tau = \frac{RT}{N}\cdot\frac{1}{3\pi\eta r} \qquad \text{...(4)}$$



(Fig. 4.18)

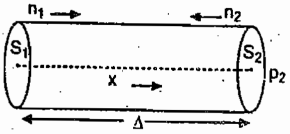
The value of $\overline{(\Delta x)^2}$ was measured by Perrin; who instead of observing different particles, watched the motion of a single particle for a long time using a very efficient camera with mutually perpendicular lines on the film as on a graph paper. The experiment was repeated for a large number of particles and the mean value $\overline{(\Delta x^2)}$ for specified time interval (*viz* 30 seconds) was calculated. Perrin's observation, verified equation (4). By substituting the values of $\eta$, $r$, temperature $T$, the value of Avagadro number N may be estimated.

## 5.17 Einstein's Theory of the Translational Brownian Motion

An adequate theory of the Brownian movement phenomenon was first developed by Einstein and published in the memorable year of 1905. He succeeded in formulating a quantitative theory for the Brownian movement on the basis of the fact that the Brownian particles in due course of time tend to diffuse into the medium on account of their random motion. As a consequence of Brownian motions executed by the individual particles, the ordinary process diffusion must arise. A connection must exist, therefore between the properties of Brownian motion and the ordinary diffusion coefficient of a colloid. Einstein procedue was to establish a relation between them.

Einstein determined the diffusion coefficient in two ways : (i) from the irregular random motion of the suspended particles, (ii) from the difference in osmotic pressure between different parts due to differences in concentration of the suspended particles which gives rise to the phenomenon of diffusion.

**(i) Calculation of diffusion coefficient of random molecular motion** : Let us suppose that the molecular concentration has a gradient along the X-axis causing diffusion of the particles and that every particle suffers the displacement Δ in time $t$. Imagine a cylinder with its axis parallel to the X-axis and its end surfaces $S_1$ and $S_2$ and area of cross section $A$, separated by a distance Δ as shown in fig. 5.19



(Fig. 5.19)

Let the molecular concentration at $S_1$ and $S_1$ be $n_1$ and $n_2$ $(n_1 > n_2)$. Then the number of particles crossing the surface $S_1$ to the right in time $t$ is $\frac{1}{2}\Delta A n_1$, because only half of the particles contained in a cylinder of volume $\Delta A$ situated to the left of $S_1$ will cross it in time $t$ (the other half going towards left). Similarly the number of particles crossing the end face $S_2$ to the left in time $t$ is $\frac{1}{2}\Delta A n_2$. Hence the excess of particles crossing a middle layer to the right.

$$= \frac{1}{2}(n_1 - n_2)\,\Delta A$$

But $\frac{n_1 - n_2}{\Delta} = -\frac{dn}{dx}$, the gradient of concentration.

Hence the number of particles crossing a plane between $S_1$ and $S_2$ per unit area per second

$$= -\frac{1}{2}\cdot\frac{\Delta^2}{t}\cdot\frac{dn}{dx}$$

From the definition of diffusion coefficient, this number must to equal to $-D\frac{dn}{dx}$. Therefore

$$-D\frac{dn}{dx} = -\frac{1}{2}\frac{\Delta^2}{t}\cdot\frac{dn}{dx}$$

$$D = \frac{\Delta^2}{2t} \qquad \ldots(1)$$

**(ii) Calculation of diffusion coefficient from the difference in osmotic pressure between different parts due to differences is concentration of the suspended particles.** Let the osmotic pressure acting on the end surfaces $S_1$ and $S_2$ be $P_1$ and $P_2$ respectively. From the gas laws $P_1 = n_1kT$ and $P_2 = n_2kT$ where $k$ is the Boltzmann constant and $T$ the absolute temperature. Due to this difference of pressure, the cylinder will experience a force equal to

$$(P_1 - P_2)\,A = (n_1kT - n_2kT)\,A$$

$$= (n_1 - n_2)\,kTA.$$

This action of this force is to push the cylinder to the right *i.e.*, in the positive direction of the X-axis. In $n$ is the mean concentration, then this force acts on $n\Delta A$ particles contained in the cylinder. Thus the force acting on a single particle is given by

$$f = \frac{(n_1 - n_2)\,kTA}{n\Delta A}$$

---

$$= \frac{kT}{n}\cdot\frac{n_1 - n_2}{\Delta} = \frac{kT}{n}\left(-\frac{dn}{dx}\right)$$

$$= -\frac{1}{n}kT\frac{dn}{dx}$$

As the particle is suspended in a viscous medium, we may assume that the law of viscous resistance is that given by Sir George Stroke for spherical particles of radius $r$. Using Stoke's law.

$$f = 6\pi\eta r v = -\frac{1}{n}kT\frac{dn}{dx}$$

$$nv = -\frac{kT}{6\pi\eta r}\cdot\frac{dn}{dx}$$

where $v$ is the velocity of the particle and η the coefficient of viscosity of the fluid. This expression represents the number of particles moving to the right per second per unit area and from the definition of diffusion coefficient must be equal to $-D\frac{dn}{dx}$ *i.e.*,

$$\Rightarrow \qquad nv = -D\frac{dn}{dx} \text{ or } -\frac{kT}{6\pi\eta r}\cdot\frac{dn}{dx} = -D\frac{dn}{dx}$$

$$\text{or} \qquad D = \frac{kT}{6\pi\eta r} = \frac{RT}{N}\left(\frac{1}{6\pi\eta r}\right) \qquad \left(\text{Since } k = \frac{R}{N}\right) \qquad \ldots(2)$$

Eliminating $D$ between eqn. (1) and (2), we get

$$\frac{\Delta^2}{2t} = \frac{RT}{N}\left(\frac{1}{6\pi\eta r}\right)$$

$$\text{or} \qquad \Delta^2 = \frac{RT}{N}\left(\frac{t}{3\pi\eta r}\right) \qquad \ldots(3)$$

Thus the average squared displacement of a particle due to Brownian movement along the X-axis in a time $t$ is given by an equation containing the gas constant $R$, the absolute temperature $T$, the Avogadro number $N$, the coefficient of viscosity η and the radius of the particles $r$. As all these quantities can be measured, it may experimentally be verified. Einstein's equation (3) has actually been confirmed experimentally in numerous ways and has been used to determine the Boltzmann constant $k$ or the Avogadro's number $N = R/k$.

## 5.18 Experimental Verification of Brownian Movement Equation and Determination of Avogadro number

The French physicist, Jean Perin, tested the hypothesis that the suspended particles, which dance about in a stationary liquid in Brownian movement behave like large gas molecules. He showed that these particles have all the properties of a gas including equipartition of energy. He linked an emulsion to a miniature ponderable atomsphere in which the number of particles per unit volume varied with height in the same manner as it does in the earth's atmosphere.

The Brownian particles form a gas in equilibrium under the action of force of gravity. Let us consider the equilibrium of a vertical imaginary cylinder in the gas of unit crosssection and having end faces at heights $z$ and $z + dz$, $z$ increasing vertically upwards. If $P$ and $P + dP$ are the pressures at two faces and ρ the density of the gas inside the cylinder, the force due to gravity

$$mg = 1\,dz\,\rho g = g\rho\,dz.$$

For the equilibrium of the cylinder, the net force on the layer

$$(P + dP) - P + g\rho\,dz = 0$$

$$\text{or} \qquad dP = -g\rho\,dz.$$

The negative sign here denotes that the pressure decreases as the height increases. If $m$ is the mass of a single molecule and $n$ the average number of milecules per unit volume, then

$$\rho = mn = \frac{mN}{V},$$

where $N$ is the Avogadro number, $V$ the gram molecular volume.

Hence,

$$dP = -\frac{mgN}{V} dz$$

If these particles obey the gas laws, then applying $PV = RT$, the expression becomes

$$\frac{dP}{P} = -\frac{mgN}{RT} dz.$$

Integrating we obtain

$$\int_{P_0}^{P} \frac{dP}{P} = -\int_{z_0}^{z} \frac{mgN}{RT} dz.$$

or

$$\log\left(\frac{P}{P_0}\right) = -\frac{mgN}{RT}(z - z_0)$$

or

$$P = P_0 e^{-(mg N/RT)(z - z_0)}$$

Further, since the number of molecules per unit volume, $n_0$ and $n$ are proportional to $P_0$ and $P$ respectively,

$$n = n_0 e^{-(mgN/RT)(z - z_0)} \qquad \text{...(1)}$$

This is the well known *law of atmospheres* and indicates that the density of particles increases exponentially as the height decreases.

In the case of colloidal suspensions, the force of gravity acts on the particles which are buoyed up by the liquid in which they are suspended. If $d$ and $d'$ are the densities of the particles and the interamolecular liquid, the effective mass of the particle $= \frac{4}{3}\pi r^3 (d - d')$ where $r$ is the radius of the particles. Using this value of $m$, we get

$$\frac{n}{n_0} = e^{-4/3\, \pi r^3 (d - d')(gN/RT)(z - z_0)}$$

or

$$\log\frac{n}{n_0} = -\frac{4\pi r^3 (d - d') gN (z - z_0)}{3RT}$$

or

$$N = \frac{3RT}{4\pi r^3 (d - d') g (z - z_0)} \log\frac{n_0}{n} \qquad \text{...(2)}$$

This formula furnishes a convenient method for the determination of $N$. Perrin, working with the colloidal suspensions of gum mastic and gum gamboge, made a direct measurement of all the quantities in eq. (2) except $N$ and found the value of $N$ to be $6{\cdot}5$ to $7{\cdot}2 \times 10^{23}$.

Perrin then observed the motion of individual particles, projecting them on a screen for this purpose and showed that the average squared displacement of a particles during a time $t$ was approximately proportional to $t$, as required' by Einstein's equation

$$\overline{\Delta}^2 = \frac{RT}{N}\left(\frac{t}{3\pi\eta r}\right) \qquad \text{...(3)}$$

Perrin found that making $t = 220$ seconds; $\Delta^2$ was about four times what it was for 30 seconds *i.e.*,

$$\frac{\overline{\Delta}^2_{20}}{\overline{\Delta}^2_{120}} = \frac{30}{120} = \frac{1}{4}$$

He then measured the diameter of Brownian particle and from the known viscosity of water, calculated $N$ by means of Einsteins equation (3). The best value found in this manner was $6{\cdot}8 \times 10^{23}$.

*The fair agreement of Perrins value of N obtained from the law of atmospheres and from Einsteins equation verifies the equation with in the limits of experimental errors.* It gives the striking confirmation of the Kinetic Theory and shows conclusively that all the gas laws can be applied to Brownian particles

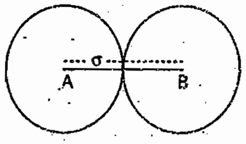
Perrin further *verified the variation of* $\overline{\Delta}^2$ *with temperature as* demanded by Einsteins equation. If $\sqrt{\overline{\Delta}_1^2}$ and $\sqrt{\overline{\Delta}_2^2}$ are the average displacements at two temperatures $T_1$ and $T_2$ at which viscosities are $\eta_1$ and $\eta_2$ then

$$\sqrt{\left(\frac{\overline{\Delta}_1^2}{\overline{\Delta}_2^2}\right)} = \sqrt{\left(\frac{T_1\eta_2}{T_2\eta_1}\right)}$$

According to it, the variation for $\sqrt{\left(\frac{\overline{\Delta}_2^2}{\overline{\Delta}_1^2}\right)}$ in one suspension for a temperature interval from 17°C to 90°C. should have been 2·05. Perrin actually observed it to be 2·2, thus leading to a verification of Einstein's equation.

## 5.19 Molecular Diameters

The term molecular diameter originates from the original picture of molecule as hard elastic spheres. When two such similar molecular spheres are placed side by side such that they are in contact (fig 5.20) then the distance $AB$ between their centres is called the molecular diameter. Maxwell defined the molecular diameter, as *the distance between the centres of two molecules when they act on another so as to have an encounter.* The definition is not entirely satisfactory because the molecules are not elasic spheres but actually, as we know today, consist of a positive nucleus surrounded by planetary electrons with orbital motions Moreover the electrical fields of force between the electrons and nuclei influence the molecular motion and hence when molecules act on each other at a distance by attractive or repulsive forces. The distance between their centres is not a definite quantity but varies during an encounter. In case of gases also the distance of approach is affected by the conditions of impact due to velocity distribution. But still, for simplicity, we may take the simple picture of elastic spheres of diameter σ for the present.



(Fig. 5.20)

Various kinetic theory methods have been employed in order to determine the molecular diameters. In section 5.20 we have shown that *for spherical molecules, the mean free path* is given by

$$\lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2 n} = \frac{0{\cdot}707}{\pi\sigma^2 n}$$

Since $\lambda$ can be determined experimentally, we are in a position to calculate $\sigma$ from the above equation. Let us take the case of hydrogen, as an example. For hydrogen, the mean free path $\lambda = 1{\cdot}45 \times 10^{-5}$ cm. and $n = 2{\cdot}705 \times 10^{19}$ per cm$^3$. Therefore the molecular diameter

$$\sigma = \sqrt{\left(\frac{0{\cdot}707}{\pi n\lambda}\right)} = \sqrt{\left(\frac{0{\cdot}707}{3{\cdot}14 \times 2{\cdot}705 \times 10^{19} \times 1{\cdot}45 \times 10^{-5}}\right)}$$

$$= 2{\cdot}38 \times 10^{-8} \text{ cm} = 2{\cdot}38 \text{ Å}$$

The *expressions for viscosity, conductivity and coefficient of diffusion* in terms of mean free path (derived in previous sections) can also be employed to determine $\sigma$. Taking for example the expression for viscosity $\eta$ which is given by $\eta = \frac{1}{3}\rho\bar{v}\lambda$

but $$\bar{v} = \sqrt{\left(\frac{8kT}{m\pi}\right)} \text{ and } \lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2 n} = \frac{V}{\sqrt{2}\,\pi\sigma^2 N};$$

where the molecular density $n = \frac{N}{V}$, $N$ being the Avogadro number and $V$ the gram molecular volume. Since $\rho = mn$, we have

$$\eta = \frac{1}{3}\frac{mnV}{\sqrt{2}\,\pi\sigma^2 N}\cdot\sqrt{\left(\frac{8kT}{m\pi}\right)}$$

$$= \frac{2\sqrt{(MRT)}}{3\pi^{3/2} N\sigma^2} \qquad \text{...(1)}$$

where $M$ is the molecular weight. Thus the product $N\sigma^2$ can be found with the help of eqn. (1) from the experimentally determined value of $\eta$ and if $N$ is known from other phenomenon, we can determine the molecular diameter $\sigma$.

Molecular diameter can also be determined by a study of the *deviation of gases from Boyle's law.* The term $b$ which is a correction term in Vander Waal's equation for the finite volume of the molecules present may at first be supposed to be the total unavailable space for molecular motion or the total volume of the sphere of exclusion which are spheres of radius equal to the diameter $\sigma$ of the molecules *i.e.,*

$$b = \frac{4}{3}\pi N\sigma^3.$$

But actually $b$ is only one-half of the value given above because if the centre of one molecule is kept out of this volume, it ensures that the centre of another molecules be kept at least at a distance of $\sigma$ from the molecule with which it is colliding. Thus $\frac{4}{3}\pi\sigma^3$ is the unavailable volume per pair of molecules and since there are $\frac{N}{2}$ pairs of molecules in one gram mole, the total volume excuded because of finite size of the molecules is

$$b = \frac{N}{2} \times \frac{4}{3}\pi\sigma^3 = \frac{2}{3}\pi\sigma^2 N \qquad \text{...(2)}$$

As $b$ can be determined experimentally and hence if $N$ is known $\sigma$ may be evaluated.

The value of the molecular diameter of $\sigma$ some of the common gases has been found to be the order of 3Å. Table below gives some of the values of $\sigma$ obtained by various methods.

| Gas | Values of $\sigma \times 10^{-8}$ cm | | | |
|---|---|---|---|---|
| | Viscosity | Conduction of heat | Diffusion | Values of $b$ |
| Hydrogen | 2·47 | 2·40 | 2·72 | 2·54 |
| Nitrogen | 3·50 | 3·31 | 3·84 | 3·56 |
| Carbon dioxide | 4·18 | 4·32 | 4·38 | 3·42 |
| Oxygen | 3·39 | 3·11 | 3·64 | 2·90 |
| Carbon dioxide | 3·74 | 3·74 | 3·74 | 3·32 |

It will be seen that the values obtained from different methods for the molecular diameter are in satisfactory agreement.

## SOLVED EXAMPLES

**Ex. 4.** *The mass of an oxygen molecule is* $5{\cdot}28 \times 10^{-26}$ *kg., and its mean* $< v >$ *at N.T.P. is* $4{\cdot}25 \times 10^2$ *m/s. Calculate the average kinetic energy of an oxygen molecule at* $0^\circ$C.

**Ans.** Average speed $$< v > = \sqrt{\left(\frac{8kT}{m\pi}\right)} \qquad \text{...(2)}$$

r.m.s. speed $$v_{r.m.s.} = \sqrt{\left(\frac{3kT}{m}\right)} \qquad \text{...(3)}$$

$$\therefore \quad \frac{v_{r.m.s.}}{< v >} = \frac{\sqrt{[3kT/m]}}{\sqrt{[8kT/m\pi]}} = \sqrt{\left(\frac{3\pi}{8}\right)}$$

$$\therefore \quad v^2_{r.m.s.} = \frac{3\pi}{8}(< v >)^2$$

$\therefore$ Average kinetic energy of oxygen molecule

$$= \frac{1}{2} m v^2_{r.m.s.} = \frac{1}{2} m \cdot \frac{3\pi}{8} \cdot (< v >)^2 = \frac{3}{16} m\pi (< v >)^2$$

$$= \frac{3}{16} \times (5{\cdot}28 \times 10^{-26} \text{ kg}) \times 3{\cdot}14 \times (4{\cdot}25 \times 10^2 \, m/s)^2$$

$$= 5{\cdot}614 \times 10^{-21} \text{ joule}$$

**Ex. 5.** *The mean free path of the molecules of a gas is* $2 \times 10^{-7}$ *meter at pressure p and temperature 200 K. Calculate its value at (i) p, 400 K, (ii) 2p, 200 K, (iii)* $\frac{1}{2}p$, *400 K.*

**Solution.** The mean free path $\lambda$, in terms of number of gas molecules per unit volume ($n$) and molecular diameter ($\sigma$) is given by

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

From the gas equation $pV = RT$, we can show that

$$p = nkT,$$

where $k$ is Boltzmann's constant. Thus

$$\lambda = \frac{kT}{\sqrt{2}\,\pi\, p\, \sigma^2}.$$

At pressure $p$ and $T = 200$ K; we have

$$\lambda = \frac{k\,(200)}{\sqrt{2}\,\pi p \sigma^2} = 2 \times 10^{-7} \text{ metre.}$$

(i) At $p$, 400 K; we have

$$\lambda = \frac{k\,(400)}{\sqrt{2}\,\pi\, p\, \sigma^2} = \mathbf{4 \times 10^{-7}} \textbf{ metre.}$$

(ii) At $2p$, 200 K; we have

$$\lambda = \frac{k\,(200)}{\sqrt{2}\,\pi\,(2p)\,\sigma^2} = \mathbf{1 \times 10^{-7}} \textbf{ metre.}$$

(iii) At $p/2$, 400 K; we have

$$\lambda = \frac{k\,(400)}{\sqrt{2}\,\pi\,(p/2)\,\sigma^2} = \mathbf{8 \times 10^{-7}} \textbf{ metre.}$$

**Ex. 6.** *Calculate the diameter of a molecule of nitrogen if the mean free path $\lambda = 0{\cdot}80 \times 10^{-5}$ cm and $n = 2{\cdot}7 \times 10^{19}$ molecules/cm$^3$ at normal temperature and pressure.*

**Solution.** Let $\sigma$ be the diameter of the molecule. The mean free path is

$$\lambda = \frac{1}{\sqrt{2}\,\pi n \sigma^2} = \frac{1}{1{\cdot}41\,\pi\, n\, \sigma^2}.$$

$$\therefore \quad \sigma = \sqrt{\frac{1}{1{\cdot}41\,\pi\, n\, \lambda}}$$

$$= \sqrt{\frac{1}{1{\cdot}41 \times 3{\cdot}14 \times (2{\cdot}7 \times 10^{19}/cm^3) \times (0{\cdot}80 \times 10^{-5}\text{ cm})}}$$

$$= 3{\cdot}2 \times 10^{-8}\text{ cm} = \mathbf{3{\cdot}2\text{ Å}}.$$

**Ex. 7.** *The molecular diameter of a gas is $3 \times 10^{-10}$ m. Calculate the mean free path at temperature 27°C and pressure 1 atmosphere.*

**Solution.** The mean free path at temperature $T$ and pressure $P$ is given by

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P} = \frac{kT}{1{\cdot}41\,\pi\,\sigma^2\, p}$$

Given $T = 27°\text{C} = 300$ K, $P = 1$ atmos $= 1{\cdot}01 \times 10^5\ N/m^2$

$$\sigma = 3 \times 10^{-10}\ m$$

and

$$k = 1{\cdot}38 \times 10^{-23}\ J/K$$

$$\therefore \quad \lambda = \frac{1{\cdot}38 \times 10^{-23} \times 300}{1{\cdot}414 \times 3{\cdot}14 \times (3 \times 10^{-10})^2 \times 1{\cdot}01 \times 10^5}$$

$$= \mathbf{1{\cdot}02 \times 10^{-7}\ m.}$$

**Ex. 8.** *Given : effective molecular diameter $2{\cdot}0 \times 10^{-8}$ cm, average speed of gas molecules at a given temperature is $1{\cdot}0 \times 10^5$ cm/s and number of molecules per cm$^3$ is $3 \times 10^{19}$. Calculate the mean free path and the corresponding collision frequency.*

**Solution.** The mean free path $\lambda$, in terms of molecular density $n$ and molecular diameter $\sigma$, is

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

Here $\qquad n = 3 \times 10^{19}/\text{cm}^3$ and $\sigma = 2{\cdot}0 \times 10^{-8}$ cm.

$$\therefore \quad \lambda = \frac{1}{1{\cdot}41 \times 3{\cdot}14 \times (3 \times 10^{19}/\text{cm}^3) \times (2{\cdot}0 \times 10^{-8}\text{ cm})^2}$$

$$= \mathbf{1{\cdot}88 \times 10^{-5}\text{ cm.}}$$

The mean free path is the mean distance travelled by the molecule between two successive collisions. Therefore, the mean time-interval between two collisions is the mean free path divided by mean molecular speed. Hence, the number of collisions per second *i.e.* collision frequency is

$$\frac{\bar{v}}{\lambda} = \frac{1{\cdot}0 \times 10^5\text{ cm/s}}{1{\cdot}88 \times 10^{-5}\text{ cm}} = \mathbf{5{\cdot}3 \times 10^9\ \text{second}^{-1}}.$$

**Ex. 9.** *The diameter of an oxygen molecule is roughly 3Å. Estimate the mean free path and mean time between collisions for oxygen gas at N.T.P. The number of molecules per cm$^3$ at N.T.P. is $3 \times 10^{19}$. Given : Avogadro number $N = 6{\cdot}02 \times 10^{26}$ per kg mole, Boltzmann's constant $k = 1{\cdot}38 \times 10^{-23}$ J/K and molecular weight $M$ of oxygen = 32 g/mole.*

**Solution.** The mean free path $\lambda$, in terms of molecular density $n$ and molecular diameter $\sigma$, is given by

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

Here $n = 3 \times 10^{19}/\text{cm}^3 = 3 \times 10^{25}/\text{m}^3$ and $d = 3\text{Å} = 3 \times 10^{-10}$ m.

$$\therefore \quad \lambda = \frac{1}{1{\cdot}41 \times 3{\cdot}14 \times (3 \times 10^{25}/\text{m}^3) \times (3 \times 10^{-10}\text{ m})^2}$$

$$= \mathbf{8{\cdot}36 \times 10^{-8}\text{ m.}}$$

The mean free path is the distance travelled by the molecule between two successive collisions. Therefore, the mean time-interval between two collisions is $\lambda/\bar{v}$ where $\bar{v}$ is mean molecular speed.

Now, the mean molecular speed is given by

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

where $m$ is the mass of the molecule and is given by

$$m = M/N = \frac{32}{6{\cdot}02 \times 10^{26}} = 5{\cdot}31 \times 10^{-26}\text{ kg.}$$

The normal temperature is $T = 273$ K. Thus, we have

$$\bar{v} = \sqrt{\frac{8 \times (1{\cdot}38 \times 10^{-23}\text{ Joule/K}) \times 273\text{ K}}{3{\cdot}14 \times (5{\cdot}31 \times 10^{-26}\text{ Kg})}}$$

$$= 4{\cdot}25 \times 10^2\text{ m/s.}$$

Therefore, mean time between collisions is

$$\frac{\lambda}{\bar{v}} = \frac{8{\cdot}36 \times 10^{-8}\text{ m}}{4{\cdot}25 \times 10^2\text{ m/sec.}} = \mathbf{1{\cdot}97 \times 10^{-10}}\text{ s.}$$

**Ex. 10.** *Calculate the mean free path of argon molecules at 25°C and 1 atmosphere pressure. Given : $\sigma = 2{\cdot}56$ Å and $k = 1{\cdot}38 \times 10^{-23}$ joule/K.*

**Solution.** Let us first calculate the number of molecules per unit volume of argon gas for the conditions stated. For 1 mole of gas, the equation of state is

$$pV = RT.$$

But $R = Nk$, where $N$ is number of molecules in 1 mole of gas (Avogadro's number). Thus

$$pV = NkT.$$

The number of molecules per unit volume is therefore

$$n = \frac{N}{V} = \frac{p}{kT}.$$

Here $p = 1$ atmos $= 1{\cdot}013 \times 10^5$ newton/meter$^2$ and $T = 25°\text{C} = 298$ K.

$$\therefore \quad n = \frac{1{\cdot}013 \times 10^5 \text{ N/m}^2}{(1{\cdot}38 \times 10^{-23} \text{ joule/K}) \times 298 \text{ K}} = 2{\cdot}46 \times 10^{25}/\text{m}^3.$$

Now, the mean free path is

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

Substituting the above value of $n$ and given value of

$\sigma$ (= 2·56 Å = $2{\cdot}56 \times 10^{-10}$ m)

$$\lambda = \frac{1}{1{\cdot}41 \times 3{\cdot}14 \times (2{\cdot}46 \times 10^{25}) \times (2{\cdot}56 \times 10^{-10})^2}$$

$$= \mathbf{1{\cdot}4 \times 10^{-7}\ m.}$$

**Ex. 11.** *The mean free path of the molecules of a gas at 25°C is $2{\cdot}63 \times 10^{-5}$ metre. If the radius of the molecule is $2{\cdot}56 \times 10^{-10}$ meter, find the pressure of the gas. $k = 1{\cdot}38 \times 10^{-23}$ joule/degree.*

**Solution.** In usual notations,

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

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

$$= \frac{1}{1{\cdot}41 \times 3{\cdot}14 \times (2{\cdot}63 \times 10^{-5} \text{ m}) \times (5{\cdot}12 \times 10^{-10} \text{ m})^2}$$

$$= 3{\cdot}28 \times 10^{22}/\text{m}^3.$$

We know that the number of molecules per unit volume of the gas is given by

$$n = \frac{p}{kT}.$$

Putting the above value of $n$ and $T = 25°\text{C} = 298$ K, we have

$$p = nkT$$

$$= (3{\cdot}28 \times 10^{22}/\text{m}^3)\,(1{\cdot}38 \times 10^{-23} \text{ joule/K})\,(298 \text{ K})$$

$$= 135 \text{ newton/meter}^2$$

$$= \frac{135 \text{ N/m}^2}{(13{\cdot}6 \times 10^3 \text{ kg/m}^3)\,(9{\cdot}8 \text{ N/kg})}$$

$$= 1{\cdot}0 \times 10^{-3} \text{ meter}$$

**= 1·0 mm of mercury.**

**Ex. 12.** *The molecular diameter of nitrogen is 3·5 Å. Calculate (i) collision cross-section, (ii) mean free path and (iii) collision frequency for nitrogen at N.T.P. (Boltzmann constant $k = 1{\cdot}38 \times 10^{-23}$ J/K; Avogadro's number $N = 6{\cdot}025 \times 10^{23}$ per gm mole and mass of hydrogen atom = $1{\cdot}67 \times 10^{-24}$ gm.)*

**Solution.** (i) If a molecule of diameter $\sigma$ is moving with average speed $\bar{v}$, its sphere of influence sweeps out in one second a cylinder of base area $\pi\sigma^2$ and length $\bar{v}$. The quantity $\pi\sigma^2$ is called the **collision cross-section**, which is thus

$$3{\cdot}14 \times (3{\cdot}5 \text{ Å})^2 = \mathbf{38{\cdot}46\ Å^2}.$$

(ii) The number of molecules per unit volume in a gas is given by

$$n = \frac{p}{kT}.$$

At N.T.P.,

$p = 0{\cdot}76$ m of Hg $= 0{\cdot}76 \times 13{\cdot}6 \times 10^3 \times 9{\cdot}8$ N/m$^2$ and $T = 273$ K.

$$\therefore \quad n = \frac{0{\cdot}76 \times 13{\cdot}6 \times 10^3 \times 9{\cdot}8}{(1{\cdot}38 \times 10^{-23}) \times 273} = 2{\cdot}69 \times 10^{25}/\text{m}^3.$$

The mean free path is therefore

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

$$= \frac{1}{1{\cdot}41 \times 3{\cdot}14 \times (2{\cdot}69 \times 10^{25}/\text{m}^3) \times (3{\cdot}5 \times 10^{-10} \text{ m})^2}$$

$$= \mathbf{6{\cdot}85 \times 10^{-8}\ m.}$$

(iii) The mean speed of a molecule of mass $m$ in a gas at temperature T Kelvin is given by

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

Here $m = 28 \times (1{\cdot}67 \times 10^{-24} \text{ gram}) = 28 \times 1{\cdot}67 \times 10^{-27}$ kg where 28 is molecular weight of nitrogen and $T = 273$ K.

$$\therefore \quad \bar{v} = \sqrt{\frac{8 \times (1{\cdot}38 \times 10^{-23}) \times 273}{3{\cdot}14 \times (28 \times 1{\cdot}67 \times 10^{-27})}}$$

$$= 4{\cdot}53 \times 10^2 \text{ m/s}.$$

The frequency of collision is

$$\frac{\bar{v}}{\lambda} = \frac{4{\cdot}53 \times 10^2}{6{\cdot}85 \times 10^{-8}} = \mathbf{6{\cdot}6 \times 10^9 \text{ per second.}}$$

**Ex. 13.** *Calculate the mean free path, frequency of collision and the diameter of nitrogen molecule at N.T.P. Given : coefficient of viscosity $\eta = 1{\cdot}66 \times 10^{-4}$ dyne/(cm$^2$ – vel – gradient), density*

*$\rho = 1{\cdot}25 \times 10^{-3}$ gm/cm$^3$, average speed $\bar{v} = 4{\cdot}5 \times 10^4$ cm/s and molecular density $n = 2{\cdot}7 \times 10^{19}$ per cm$^3$ for $N_2$ at N.T.P.*

**Solution.** According to the kinetic theory, the viscosity of a gas is

$$\eta = \tfrac{1}{3} mn\,\bar{v}\,\lambda,$$

where $m$ is the mass of a molecule. But $mn = \rho$ (density of the gas).

$$\therefore \quad \eta = \tfrac{1}{3} \rho\,\bar{v}\,\lambda$$

or

$$\lambda = \frac{3\eta}{\rho\,\bar{v}}.$$

Putting the given data :

$$\lambda = \frac{3 \times 1{\cdot}66 \times 10^{-4}}{1{\cdot}25 \times 10^{-3} \times 4{\cdot}5 \times 10^4} = \mathbf{8{\cdot}8 \times 10^{-6}\ cm.}$$

Since the mean free path $\lambda$ is the average distance travelled by the molecule between two successive collisions, we have

$$\text{Frequency of collision } \frac{\bar{v}}{\lambda}$$

$$= \frac{4{\cdot}5 \times 10^4}{8{\cdot}8 \times 10^{-6}} = \mathbf{5{\cdot}1 \times 10^9.}$$

The mean free path is given by

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

where $\sigma$ is the diameter of the molecule.

$$\therefore \quad \sigma = \sqrt{\frac{1}{\sqrt{2}\,\pi n \lambda}}$$

$$= \sqrt{\frac{1}{1{\cdot}41 \times 3{\cdot}14 \times (2{\cdot}7 \times 10^{19}) \times (8{\cdot}8 \times 10^{-6})}}$$

$$= \mathbf{3{\cdot}1 \times 10^{-8}\ cm = 3{\cdot}1\ \text{Å}.}$$

**Ex. 14.** *The coefficient of viscosity of oxygen at NTP is $1{\cdot}96 \times 10^{-4}$ gm/(cm-sec) and its molecular weight $M = 32$.. Calculate the diameter and collision cross-section of $O_2$ molecule. Given : Boltzmann constant $k = 1{\cdot}38 \times 10^{-16}$ erg/degree and Avogadro's number $N = 6{\cdot}025 \times 10^{23}$ per gram mole.*

**Solution.** The mass of the $O_2$ molecule is

$$m = \frac{M}{N} = \frac{32}{6{\cdot}025 \times 10^{23}} = 5{\cdot}31 \times 10^{-23}\ \text{gram}.$$

The number of $O_2$ molecules per unit volume of the gas at NTP (273 K and 1 atm-pressure) is

$$n = \frac{p}{kT} = \frac{76 \times 13{\cdot}6 \times 980\ \text{dynes/cm}^2}{(1{\cdot}38 \times 10^{-16}\ \text{erg/K}) \times 273\ \text{K}} = 2{\cdot}69 \times 10^{19}/\text{cm}^3.$$

The average speed of $O_2$ molecules at 273 K is

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8 \times (1{\cdot}38 \times 10^{-16}) \times 273}{3{\cdot}14 \times (5{\cdot}31 \times 10^{-23})}} = 4{\cdot}25 \times 10^4\ \text{cm/sec}.$$

Now, according to kinetic theory, the viscosity of a gas in terms of mean free path, is given by $\eta = \frac{1}{3} m\,n\,\bar{v}\,\lambda$.

$$\therefore \quad \lambda = \frac{3\eta}{m\,n\,\bar{v}}$$

$$= \frac{3 \times (1{\cdot}96 \times 10^{-4})}{(5{\cdot}31 \times 10^{-23}) \times (2{\cdot}69 \times 10^{19}) \times (4{\cdot}25 \times 10^4)}$$

$$= \mathbf{9{\cdot}68 \times 10^{-6}\ cm.}$$

The mean free path $\lambda$ is given by

$$\lambda = \frac{1}{\sqrt{2}\,\pi\,n\,\sigma^2} = \frac{1}{1{\cdot}41\,\pi\,n\,\sigma^2}.$$

Therefore, the diameter of $O_2$ molecule is

$$\sigma = \sqrt{\frac{1}{1{\cdot}41\,\pi\,n\,\lambda}}$$

$$= \sqrt{\frac{1}{1{\cdot}41 \times 3{\cdot}14 \times (2{\cdot}69 \times 10^{19}) \times (9{\cdot}68 \times 10^{-6})}}$$

$$= 3 \times 10^{-8}\ \text{cm} = \mathbf{3\text{Å}}.$$

The collision cross-section of $O_2$ molecules is

$$\pi\,\sigma^2 = 3{\cdot}14 \times (3 \times 10^{-8}\ \text{cm})^2 = \mathbf{28 \times 10^{-16}\ cm^2.}$$

**Ex. 15.** *Calculate the radius of an oxygen molecule if its coefficient of thermal–conductivity $K = 24 \times 10^{-3}$ joule/(meter-sec-deg) at $0^\circ$C and specific heat at-constant volime $C_v = 20{\cdot}9 \times 10^3$ joule/kilomole-degree. Boltzmann constant $k = 1{\cdot}38 \times 10^{-23}$ joule/degree and mass of an oxygen molecule $= 5{\cdot}31 \times 10^{-26}$ kg.*

**Solution.** The average velocity of oxygen molecules at $0^\circ$C ($= 273$ K) is given by

$$\bar{v} = \sqrt{\frac{8kT}{\pi\,m}} = 425\ \text{meter/sec}.$$

If $\sigma$ is the molecular diameter, then the coefficient of thermal conductivity is given by

$$K = \frac{1}{3\sqrt{2}}\,\frac{m\,\bar{v}\,c_v}{\pi\,\sigma^2}:$$

$$\text{Hence } c_v = \frac{C_v}{M} = \frac{20{\cdot}9 \times 10^3}{32} = 0{\cdot}653 \times 10^3\ \text{joule/kg-degree}.$$

$$\therefore \quad \sigma^2 = \frac{m\,\bar{v}\,c_v}{3\sqrt{2}\,\pi\,K}$$

$$= \frac{(5{\cdot}31 \times 10^{-26}) \times 425 \times (0{\cdot}653 \times 10^3)}{3 \times 1{\cdot}41 \times 3{\cdot}14 \times (24 \times 10^{-3})} = 4{\cdot}6 \times 10^{-20}.$$

$$\therefore \quad \sigma = 2{\cdot}2 \times 10^{-10}\ \text{meter} = 2{\cdot}1\ \text{Å}.$$

$$\therefore \quad \text{radius} = \mathbf{1{\cdot}05\ \text{Å}.}$$

**Ex. 16.** *The coefficient of self-diffusion of oxygen at 273 K and 1 atmosphere pressure is $1{\cdot}8\times10^{-5}\ m^2/s$. Estimate mean free path. The gas constant is $8{\cdot}3\times10^3$ Joule/kg-mole-K and molecular weight of oxygen is 32.*

**Solution.** The average velocity of oxygen molecules at 273 K is given by

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

mass of the molecule, $m=\frac{M}{N}$, where $M$ is molecular weight and $N$ is Avogadro's number. and $k=\frac{R}{N}$

$$\bar{v}=\sqrt{\frac{8\,(R/N)}{\pi\,(M/N)}}$$

$$=\sqrt{\frac{8RT}{\pi M}}$$

$$=\sqrt{\frac{8\times(8{\cdot}3\times10^3)\times273}{3{\cdot}14\times32}}=4{\cdot}25\times10^2\ \text{m/s}$$

Now, the coefficient of self-diffusion $D$ is related to the mean free path $\lambda$ by

$$D=\tfrac{1}{3}\lambda\,\bar{v}$$

so that

$$\lambda=\frac{3D}{\bar{v}}$$

$$=\frac{3\times1{\cdot}8\times10^{-5}\ \text{m}^2/\text{s}}{4{\cdot}25\times10^2\ \text{m/s}}=\mathbf{1{\cdot}27\times10^{-7}\ m.}$$

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## EXERCISES

### SHORT ANSWER QUESTIONS

1. State assumptions of kinetic theory of gases.
2. State the law of distribution of velocities in a monoatomic gas.
3. Explain concept of temperature on the basis of kinetic theory of gases.
4. What do you mean by root mean square velocity, mean velocity and most probable velocity ?
5. Out of root mean square velocity, mean velocity and most probable velocity which one is related directly to mean kinetic energy of molecules of gas ?
6. Write equation of state for an ideal gas
   (i) for 1 mole (ii) for $n$ moles and (iii) for $n$-molecules.
7. Define mean free path. Write an expression for it. On what factors does the mean free path depend ?
8. What is the effect of temperature and pressure on mean free path ?
9. What do you mean by transport phenomena ?
10. What will be the meaning of mean free path if we treat molecules as centres of force at a distance and reject the idea of actual collision ?

11. Explain why, there is a time-lag between opening an ammonia bottle in one corner of a room and smelling it in the other corner.
12. A gas is filled in a box whose opposite walls are maintained at different temperatures. Heat-conduction then takes place through the gas; explain.
13. Prove for a gas the relation $K/\eta=c_v$, where K is coefficient of thermal conductivity, $\eta$ is coefficient of viscosity and $c_v$ is specific heat at constant volume.
14. The air that leaks into vacuum system almost always contains a larger fraction of hydrogen and helium than that found in the outside atmosphere. How can this observation be understood on the basis of kinetic theory ?

### LONG ANSWER QUESTIONS

1. Derive Maxwell's distribution low of velocities and discuss its experimental varification. *(Ranchi 2004)*
2. Discuss the main assumptions of kinetic theory of gases and obtain expression for the number of molecules lying between speed $v$ and $v+dv$.
3. Outline the essential features of kinetic theory of gases. Discuss any direct evidence that may be in favour of the fundamental hypothesis that the ultimate particles of matter are in rapid and irregular motion.
4. The distribution of one component of velocity in a perfect monoatomic gas is given by $f(u)=ae^{-bu^2}$ where $a$ and $b$ are functions of temperaure
   (i) What does $f(u)$ stand for
   (ii) Deduce the values of $a$ and $b$ given by
   $$\int_0^\infty e^{-bu^2}\,du=\frac{1}{2}\sqrt{\left(\frac{\pi}{b}\right)};\ \int_0^\infty u^2e^{-bu^2}\,du=\frac{1}{2}\sqrt{\left(\frac{\pi}{b^3}\right)}$$
   (iii) Dedue the relation
   $$f(c)=4\pi a^2e^{-bc^2}c^2.$$
   (iv) Show typical distribution curves for $u$ for a given gas at two temperatures say 80K and 800K. Show also the corresponding curve for $c$. *(Meerut 2005; Agra 2004)*
5. Show that in an assembly of particles the number $n_r$ of particle having energy equal to $\varepsilon_r$ is given by the relation
   $$n_r=Ne^{-\varepsilon_r/kT}$$
   where $N$ is the total number of particles. *(Agra 1997)*
6. Deduce the Maxwell-Boltzmann law for the distribution of velocities of the particles of a gas. Apply it to calculate the width of spectral lines due to Doppler shift. *(Agra 2003)*
7. Find the number of atoms that strike a unit area per unit time assuming that the atoms in a gas satisfy the Maxwell distribution. Find the number of molecules escaping through an infinitesimal hole of area $A$ and the rate of loss of energy in the vessel. *(Garhwal 2000; Agra 2000)*
8. Derive Maxwell-Boltzmann velocity districution law. Mention the cases where it fails and explain why. *(Meerut 1999; Delhi 2001)*

9. Show that the probability of a gas molecule with $x$ components of velocity between $v_x$ and $v_x + dv_x$ is equal to

$$P(v_x)\,dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\,dv_x.$$

where the symbols have their usual meaning.

10. The probability of a molecule having $x$ component of velocity in the range $v_x$ to $v_x + dv_x$ is given by

$$P(v_x)\,dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} \cdot e^{-mv_x^2/2kT}\,dv_x.$$

where the symbols have their usual meaning. (a) Show that

(i) the function $P$ is symmetrically distributed about $v_x = 0$

(ii) maximum value of $P = \left(\frac{m}{2\pi kT}\right)^{1/2}$

(iii) the average value of $v_x^2 = \frac{kT}{m}$

(b) Find the value of $v_x$ for which the probability falls to

(i) 1/2 times

(i) 1/10 times, the maximum value $\left[\text{Ans. (i) } \sqrt{\left(\frac{1{\cdot}38\,kT}{m}\right)},\ \text{(ii) } \sqrt{\left(\frac{9{\cdot}2\,kT}{m}\right)}\right]$

11. Show that the number of gas molecules with speed between $v$ and $v + dv$ is equal to

$$N_v\,dv = 4\pi N\left(\frac{m}{2\pi kT}\right)^{1/2} v^2 e^{-mv^2/2kT}\,dv.$$

12. Show that the number of molecules lying in the energy range $\in$ to $\in + d\varepsilon$ is given by

$$n(\in)\,d\in = 2\pi N\left(\frac{1}{\pi kT}\right)^{3/2} \in^{1/2} e^{-\varepsilon/kT}\,d\varepsilon.$$

Also find an expression for the most probable and mean energy. What is the significance of the fact that the energy wise distribution is independent of mass of the molecules. Give a typical plot of this distribution for two different temperatures.

13. What do you understand by the term "mean free path". Show that if the molecular diameter is $\sigma$ and molecular density is $n$ per unit volume, the mean free path $\lambda$ is given by

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

*(Patna 2004)*

Give an experimental method for the determination of $\lambda$. *(Purvanchal 2006; Delhi 2004)*

14. (a) What is the meaning of mean free path of molecule of a gas? How does mean free path of a gas molecule depend on temperature and pressure.

(b) The diamater of a gas molecule is 3Å. Calculate the mean free path at N.T.P. using Maxwell formula for mean free path. *(Rohilkhand 2006; Agra 1995)*

15. Outline the assumptions of the kinetic theory of gases. Examine their validity. What is the concept of temperature and mean free path. How the mean free path of molecules can be determined experimentally.

16. What is meant by free path of a molecule of a gas. Obtain the probability of a free path of a given length.

17. Define mean free path and obtain the law of distribution of free paths.

18. What are transport phenomena ? Deduce expression for coefficient of viscosity of a gas on the basis of kinetic theory. Discuss effect of temperature and pressure on it. *(Delhi 2004, Patna 2004)*

19. Deduce an expression for the viscosity of a gas. State the limitation of the deduction. *(Agra 1997)*

20. Deduce an expression for the viscosity of gases in terms of mean free path, density and temperature. Discuss the effect of pressure and temperature. *(Rohilkhand 2004)*

21. Discuss Maxwell's law that the viscosity of a gas is independent of the density and show how it affords evidence in favour of the truth of kinetic theory. Explain why the law can no longer be regarded as valid at very low pressures.

22. Derive from kinetic theogy an expression for the thermal conductivity of a monoatomic gas. Discuss the modification necessary for polyatomic gases. *(Agra 1997; Delhi 1999)*

23. Investigate relation betweent the coefficient of thermal conductivity K and viscosity $\eta$ of a gas and show that $K = \eta\, C_V$ where $C_V$ is the specific heat at constant volume.

24. Give an elementary theory of thermal conduction in a gas. Discuss why hydrogen gas has large thermal conductivity.

25. Give an elementary theory of self diffusion and hence show that the diffusion is directly proportional to the square root of absolute temperature and is inversely proportional to pressure.

26. Explain Brownian motion ? Discuss Langevin's theory of translational Brownian motion. *(Patna 2004)*

27. What is Brownian motion. Give Einsteins's theory of Brownian movement. *(Rohilkhand 2002)*

28. Derive Einstein's expression for the diffusion coefficient

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}$$

How will you determine $N$ with the help of Brownian movement in gases. *(Agra 2006)*

29. Give Einstein's theory of Brownian movement. How has it been experimentally verified. *(Agra 2001)*

30. Give Einstein theory of translational Brownian motion. Discuss how Avogadro number can be determined by a study of this phenomenon. *(Agra 2002)*

31. Show that the pressue $P$ at a given point in a vertical column of gas at uniform temperature $T$ is given by

$$P = P_0\, e^{-Mgh/RT}$$

where $h$ is the height of the given point above the level where the pressure is $P_0$ and $M$ is the molecular weight.

32. Give an outline of Einstein's theory of the translational Brownian motion. Estimate the size of particles most suitable for an experimental study.

33. Write notes on the following :
    (i) Determination of Avogadro number.
    (ii) Molecular diameter and its determination.
    (iii) Brownian Motion. *(Agra 2002; Rohilkhand 2003)*
    (iv) Maxwell's law of distribution of velocities. *(Delhi 2000; Meerut 2005)*
    (v) Maxwell's speed distribution.
    (vi) Molecular collision and mean free path
    (vii) Transport phenomenon is gases.

## NUMERICAL PROBLEMS

1. Find the number of oxygen molecules per kg. mol. at 0°C with speeds between (i) 100 and 101 m/s. (ii) 500 and 501 m/s.

2. The diameter of the molcules of a gas is $3 \times 10^{-8}$ cm. Calculate the mean free path at N.T.P. $[k = 1{\cdot}38 \times 10^{-23}\ \text{J/K}]$ **[Ans.** $9{\cdot}0 \times 10^{-8}$ m.]

3. The mean free path of molecules of a gas at pressure $p$ and temperature $T$ is $\lambda$. What will be the mean free path if
   (i) the pressure is kept constant and the temperature is doubled.
   (ii) the temperature is kept constant and the pressure is doubled.

4. The mean free path of molecules of a certain gas at pressure $p$ and temperature $T$ is $2 \times 10^{-5}$ cm. Deduce the mean free path under the conditions (i) $p, 2T$ (ii) $(2p, T)$
   Also deduce the probability that under conditions $(p, T)$ a molecule would traverse distance $6 \times 10^{-5}$ cm. without collision. **[Ans.** $4 \times 10^{-5}$ cm, $10^{-5}$ cm., $c^{-3}$]

5. The mean free paths of argon and nitrogen at 20°C and 75 cm. of Hg are $9{\cdot}9 \times 10^{-6}$ cm. and $27{\cdot}5 \times 10^{-6}$ cm. respectively, (a) Find the ratio of the effective cross-section diameters of argon and nitrogen. (b) What will be the mean free path of argon at 20°C and 15 cm of Hg and at – 40°C and 75 cm. of Hg. **[Ans.** (a) 1·66, (b) $49{\cdot}5 \times 10^{-6}$ cm., $7{\cdot}87 \times 10^{-6}$ cm]

6. Determine the mean free path of molecular hydrogen at N.T.P. Given that the density of hydrogen is $8{\cdot}96 \times 10^{-5}$ g/c.c. and the coefficient of viscosity is $8{\cdot}6 \times 10^{-4}$ dyne per cm$^3$ per unit velocity gradient.

7. The density of nitrogen at N.T.P. is $1{\cdot}25\ \text{kg/m}^3$ end its coefficient of viscosity is $1{\cdot}66 \times 10^{-5}$ M.K.S. units. Determine mean free path of a molecule of gas. **[Ans.** $8{\cdot}084 \times 10^{-5}$ m]

8. At what temperature will the mean free path of the molecules of a given mass of a perfect gas be twice that at 27°C, when the pressure kept constant. Find the pressure at which the mean free path will be 1000 times greater than that at a pressure of 1 atmosphere. *(Agra 1983)*
   **[Ans.** 327°C, 0·76 mm. of mercury]

9. Calculate the mean free path, frequency of collisions and the molecular diameter of nitrogen gas. Given $\eta = 1{\cdot}66 \times 10^{-6}$ dynes per sq. cm. per unit velocity radient, $v = 45 \times 10^4$ cm per sec. and $\rho = 1{\cdot}25 \times 10^3$ gm. per c.c. **[Ans.** $9 \times 10^{-6}$ cm $5 \times 10^6$, $3 \times 10^{-8}$ cm.]

10. Find the difference in the mean free path of helium at atmospheric pressure at 0°C and 100°C. Given viscosity of helium = 0·00019 C.G.S. unit at 0°C and 0·00024 at 100°C and density of helium at 0°C = 0·0001785 gm. per c.c. **[Ans.** $1{\cdot}3 \times 10^{-5}$ cm]

11. In his experiment on water suspension of gamboge at 20°C, Perrin observed an average of 49 particles per unit area in a layer at one level and 14 particles per unit area at a level 60 microns (1 micron $= 10^{-6}$ m) higher. If the density of gamboge is 1·194 gm/c.c. and the radius of each spherical particles is 0·212 micron, calculate (*a*) the mass of each particle and (*b*) Avogadro's number. **[Ans.** $4{\cdot}74 \times 10^{-17}$ kg, $6{\cdot}7 \times 10^{26}$]

## MULTIPLE CHOICE QUESTIONS : SELECT THE RIGHT CHOICE

1. The first evidence in favour of molecular structure of gas come from the experimental conservation of :
   (a) Brownian movement of colloidal particles
   (b) Tracks of particles in cloud chamber
   (c) Motion of molecules in a conduction phenomenon
   (d) Gas equation

2. The average velocity of molecules in a gas in equilibrium is ($T$ is absolute temperature) :
   (a) proportional to $\sqrt{T}$ (b) proportional to $T$
   (c) proportional to $T^2$ (d) zero

3. The mean free path of a gas molecule is inversely proportional to :
   (a) square of diameter of the molecule
   (b) square root of diameter of the molecule
   (c) molecular diameter
   (d) four power of the molecular diameter

4. The mean free path of a gas is given by ($n$ = number of molecules per m$^3$ and $\sigma$ is molecular diameter) :
   (a) $\lambda = \dfrac{1}{\pi n \sigma^2}$ (b) $\dfrac{1}{\sqrt{2}\,\pi n \sigma^2}$ (c) $\dfrac{\sigma^2}{\pi n}$ (d) $\dfrac{1}{2}\dfrac{n}{\pi\sigma^2}$

5. The mean free path of a gas ($T$ = absolute temperature) :
   (a) varies as $T$ (b) varies as $T^{-1}$
   (c) varies as $T^2$ (d) is independent of $T$

6. The mean free path of a gas ($p$ = pressure) :
   (a) varies as $P$ (b) varies as $P^{-1}$
   (c) varies as $\sqrt{P}$ (d) is independent of $P$

7. The satisfactory explanation of Browinian motion was given by :
   (a) Maxwell (b) Brown (c) Langevin (d) Einstein

8. The mean free path of molecules of a certain gas at pressure $P$ and temperature $T$ is $2 \times 10^{-7}$ m. The mean free path at pressure $P \times 10^{-6}$ and temperature $T$ is : *(Rohilkhand 2003)*
   (a) $2 \times 10^{-1}$ m (b) $2 \times 10^{-3}$ m (c) $2 \times 10^{-4}$ m (d) $2 \times 10^{-10}$ m

9. Diffusion is mainly due to :
   (a) Temperature gradient (b) pressure gradient
   (c) concentration gradient (d) velocity gradient
10. The conduction is mainly due to :
   (a) Temperature gradient (b) pressure gradient
   (c) concentration gradient (d) velocity gradient
11. The viscosity is due to :
   (a) Temperature gradient (b) pressure gradient
   (c) concentration gradient (d) velocity gradient
12. The coefficient of viscosity of a gas :
   (a) is independent of pressure
   (b) increases with increase of pressure
   (c) decreases with increase of pressure
   (d) varies as $(\text{Pressure})^{-3/2}$ at given temperature
13. The coefficient of viscosity of gas :
   (a) varies as $\sqrt{T}$ (b) varies as $T$
   (c) varies as $T^{-3/2}$ (d) is independent of temperature
14. The relation between coefficient of conductivity ($K$) and coefficient of viscosity ($\eta$) is :
   (a) $\frac{k}{\eta} = C_p$ (b) $\frac{K}{\eta} = \frac{1}{C_p}$ (c) $\frac{K}{\eta} = C_v$ (d) $\frac{K}{\eta} = \frac{1}{C_v}$
15. The relation between coefficient of viscosity ($\eta$) and diffusion coefficient ($P$) is ($\rho$ = density of gas, $N_A$ = Avogadro number)——
   (a) $D = \rho\eta$ (b) $D = N_A\eta$ (c) $D = \rho^2\eta$ (d) $D = \frac{\eta}{\rho}$
16. The diffusion coefficient :
   (a) varies as $P$ (b) varies as $P^{-1}$
   (c) varies as $P^{3/2}$ (d) is independent of $P$
17. The diffusion coefficient :
   (a) varies as $T$ (b) varies as $T^{-3/2}$
   (c) varies as $T^{3/2}$ (d) is independent of $T$
18. The relation between coefficient of diffusion ($D$) and mean free path ($\lambda$) is :
   (a) $D = \frac{1}{2}\lambda\bar{v}$ (b) $D = \frac{1}{3}\lambda\bar{v}$ (c) $D = \frac{1}{6}\lambda\bar{v}$ (d) $D = \frac{\bar{v}}{6\lambda}$

**ANSWERS**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. (a) | 2. (d) | 3. (a) | 4. (b) | 5. (a) | 6. (b) | 7. (d) | 8. (a) |
| 9. (c) | 10. (a) | 11. (d) | 12. (a) | 13. (a) | 14. (c) | 15. (d) | 16. (b) |
| 17. (c) | 18. (b) | | | | | | |

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# 6

# PRINCIPLES OF STATISTICAL MECHANICS : CLASSICAL STATISTICS

## 6.1 Introduction to Statistical Mechanics

Upto the end of seventeenth century the physical phenomena were explained by the use of ordinary laws of mechanics. But in certain cases particularly where the system contained a large number of particles these ordinary laws could not be used either due to mathematical complications or due to their being insufficient for the interpetations of observed phenomenon. For example, we can obtain complete information concerning the motion of a mechanical system containing a large number of particles by solving the equations of motion which are equal in number to the degree of freedom of the system by the use of initial conditions of position and velocity of the mutual forces between the particles which are not known. Therefore, it is impossible to apply the ordinary laws of mechanics to a physical system containing a large number of particles. Moreover the problem of an atom with two electrons presents such great mathematical complications that no body, so far, has solved it completely by the use of ordinary laws of machanics. Therefore, it is impossible to solve the problem of a macroscopic body consisting of about $10^{23}$ atoms with their electrons. Such problems have been successfully solved by the *methods of Statistical Mechanics*.

Statistical Mechanics is the branch of science which establishes the interpretation of the macroscopic behaviour of a system in terms of its microscopic properties. As its name implies. Statistical Mechanics is not concerned with the actual motion of individual particle of the system; but investigates instead some average or most probable or statistical properties of the system without going into the interior details of the characteristics of its constituents. *The larger is the number of particles in the physical system considered, the more nearly correct are the statistical predictions. The smaller is the number particles* (or degrees of freedom) *in a mechanical system, the methods of Statistical Mechanics cease to have meaning.* From the size of Avogadro Number $N_0 = 6 \times 10^{23}/\text{g}$ mole, it is clear that even a small volume of the matter contains many atoms or molecules. Obviously, it is impossible to follow the motion of all the individual particles, but the situation is ideal for the application of the methods of Statistical Mechanics.

The methods of Statistical Mechanics are applied to draw inferences and making the deductions of some average or most probable properties of large assemblies of electrons, atoms, molecules, quanta etc. Before the advent of the quantum theory Maxwell, Boltzman. Gibbs etc. applied statistical methods making the use of classical physics. These statistical methods are known as *classical statistics or Maxwell-Boltzmann statistics.* The classicial statististics explained successfully many observed physical phenomenon like temperature, pressure, energy etc. : but could not explain adequately several other experimentally observed phenomenon like black-body radiation, specific heat at low temperature etc. For explaining such phenomenon Bose, Einsteins, Fermi and Dirac made new approach by using new quantum idea of discrete exchange of energy between systems. The new statistics, known as *quantum statistics*, was subdivided into two categories:

(i) Bose-Einstein statistics,

(ii) Fermi-Dirac statistics.

The first of these holds goods for photons, while the other for elementary material particles. The classical statistics is only the limiting case of quantum statistics.

## 6.2 Probability

***The probability of an event may be defined at the ratio of the number of cases in which the event occurs to the total number of cases. i.e.,***

The probability of an event

$$= \frac{\text{Number of cases in which the event occurs}}{\text{Total number of cases}}$$

Thus if an event can happen in $a$ ways and fails to happen in $b$ ways, then the probability of happening the event $= \frac{a}{a+b}$

and the probability of failing the ovent $= \frac{b}{a+b}$

Here it has been assumed that $(a+b)$ ways have the same change of occurrance.

It should be noted that the sum of these two probabilities is always one since the event must either happen or fail.

**Theorem of Composite Probability**

This theorem states that the product of probabilities of a composite event is equal to the product of probabilities of individual and independent events.

**Proof :** Suppose there are two balls : one red and other white and two boys $A$ and $B$ are playing with them. The probability of getting either ball with either boy is $\frac{1}{2}$. Now there are four possible cases :

| | $A$ | $B$ | Probability |
|---|---|---|---|
| (i) | Red ball | White ball | $\frac{1}{4}$ |
| (ii) | White ball | Red ball | $\frac{1}{4}$ |
| (iii) | Both balls | — | $\frac{1}{4}$ |
| (iv) | — | Both balls | $\frac{1}{4}$ |

The probability of each case is $\frac{1}{4}$, which is the product of $\frac{1}{2}$ and $\frac{1}{2}$. Thus the probability of $A$ (or $B$) getting both balls simultaneously is $\frac{1}{4}$.

[Note that it is not equal to sum $\left(\frac{1}{2}+\frac{1}{2}\right)$ of probabilities of individual and independent events].

Let there be three boys A, B, C who want to get a particular white ball. Cleary the probability of A getting the white ball is 1/3. If there is another red ball which is to be distributed similarly; then the probability of A getting it again is 1/3. Thus the probability of A getting both the balls simultaneously is $\frac{1}{3} \times \frac{1}{3} = \frac{1}{9}$ because the desired event takes place only once out of 9 equally-likely ways in which the composite event takes place.

Therefore we conclude that ***the probability of a composite event is equal to the product of the probabilities of the individual and independent events.***

## 6.3 Probability Considerations of Tossing of Coins

Tossing of a coin : If we toss a coin for a large number of times and count the number of times in which the head or the tail falls uppermost, we find that the ratio of the number of heads falling uppermost to the number of tails falling uppermost is nearly unity *i.e.*, the probability of each event or the ratio of the number in which the event occurs to the total number of throws is $\frac{1}{2}$.

Tossing of two coins : (a) When the coins are *unlike or distinguishable* :

If we toss two coins, one of copper (coin number "1") and the other of silver (coin number "2") for a large number of times, then the following four events are possible :

1. The heads of both the coins fall uppermost ......... $a_1a_2$.
2. The tails of both the coins fall uppermost ......... $b_1b_2$.
3. The head of coin "1" and the tail of coin "2" all upper-most ......... $a_1b_2$.
4. The tail of coin "1" and the head of coin ~~"2" fall uppermost~~ ......... ~~$b_1a_2$.~~

where $a$ denotes that the heads fall uppermost while $b$ denotes that the fails fall uppermost, *i.e.*, $a_1$ denote that the head of coin "1" falls uppermost, $b_1$ denotes that the tail of coin "1" falls uppermost and so on.

The total number of possible events is obviously equal to

$$a_1a_2 + a_1b_2 + a_2b_1 + b_1b_2 = (a_1 + b_2)(a_2 + b_2).$$

As the events are independent and equally likely, therefore the probability of each event is $\frac{1}{4}$. This can also be explained of follows :

If we toss coin number 1, the probability of getting its head up is $\frac{1}{2}$, if we toss coin "2" the probability getting its head up is $\frac{1}{2}$.

Therefore the probability of getting the heads of both the coins uppermost in the simultaneous toss of the two coins $= \frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$, since the probability of a composite event is the product of the probability of the individual and independent component events. Now the tossing of the two unlike coins may be shown by the following table :

| S. No. | Event | Symbol | Probability |
|---|---|---|---|
| 1. | The heads of both the coins fall uppermost | $a_1a_2$ | 1/4 |
| 2. | The tails of both the coins fall uppermost | $b_1b_2$ | 1/4 |
| 3. | The head of coin "1" and the tail of coin "2" fall uppermost | $a_1b_2$ | 1/4 |
| 4. | The head of coin "2" and the tail of coin "1" fall uppermost | $a_2b_1$ | 1/4 |

(b) When the coins are *Similar and indistinguishable*

In this case $a_1 = a_2 = a$ (say)

and $b_1 = b_2 = b$ (say)

Then the possible combinations will be symbolised by $a^2, b^2$ and $ab$ since the events (3) and (4) cannot be distinguisned in this case.

The total number of possible events

$$= (a_1 + b_1)(a_2 + b_2) = (a + b)(a + b)$$

$$= a^2 + b^2 + 2ab.$$

In this case the probability of getting the heads or tails of both the coins uppermost $= \frac{1}{4}$ and the probability of getting the head of one coin and the tail of other coin uppermost *i.e.*, the probability of $ab = 2 \times \frac{1}{4} = \frac{1}{2}$.

The results and summarised in the following table :

| S. No. | Event | Symbol | Weight | Probability |
|---|---|---|---|---|
| 1. | The heads of both the coins fall uppermost | $a^2$ | 1 | 1/4 |
| 2. | The tails of both the coins fall uppermost | $b^2$ | 1 | 1/4 |
| 3. | One head and one tail fall uppermost | $ab$ | 2 | 1/2 |

Tossing of the *three unlike or distinguishable coins.*

When three unlike coins "1", "2" and "3" are tossed for a large number of times, the number of equally likely possible events is 8. If $a_1$, $a_2$ and $a_3$ represent that the heads of coins "1", "2" and "3" fall uppermost respectively and $b_1, b_2$ and $b_3$ represent that the tails of coins "1", "2" and "3" fall uppermost respectively, then the total numeber of possible events

$$= (a_1 + b_1)(a_2 + b_2)(a_3 + b_3).$$

As all the events are independent and equally likely the probability of each of the events is 1/8.

The results are shown in the following table :

| S. No. | Event | Symbol | Probability |
|---|---|---|---|
| 1. | The heads of all the coins fall uppermost | $a_1a_2a_3$ | 1/8 |
| 2. | The tails of all coins fall uppermost | $b_1b_2b_3$ | 1/8 |
| 3. | The heads of coins "1" and "2" and the tail of "3" fall uppermost | $a_1a_2b_3$ | 1/8 |
| 4. | The heads of coins "1" and "3" and the tail of "2" fall uppermost | $a_1b_2a_3$ | 1/8 |
| 5. | The heads of coins "2" and "3" and the tail of "1" fall uppermost | $b_1a_2a_3$ | 1/8 |
| 6. | The heads of coin "1" and the tails of coins "2" and "3" fall uppermost | $a_1b_2b_3$ | 1/8 |
| 7. | The heads of coin "2" and the tails of coins "1" and "3" fall uppermost | $b_1a_2b_3$ | 1/8 |
| 8. | The heads of coin "3" and the tails of coins "1" and "2" fall uppermost | $a_3b_1b_3$ | 1/8 |

Tossing of three *similar or indistinguishable coins* :

In this case $a_1 = a_2 = a_3 = a$ (say)

and $b_1 = b_2 = b_3 = b$ (say)

Then the possible combinations will be symbolised by $a^3, b^3, a^2b$ and $ab^2$ since the events (3), (4) and (5) cannot be distinguished and the events (6), (7) and (8) can also not be distinguished.

The total number of possible events $= (a_1 + b_1)(a_2 + b_2)(a_3 + b_3)$

$$= (a + b)(a + b)(a + b) = (a + b)^3$$

$$= a^3 + b^3 + 3a^2b + 3ab^2.$$

In this case the probability of getting heads or tails of all the three coins uppermost is 1/8 while the probability of getting two heads and one tail or one head and two tails uppermost is 3 × 1/8 = 3/8.

These results may be shown by the following table :

| S. No. | Event | Symbol | Weight | Probability |
|---|---|---|---|---|
| 1. | The heads of all the coins fall uppermost | $a^3$ | 1 | 1/8 |
| 2. | The tails of all the three coins fall uppermost | $b^3$ | 1 | 1/8 |
| 3. | The heads of two coins and the tail of one coin fall uppermost | $a^2b$ | 3 | 3/8 |
| 4. | The head of one coin and the tails of two coins fall uppermost | $ab^2$ | 3 | 3/8 |

**Tossing of any number of coins :**

If $n$ unlike or distinguishable coins are tossed for a large number of times, then extending the above results; the total number of possible events are

$$(a_1 + b_1)(a_2 + b_2)(a_3 + b_3) \dots (a_n + b_n)$$

when all the $n$ coins are identical (similar of indistinguishable), then

$$a_1 = a_2 = \dots = a_n = a \text{ (say)}$$

$$b_1 = b_1 = \dots = b_n = b \text{ (say)}$$

Therefore the total number of possible events $= (a + b)^n$ and the possible combinations are given by the terms of the binomial expansion.

$$(a + b)^n = a^n + na^{n-1}b + \frac{n(n-1)}{1.2}a^{n-2}b^2 + \dots$$

$$+ \frac{n(n-1)(n-2)\dots(n-r+1)}{1.2.3\dots r}a^r b^{n-r} + \dots + b^n$$

$$= a^n + {}^nC_1 a^{n-1}b + {}^nC_2 a^{n-2}b^2 + \dots + {}^nC_{n-r}a^r b^{n-r} + \dots + {}^nC_n b^n$$

$$= \sum_{r=0}^{n} {}^nC_{n-r}a^r b^{n-r} = \sum_{r=0}^{n} {}^nC_r a^r b^{n-r}$$

$$= \sum_{r=0}^{n} {}^nC_r a^r b^s \quad \text{where } s = n - r$$

In the above expression the total number of terms representing all possible combinations is $\Sigma\, {}^nC_r = 2^n$.

Thus the probability of each equally likely possible combination $= \dfrac{1}{2^n} = 2^{-n}$.

Therefore the probability of the combination $a^r b^s$ is given by

$$P(r, s) = \frac{{}^nC_r}{2^n} = \frac{n!}{r!\,s!}\cdot\frac{1}{2^n} \qquad \ldots(1)$$

**Combination possessing maximum probability.**

If $n$ similar coins are tossed for a large number of times, let us then find which of the $(n+1)$ combinations $a^r b^s$ has the maximum probability.

We know from elementary algebra that if $n$ is even, the value of ${}^nC_r$ is greatest when $r = \dfrac{n}{2}$.

Hence the maximum value of probability is given by

$$P_{\max.} = \frac{n!}{\frac{n}{2}!\,\frac{n}{2}!}\times\frac{1}{2^n}$$

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

**Combination possessing the minimum probability.**

If $n$ similar coins are tossed for a large number of times, let us then find which of the $(n+1)$ combinations $a^r b^s$ has the minimum probability.

We know from elementary algebra that ${}^nC_r$ is minimum if $r$ is equal to either zero or $n$.

If $r = 0$ the probability is

$$P_{\min} = \frac{n!}{r!\,\overline{n-r}!}\cdot\frac{1}{2^n}$$

$$= \frac{n!}{0!\,\overline{n-0}!}\cdot\frac{1}{2^n} \qquad \text{since } 0! = 1$$

$$= \frac{1}{2^n}. \qquad \ldots(A)$$

If $r = n$, probability is

$$P_{\min.} = \frac{n!}{r!\,\overline{n-r}!}\cdot\frac{1}{2^n}$$

$$= \frac{n!}{n!\,\overline{n-n}!}\cdot\frac{1}{2^n} \qquad \text{since } 0! = 1$$

$$= \frac{1}{2^n}. \qquad \ldots(B)$$

From (A) and (B), we see that minimum probability is given by

$$P_{\min.} = \frac{1}{2^n}. \qquad \ldots(3)$$

## SOLVED EXAMPLES

**Ex. 1.** *Eight similar coins are tossed for a large number of times. Calculate.*
*(a) the probability of getting the heads of 5 coins uppermost,*
*(b) the probability of most probable combination,* **(Rohtak 1977)**
*(c) the probability of least probable combination.*

**Solution.** The probability of the combination $a^r b^s$ is given by

$$P = \frac{n!}{r!\,s!}\cdot\frac{1}{2^n} \qquad \ldots(1)$$

where $s = n - r$

(a) In this case $n = 8$, $r = 5$ and $s = 3$.

Therefore the probability of getting the heads of 5 coins uppermost.

$$= \frac{8!}{5!\,3!}\times\frac{1}{2^8} = \frac{7}{32}$$

(b) In the case of most probable combination

$$r = \frac{n}{2} = \frac{8}{2} = 4.$$

The probability of most probable combination is given by

$$P_{\max.} = \frac{8!}{[4!]^2}\times\frac{1}{2^8}$$

$$= \frac{5\times6\times7\times8}{1\times2\times3\times4}\times\frac{1}{2^8}$$

$$= \frac{70}{256} = \mathbf{\frac{35}{128}}$$

(c) The probability of least probable state $(r = 0)$ is given by

$$P_{\min.} = \frac{1}{2^n} = \frac{1}{2^8}$$

$$= \mathbf{\frac{1}{256}}$$

**Ex. 2.** *Calculate the probability that in tossing a coin 10 times we get (i) all heads, (ii) 5 heads, 5 tails, (iii) 3 heads, 7 tails, (iv) 7 heads, 4 tails.* **(Purvanchal 2004; Agra 1999)**

**Solution.** It we toss a coin $n$ times, probability of getting $r$ head and $s$ tails is given by

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

(i) Here $r = 10$; $s = 0$, $n = 10$

$$\therefore \quad P(10, 0) = \frac{10!}{10!\,0!}\cdot\frac{1}{2^{10}}$$

$$= \frac{1}{2^{10}} = \mathbf{\frac{1}{1{,}024}}.$$

(ii) Here $n = 10$, $r = 5$, $s = 5$.

$$\therefore \quad P(5, 5) = \frac{10!}{5!\,5!}\cdot\frac{1}{2^{10}}$$

$$= \frac{10 \times 9 \times 8 \times 7 \times 6}{1 \times 2 \times 3 \times 4 \times 5} = \frac{\mathbf{255}}{\mathbf{1{,}034}}.$$

(iii) Here $n = 10, r = 3, s = 7$.

$\therefore$

$$P(3, 7) = \frac{10\,!}{3\,!\,7\,!} \times \frac{1}{2^{10}}$$

$$= \frac{10 \times 9 \times 8}{1 \times 2 \times 3} \times \frac{1}{2^{10}} = \frac{120}{2^{10}}$$

$$= \frac{\mathbf{120}}{\mathbf{1{,}024}}.$$

(iv) Here $n = 10, r = 7, s = 3$.

$\therefore$

$$P(7, 3) = \frac{10\,!}{7\,!\,3\,!} \times \frac{1}{2^{10}}$$

$$= \frac{\mathbf{120}}{\mathbf{1{,}024}}$$

**Ex. 3.** *If $P(r)$ is the probability of getting r heads and $(N - r)$ tails in tossing N coins, $P(s)$ is the probability of getting 's' heads and $(M - s)$ tails in tossing M coins, state the probability of getting r heads out of N tosses and s heads out of M tosses simultaneously in one pair of trials.*

**Solution.** The probability of getting $r$ heads and $N - r$ tails in tossing $N$ coins $= P(r)$.

The probability of getting $s$ heads and $M - s$ tails in tossing $M$ coins $= P(s)$.

As we know that the probability of a composite event is the product of probabilities of individual and independent component events, therefore the probability of getting $r$ heads out of $N$ tosses and $s$ heads out of $M$ tosses simultaneously in one pair of trials.

$$= P(r) \times P(s)$$

$$= \mathbf{P(r)\,P(s)}.$$

**Ex. 4.** *Two similar dice A and B each having six equally likely faces marked as 1, 2, 3, 4 5, 6 are thrown simultaneously. Calculate the probability of getting the faces of both the dice up marked with same number.*

**Solution.** The probability of $A$ getting the face marked 1 up

$$= \frac{1}{6}.$$

Since the dice has equally likely six faces. Similarly the probability of $B$ getting the face marked 1 up $= 1/6$.

We know that the probability of a composite event is equal to the product of the probability of individual and independent component events. Therefore the probability of getting the faces of both the dice marked with number 1 upwards.

$$= \frac{1}{6} \times \frac{1}{6} = \frac{1}{36}.$$

Similarly the probability of getting the faces marked '2' upwards of both the dice simultaneously.

$$= \frac{1}{36}.$$

Similarly for the faces marked with 3, 4, 5 and 6.

Thus there are 6 favourable independent events in which the dice will have the faces marked with the same number upwards. Hence the probability of getting the faces of both the dice marked with the same number upwards is

$$= \frac{1}{36} + \frac{1}{36} + \frac{1}{36} + \frac{1}{36} + \frac{1}{36} + \frac{1}{36}$$

$$= \frac{6}{36} = \frac{1}{6}.$$

## 6.4. Distribution of $n$ molecules in two halves of a box

If there are $n$ molecules to be distributed between two halves of a box with equal-probability, then the problem is similar to the tossing of $n$ coins. As in the case of tossing of a coin, either head or tail may be uppermost, in the case of the distribution of a molecule in two halves of a box, the molecule may either go in first half or in the other half. If $a$ and $b$ denote that a molecule will be in first half and second half of a box respectively; then the possible combinations in the distribution of $n$ molecules will be.

$$(a + b)^n = a^n + {}^nC_1\, a^{n-1} b + {}^nC_2\, a^{n-2} b^2 + \ldots + {}^nC_r\, a^r b^{n-r} + \ldots + {}^nC_n b^n$$

The total number of terms representing all possible combinations is

$$\Sigma\, {}^nC_r = 2^n,$$

$\therefore$ The probability of distribution $(r, n - r)$ is given by

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

The probability of most probable distribution is

$$P_{\max} = \frac{n\,!}{(n/2)\,!\,(n/2)\,!} \cdot \frac{1}{2^n} = \frac{n\,!}{(n/2\,!)^2} \cdot \frac{1}{2^n} \qquad \ldots(2)$$

The probability of least probable distribution is

$$P_{\min} = \frac{n\,!}{n\,!\,(n - n)\,!} \cdot \frac{1}{2^n} = \frac{1}{2^n}. \qquad \ldots(3)$$

## SOLVED EXAMPLES

**Ex. 5.** *If twelve particles are distributed randomly between two boxes A and B with equal probability, then calculate :*

*(a) The probability of the distribution (8, 4).*

*(b) The probability of the most probable distribution.*

*(c) The probability of the least probable distribution.*

**Solution.** The probability of distribution $(r, s)$ is given by

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

where $s = n - r$.

(a) In this case $n = 12$, $r = 8$ and $s = 4$ therefore the probability of distribution (8, 4) is given by

$$P(8, 4) = \frac{12\,!}{8\,!\,4\,!} \cdot \frac{1}{2^{12}}$$

$$= \frac{9 \times 10 \times 11 \times 12}{1 \times 2 \times 3 \times 4} 2^{-12}$$

$$= 495 \times 2^{-12}.$$

(b) In the case of most probable distribution $r = (n/2)$

$$r = \frac{12}{2} = 6 \text{ since } n = 12$$

and $$s = n - r = 12 - 6 = 6.$$

The probability of most probable distribution is given by

$$P_{\max} = \frac{12\,!}{6\,!\,6\,!} \cdot \frac{1}{2^{12}}$$

$$= \frac{7 \times 8 \times 9 \times 10 \times 11 \times 12}{1 \times 2 \times 3 \times 4 \times 5 \times 6} \times 2^{-12}$$

$$= 924 \times 2^{-12}.$$

(c) In the case of least probable distribution, we have

$$P_{\min} = \frac{1}{2^n} = \frac{1}{2^{12}}$$

$$= 2^{-12}.$$

**Ex. 6.** *Find the probability that in tossing a coin 12 times, we get (i) 4 head, 8 tails, (ii) 6 heads, 6 tails.*

***(Garhwal 2005; Rohilkhand 2004)***

**Solution.** The probability of distribution $(r, s)$ is given by

$$P(r, s) = \frac{n\,!}{r\,!\,s\,!} \cdot \frac{1}{2^n}. \qquad \text{such that } r + s = n$$

(i) Here $n = 12, r = 4, s = 8$

$$\therefore \qquad P(4, 8) = \frac{12\,!}{4\,!\,8\,!} \cdot \frac{1}{2^{12}} = 495 \times 2^{-12}$$

(ii) Here $n = 12, r = s = 6$

$$\therefore \qquad P(6, 6) = \frac{12\,!}{6\,!\,6\,!} = 924 \times 10^{-12}.$$

## 6.5 Cases with weightage; General case

So far we have considered the case in which the probability of happening and failing the event is the same; but there are cases in which the probability of happening and failing the event is different.

For example if a dice is tossed, the probability that the dice lands with any particular number (out of 1, 2, 3, 4, 5, 6) uppermost is $\frac{1}{6}$, hence the probability that the particular number will not be uppermost is $\left(1 - \frac{1}{6}\right) = \frac{5}{6}$.

Hence if '$a$' is the probability of the happening of an event and $b$ the probability of its failure in a single trial such that $b = 1 - a$; then if the trial is repeated $n$ times we have to find the probability of exactly $r$ successes under the condition that each trial is independent of the other trial.

Now by the theorem of the probability of a composite event, the probability of $r$ successes and $(n - r)$ failures in a specified order is

$$= (a \times a \times a \,.\, r \text{ times}) \times \{b \times b \times b \ldots (n - r) \text{ times}\}$$

$$= a^r b^{n-r}.$$

But there are ${}^nC_r$ ways in which $r$ successes and $(n - r)$ failures can occur.

Therefore the probability of exactly $r$ successes out of $n$ trials is

$$P(r) = {}^nC_r \,.\, a^r b^{n-r}$$

*i.e.,* $$P(r) = \frac{n\,!}{r\,!\,n - r\,!} a^r b^{n-r}. \qquad \ldots(1)$$

Thus the probabilities of 0, 1, 2, ... $n$ successes respectively are

$$b^n, {}^nC_1 a b^{n-1}, {}^nC_2 a^2 b^{n-2}, \ldots {}^nC_r a^r b^{a-r}, \ldots, {}^nC_n a^n$$

which are successive terms of the binomial expansion.

$$(b + a)^n = b^n + {}^nC_1 b^{n-1} + {}^nC_2 a^2 b^{n-2} + \ldots + {}^nC_r a^r b^{n-r} + \ldots + a^n.$$

Obviously ${}^nC_r a^r b^{n-r}$ is the $(r + 1)$th term in the binomial expansion of $(b + a)^n$. Thus the probability that the event will happen exactly $r$ times in $n$ trials is the $(r + 1)$th term in the binomial expansion of $(b + a)^n$.

The probability distribution of the number of successes thus determined is called **"Binomial distribution"**.

**Binomial Theorem of probability :** The theorem is used to determine the probability of happening the event $r$ times out of $n$ trials, if the probability of an event in one trial is known. It states if $a$ is the probability of happening an event and $b$ that of failing that event, then the probability that an event happens exactly $r$ times in the total $n$ trials is the $(r + 1)$th term in the expansion of $(b + a)^n$.

**Proof :** Let $a$ be the probability of happening and $b$ that of failing the event. Then out of $n$ trials $r$ can be chosen in ${}^nC_r$ ways. The probability that an event will happen in $r$ trials is

$$= [a \,.\, a \,.\, a \ldots r \text{ times}]\ [b \,.\, b \,.\, b \ldots (n - r) \text{ times}] = a^r b^{n-r}.$$

The probability of exactly $r$ successes in $n$ trials is

$$= {}^nC_r a^r b^{n-r}$$

$$= (r + 1) \text{ th terms in the binomial expansion of } (b + a)^n$$

$$P(r) = \frac{n\,!}{r\,!\,n - r\,!} a^r b^{n-r}.$$

**Examples**

(i) In the case of distribution of $n$ particles among two halves of a box the probability of going a particle in one half is a and in the other half is $b$, then the probability of distribution $(r, n - r)$ [with weightage $a$, $b$ where $b = 1 - a$] is given by

$$P(r, n - r) = \frac{n\,!}{r\,!\,n - r\,!} a^r b^{n-r} \qquad \ldots(2)$$

(ii) If a dice is tossed, the probability that the dice lands with any number (out of 1, 2, 3, 4, 5, 6) uppermost is 1/16, therefore the probability that the particular number will not be uppermost is

$$b = 1 - 1/6 = 5/6$$

$$\therefore \qquad a = 1/6 \text{ and } b = 5/6.$$

Thus if $P(r)$ is the probability that $r$ of the $n$ dice show the same number uppermost will be

$$P(r) = \frac{n!}{r!\,n-r!}(1/6)^r (5/6)^{n-r}. \qquad \ldots(3)$$

## SOLVED EXAMPLES

**Ex. 7.** *A system of n particles has only two allowed states A and B. The probability for state A is p and for state B is (1 – p). What is the probability for system to be in macrostate defined by distribution (r, n – r),* **(Rohilkhand 1996)**

**Solution.** The probability of state $A$ is $p$ and that for state $B$ is $(1-p)$. Thus the weight factors $a$ and $b$ for states $A$ and $B$ are $p$ and $(1-p)$ respectively. Therefore the probability for the distribution of $n$ particles in states $A$ and $B$ in macrostate $(r, n-r)$, from equation (2) is given by

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

**Ex. 8.** *Assume that each face of a six faced dice is equally likely to land uppermost. Consider a game which involves the tossing of five such dice. Calculate the probability that the number 4 appears uppermost :*

*(i) in exactly one dice,*

*(ii) in exactly two dice,*

*(iii) in exactly five dice,*

*(iv) in none of the five dice,*

*(v) in at least one dice.* **(Agra 2002, 1998)**

**Solution.** (i) The probability $P(r)$ that $r$ out of $n$ dice show number '4' uppermost, from eqn. (3), is given by

$$P(r) = \frac{n!}{r!\,n-r!}(1/6)^r (5/6)^{n-r}$$

(i) Here $n=5, r=1$.

$$\therefore \quad P(1) = \frac{5!}{1!\,(5-1)!}(1/6)^1 (5/6)^{5-1}$$

$$= \frac{5!}{4!}(1/6)\,(5/6)^4 = (5/6)^5$$

$$= \mathbf{0{\cdot}4}.$$

(ii) Here $n=5, r=2$

$$\therefore \quad P(2) = \frac{5!}{2!\,(5-2)!}(1/6)^2 (5/6)^3$$

$$= \frac{5!}{2!\,3!}(1/6)^2 (5/6)^3$$

$$= \mathbf{0{\cdot}16}.$$

(iii) Here $n=5, r=5$

$$\therefore \quad P(5) = \frac{5!}{5!\,0!}\left(\frac{1}{6}\right)^5 \left(\frac{5}{6}\right)^{5-5} = \left(\frac{1}{6}\right)^5 = \mathbf{1{\cdot}286 \times 10^{-4}}.$$

(iv) The probability that the number '4' does not appear uppermost in one dice = 5/6.

The probability that number '4' does not appear uppermost in all five dice simultaneously.

$$= (5/6)^5 = \mathbf{0{\cdot}4}$$

(v) The probability that the number '4' appears uppermost in at least one dice.

$$= 1 - (5/6)^5 = 1 - 0{\cdot}4 = 0{\cdot}6.$$

**Ex. 9.** *A coin is so tossed that the probability of getting 'head' in a toss is 0·7 Deduce the probability that in 5 tosses, we get (I) 2 heads, 3 tails, (ii) all tails, (iii) all heads.* **(Agra 1999)**

**Solution.** The probability of getting $r$ heads $(n-r)$ tails with weight factor '$a$' of getting head in a toss is given by

$$P(r, n-r) = \frac{n!}{r!\,n-r!}(a)^r (b)^{n-r}.$$

Given $a = 0{\cdot}7$ and $b = 1 - 0{\cdot}7 = 0{\cdot}3$, $n = 5$

(i) Here $r = 2$, $n - r = 5 - 2 = 3$

$$\therefore \quad P(2, 3) = \frac{5!}{2!\,3!}(0{\cdot}7)^2 (0{\cdot}3)^8 = \mathbf{0{\cdot}1323}$$

(ii) Here $r = 0$, $n - r = 5 - 0 = 0$

$$P(0, 5) = \frac{5!}{0!\,5!}(0{\cdot}7)^0 (0{\cdot}3)^5 = \mathbf{0{\cdot}00243}$$

(iii) Here $r = 5$, $n - r = 5 - 5 = 0$

$$\therefore \quad P(5, 0) = \frac{5!}{5!\,0!}(0{\cdot}7)^6 (0{\cdot}3)^0 = \mathbf{0{\cdot}16807.}$$

## 6.6 Phase-Space

In classical mechanics the state of a system of particles at any given time is completely specified by the knowledge of position and momentum (or velocity) of each of its particles. The instantaneous position of a single particle is determined by three independent coordinates $x, y, z$ and the instantaeous motion of a particle is described by velocity components $(v_x, v_y, v_z)$ or more conveniently by momentum components $(p_x, p_y, p_z)$. Therefore the state of a single particle is then completely specified by position coordinates $x, y, z$ and momentum components $p_x, p_y, p_z$. As a purely mathematical concept we may imagine six dimensional space in which $dx\,dy\,dz\,dp_x\,dp_y\,dp_z$ is an element of volume and the position of a point particle in this space will be described by a set of six coordinates $x, y, z, p_x, p_y, p_z$. This six dimensional space for a single particle is termed as *phase-space* and particularly the μ-space.

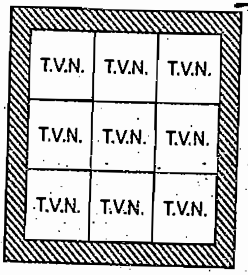
If the system contains a large number of particles such that the state of system is represented by $f$ independent position coordinates $q_1, q_2 \ldots q_f$ and $f$ momentum coordinates $p_1, p_2, \ldots\ldots\ldots q_f$, then mathematically these $2f$ combined position momentum coordinates may be allowed to define $2f$ dimensional space in which the configuration of the system is represented by $2f$ coordinates $q_1, q_2 \ldots q_f, p_1, p_2, \ldots p_f$. This $2f$ dimensional space is called the phase-space or the Γ-space. The Γ-space is considered to be a conceptual Euclidean space having $2f$ rectangular axes and an element of volume in this space is represented by $dq_1\,dq_2 \ldots\ldots dq_f\,dp_1\,dp_2 \ldots dp_f$. The Γ-space may be considered as a superposition of μ-spaces. Obviously the dimensions of the phase space depend upon the degrees of freedom of the system. The instantaneous state of a particle in the phase-space is represented by a point known as *phase point* or *representative point*. The number of phase points per unit volume is called the *phase density of these points*. An element of volume in the phase space is termed as a cell.

## 6.7 Ensembles

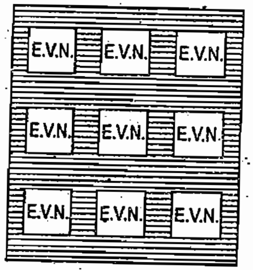
A system is defined as a collection of a number of particles. An **ensemble** *is defined as collection of a large number of microcospically identical but essentially independent systems.* By the term *macroscopically identical* we mean that each of the systems constituting an ensemble satisfies the same macroscopic conditions *e.g.*, volume, energy, pressure, total number of particles, etc. By the term *independent systems* we mean that the systems constituting an ensemble are mutually non-interacting. In an ensemble the systems play the same role as the non-interacting molecules do in a gas. The macroscopic identity of the systems constituting an ensemble may be achieved by choosing the same values of some set of macroscopic parameters which uniquely determine the equilibrium state of the system. Accordingly there may be many types of ensembles, out of them the most widely used are the microcanonical, canonical and grand canonical ensembles.

**Microcanonical ensemble :** It is the collection of a large number of essentially independent systems having the same energy $E$, volume $V$ and the number of particles $N$. For simplicity we assume that all the particles are identical. The individual systems of a microcanonical ensemble are separated by rigid, impermeable and well isulated walls (Fig. 6.1) such that the values of $E, V$ and $N$ for a particular system are not affected by the presence of other systems.

**Canonical ensemble :** It is the collection of a large number of essentially independent systems having the same temperature $T$, volume $V$ and the same number of identical particles $N$. The equality of temperature of all the systems can be achieved by bringing each in thermal contact with a large heat reservoir at constant temperature $T$ or bringing all of the systems in thermal contact with one another. The individual systems of a canonical ensemble are separated by rigid, impermeable but conducting walls (Fig. 6.2).



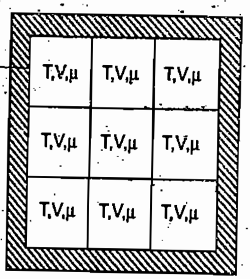
(Fig. 6.1)



(Fig. 6.2)

As the separating walls are conducting, heat can be exchanged between the systems. As a result all the systems will arrive at the common temperature $T$.

**Grand-canonical ensemble :** It is the collection of a large number of essentially independent systems having the same temperature $T$, volume $V$ and chemical potential $\mu$. The individual systems of a grand canonical ensemble are separated by rigid, permeable and conducting walls (Fig. 6.3). As the separating walls are conducting and permeable, the exchange of heat energy as well as that of particles between the systems takes place in such a way that all the systems arrive at common temperature $T$ and chemical potential $\mu$. The detailed information regarding the characteristics of these ensembles can be had after a complete study of Liouville's theorem.



(Fig. 6.3)

As the instantaneous state of any system of $f$ degree of freedom can be completely specified by the position of a suitable point, called the *phase point* or *representative point* in the $2f$ dimensional phase space; therefore, an ensemble, being the collection of a large number of microscopically independent systems, will appear as a dust cloud made up of large number of phase points in the phase space. The change in the phase *i.e.*, in position coordinates and momenta of any system can be represented by a curve or *phase line* in the phase space. Then the behaviour of an ensemble in the course of time can be represented by a large number of trajectories or phase lines in the phase space or be streaming motion of the *dust cloud* as the trajectories are described by the points according to the laws of mechanics.

It is easier to compute the behaviour of a suitable chosen ensemble than to study the behaviour of any particular system. By the knowledge of the behaviour of the ensemble, we can predict the probable behaviour of the system under consideration.

## 6.8 Density of Distribution in the Phase-Space

The use of ensembles in statistical mechanics is guided by the following points :

1. There is no need to distinguish between different systems constituting an ensemble, because the laws of statistical mechanics aim to tell us only the number of systems or elements which would be found in different states *i.e.*, in different regions of phase space at any time.

2. The number of systems in an ensemble is so large that there is a continuous changed their number in passing from one region of phase space to another.

Keeping these points in the mind the condition of an ensemble at and time can be suitably specified by the density function $\rho$ with which the phase points are distributed in the phase space. This density function is called *the density of probability distribution* or the *probability density* or *the distribution function*. In an ensemble of $f$ degrees of freedom the density of distribution $\rho$ is a function of $f$ position coordinates $q_1, q_2, \ldots, q_f$ and $f$ momenta coordinates $p_1, p_2, \ldots, p_f$ corresponding to $2f$ combined position momenta axes in the phase space. The density of distribution $\rho$ is also a function of time $t$, because due to the motion of phase points, the density of distribution will change with time at any given point. Hence we can write,

$$\rho = \rho\,(q_1, q_2, \ldots, q_f, p_1, p_2, \ldots, p_f, t)$$

or briefly
$$\rho = \rho\,(q, p, t). \qquad \ldots(1)$$

Obviously the density of distribution $\rho$ denotes the number of systems or elements $\delta N$ which are found at any given time in a given infinitesimal region of $\Gamma$-space. If the region chosen is such that the position coordinates lie between $q_i$ and $q_i + dq_i$ and momenta lie between $p_i$ and $p_i + dp_i$ $(i = 1, 2, 3, \ldots, f)$, then the *hyper volume* $d\Gamma$ of this region will be given by

$$d\Gamma = dq_1 dq_2 \ldots dq_f dp_1 dp_2 \ldots dp_f = \prod_{i=1}^{f} dq_i\, qp_i \qquad \ldots(2)$$

where $\prod_{i=1}^{f}$ stands for the product over all values of $i = 1$ to $i = f$. The number of systems $\delta N$ lying in the specified infinitesimal region can be obtained by multiplying the density of distribution $\rho$ with this hypervolume in the phase space *i.e.*,

$$\delta N = \rho\, d\Gamma = \prod_{i=1}^{f} \rho\, dq_i\, dp_i \qquad \ldots(3)$$

Integrating over the entire phase space, we can obtain total number of systems under consideration *i.e.*,

$$N = \int \rho\, d\,\Gamma = \int . \int \rho\, dq_1\, dq_2 \ldots dq_f\, dp_1\, dp_2 \ldots dp_f. \qquad \ldots(4)$$

Sometimes it is convenient to work with normalised density of distribution given by

$$\rho_N = \frac{\rho\,(q, p, t)}{\int \rho\,(q, p, t)\, d\,\Gamma} = \frac{\rho}{N}. \qquad \ldots(5)$$

In this case $\rho_N$ expresses the probability of states represented by points per unit volume element in the phase space. In other words $\rho_N$ gives the probability per unit volume of finding the phase point for a system taken at random from the ensemble in different regions of the phase space.

The function $\rho_N$ must obviously satisfy the normalisation condition,

$$\int \rho_N\, d\,\Gamma = \int \ldots \int \rho_N\, dq_1 \ldots dq_f = 1. \qquad \ldots(6)$$

Here the integral is taken over the entire phase space. The equation simply presents the fact that the sum of the probabilities of all possible states is unity.

The probability, that a phase point for a system chosen at random from the ensemble would be found at time $t$ in given infinitesimal intervals between $q_i, p_i$ and $q_i + dq_i, p_i + dp_i$ is given by

$$d\omega = \rho_N (q, p, t)\, d\Gamma = \rho_N (q, p, t) \prod_{i=1}^{f} dq_i\, dp_i \qquad \dots(7)$$

## 6.9 Liouville's Theorem

Consider an ensemble consisting of a large number of identical, non-interacting systems. We know that the instantaneous state of a system can be represented by point in the phase space. Similarly the instantaneous states of other systems constituting the ensemble can be represented by other points in the phase space. Thus the instantaneous state of the entire ensemble can be represented by a number of phase points in the phase space. The density of these points, also known as *the density of states in the phase space,* is denoted by ρ. If the state of an ensemble changes with time, the positions of phase points in the phase space will change with time. The motion of these phase points in the phase space, is of course, governed by the canonical equations.

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \; \dot{p}_i = -\frac{\partial H}{\partial q_i} \qquad \dots(1)$$

($i = 1, 2, 3, \dots f$ for a system of $f$ degrees of freedom)

Here $H = H(q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f)$ is the Hamiltonian of the system.

Due to the motion of phase points, the density of states in the phase space ρ changes with time. Liouville's theorem gives information about the rate of change of phase density in the phase space. The theorem may be stated in two parts :

1. The rate of change of density of phase points (representing systems) in the neighbourhood of a moving phase point (for which $q$'s and $p$'s are changing) in the Γ-space is zero. This part represents *the principle of conservation of density in the phase space.*

Mathematically this may be represented as

$$\frac{d\rho}{dt} = 0 \qquad \dots(2)$$

in the immediate neighbourhood of any given moving phase point.

2. Any arbitrary element of volume or extension-in-phase in the Γ-space, bounded by a moving surface and containining a number of phase points does not change with time despite the displacements and distortions. This part represent the *principle of conservation of extension in phase space.*

Mathematically this may be represented as

$$\frac{d}{dt}(\delta\Gamma) = \frac{d}{dt}\left( \prod_{i}^{f} dq_i\, dp_i \right) = 0 \qquad \dots(3)$$

**1. The principle of conservation of density in the phase space :** Consider any arbitrary hyper-volume $\delta\Gamma = \delta q_1\, \delta q_2 \dots \delta q_f\, \delta p_1\, \delta p_2 \dots \delta p_f$ in the phase space located between $q_1$ and $q_1 + \delta q_1 \dots q_f$ and $q_f + \delta q_f$, $p_1$ and $p_1 + \delta p_1 \dots, p_f$ and $p_f + \delta p_f$. The number of phase points in this volume element changes with time due to the motion of phase points. It ρ is the density of phase points, the number of phase points in this volume element at any instant $t$.

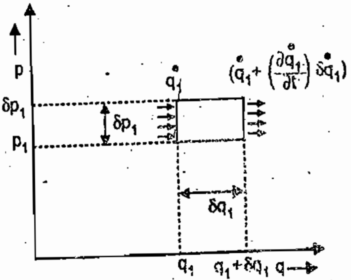
$$\delta N = \rho\, \delta\Gamma = \rho\, \delta q_1\, \delta q_2 \dots \delta q_f\, \delta p_1\, \delta p_2 \dots \delta p_f \qquad \dots(4)$$

The change in the number of phase points in the volume element per unit time,

$$\frac{d\,(\delta N)}{dt} = \frac{d}{dt}(\rho\, \delta\Gamma) = \dot{\rho}\, \delta\Gamma = \dot{\rho}\, \delta q_1\, \delta q_2 \dots \delta q_f\, \delta p_1\, \delta p_2 \dots \delta p_f \qquad \dots(5)$$

This change in number of phase points in the given hypervolume is due to the difference between the number of phase points entering the hyper volume through any face and the number of those leaving the opposite face per second.

Now consider two faces of hypervolume normal to $q_1$ axis with coordinates $q_1$ and $q_1 + \delta q_1$ as shown in fig. 6.4 (only two axes are shown in fig.). If $\dot{q}_1$ is the component of velocity of phase point at $q_1, q_2, q_t, p_1, p_2 \dots p_f$, then the number of phase points entering the first face $AD$ per second.



(Fig. 6.4)

$$= \rho \dot{q}_1\, \delta q_2 \dots \delta q_f\, \delta p_1 \dots \delta p_f \qquad \dots(6)$$

As density ρ changes with change in position and momentum coordinates and at the opposite face $BC$ the coordinate $q_1$ changes to $q_1 + \delta q_1$, therefore the density ρ changes to $\left(\rho + \frac{\partial \rho}{\partial q_1}\delta q_1\right)$ at the face $BC$. Similarly at the face $BC$ the velocity $\dot{q}_1$ change to $\left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1}\delta q_1\right)$. Therefore the number of phase points leaving the opposite face $BC$ at $q_1 + \delta q_1$ per second.

$$= \left(\rho + \frac{\partial \rho}{\partial q_1}\delta q_1\right)\left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1}\delta q_1\right)\delta q_2 \dots \delta q_f\, \delta p_1 \dots \delta p_f$$

Neglecting the term containing higher order differentials, the number of phase points leaving the opposite face $BC$.

$$\left\{\rho \dot{q}_1 + \left(\rho \frac{\partial \dot{q}_1}{\partial q_1} + \dot{q}_1 \frac{\partial \rho}{\partial q_1}\right)\delta q_1\right\}\delta q_2 \dots \delta q_f\, \delta p_1 \dots \delta p_f \qquad \dots(7)$$

Subtracting expression (7) from expression (6) we get the expression for the change in the number of phase points per second corresponding the change in coordinate $q_1$, which is

$$-\left(\rho \frac{\partial \dot{q}_1}{\partial q_1} + \dot{q}_1 \frac{\partial \rho}{\partial q_1}\right)\delta q_1 \dots \delta q_f\, \delta p_1 \dots \delta p_f \qquad \dots(8)$$

Similarly the expression for the change in the number of phase points per second corresponding to the change in coordinate $p_1$ is

$$-\left(\rho \frac{\partial \dot{p}_1}{\partial p_1} + \dot{p}_1 \frac{\partial \rho}{\partial p_1}\right)\delta q_1 \dots \delta q_f\, \delta p_1 \dots \delta p_f \qquad \dots(9)$$

To consider the change in the number of phase points per second corresponding to all position and momentum coordinates, all the terms like (8) and (9) for all position and momentum coordinates are summed up. Thus the net increase in the number of phase points in the given hypervolume per second is given by

$$\frac{d\,(\delta N)}{dt} = -\sum_{i=1}^{f}\left[\rho\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) + \left(\dot{q}_1 \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i}\right)\right] \times \delta q_1 \dots \delta q_f\, \delta p_1 \dots \delta p_f \qquad \dots(10)$$

Using equation (5) we get

$$\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{f}\left[\rho\left(\frac{\partial \dot{q}_i}{\partial q_i}+\frac{\partial \dot{p}_i}{\partial p_i}\right)+\left(\dot{q}_i\frac{\partial \rho}{\partial q_i}+\dot{p}_1\frac{\partial \rho}{\partial p_i}\right)\right] \qquad \ldots(11)$$

From canonical equations (1), we obtain

$$\frac{\partial \dot{q}_i}{\partial q_i}=\frac{\partial^2 H}{\partial q_i\,\partial p_i} \text{ and } \frac{\partial \dot{p}_i}{\partial p_i}=-\frac{\partial^2 H}{\partial p_i\,\partial q_i}.$$

Since the order of differentiation is immaterial.

*i.e.,*
$$\left[\frac{\partial^2 H}{\partial q_i\,\partial p_i}=\frac{\partial^2 H}{\partial p_i\partial q_i}\right]$$

we get

$$\frac{\partial \dot{q}_i}{\partial q_i}=-\frac{\partial \dot{p}_i}{\partial \dot{p}_i}.$$

or
$$\sum_{i=1}^{f}\left(\frac{\partial \dot{q}_i}{\partial q_i}+\frac{\partial \dot{p}_i}{\partial p_i}\right)=0. \qquad \ldots(12)$$

Substituting above in equation (11), we get

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p}=-\sum_{i=1}^{f}\left(\dot{q}_i\frac{\partial \rho}{\partial q_i}+\dot{p}_i\frac{\partial \rho}{\partial p_i}\right)\ldots\ldots$$

or
$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p}+\sum_{i=1}^{f}\frac{\partial \rho}{\partial q_i}\dot{q}_i+\sum_{i=1}^{f}\frac{\partial \rho}{\partial p_i}\dot{p}_i=0. \qquad \ldots(13)$$

This may be written as

as
$$\frac{d}{dt}\rho\,(q_1,\ldots q_f,p_1,\ldots p_f)\,t=0.$$

*i.e.,*
$$\frac{d\rho}{dt}=0. \qquad \ldots(14)$$

This equation represents *Liouville's theorem.*

According to Gibbs this expression represents the principle of conservation of density in phase space.

**2. The principle of conservation of extension in the phase space :** Consider a very small region of hypervolume $\delta\Gamma$ in the *T*-space, so that the density of phase points $\rho$ can be taken as uniform throughout the hypervolume.

The number of phase points in the hypervolume, $\delta N=\rho\,.\,\delta\Gamma$.

Differentiating with respect to *t*, we get

$$\frac{d}{dt}(\delta N)=\frac{d}{dt}(\rho\,.\,\delta\Gamma)=\frac{\partial \rho}{dt}\delta\Gamma+\rho\frac{d\,(\partial\Gamma)}{dt} \qquad \ldots(15)$$

As each phase point represents a definite system and systems can neither be created nor destroyed, therefore, the number of phase points $\delta N$ in the given region of phase space must remain fixed *i.e.,*

$$\frac{d\,(\delta N)}{dt}=0.$$

Hence equation (15) yields

$$\frac{d\rho}{dt}\delta\Gamma+\rho\frac{d\,(\delta\Gamma)}{dt}=0.$$

According to equation (14) $\frac{d\rho}{dt}=0$, therefore, it follows that

$$\frac{d\,(\delta\Gamma)}{dt}=0. \text{ or } \delta\Gamma=\text{constant} \qquad \ldots(16)$$

According to Gibbs this expression represents the principle of conservation of extension in the phase space.

## 6.10 Density of Phase Points in a Classical Ensemble

According to equation $\frac{d\rho}{dt}=0$ (*i.e.,* the principle of conservation of density in the phase space, the density of phase points representing systems in the phase space is constant in time. Therefore, this density must be the function of the constants of motion of the system. For an ensemble the total energy *E*, the number of particles *N* are the constants of motion. Hence we can write

$$\rho=\rho\,(E,N). \qquad \ldots(1)$$

Consider an ensemble consisting of *n* systems $S, S_2, \ldots, S_n$ containing $N_1, N_2, \ldots N_n$ particles respectively. Let the energy of *n* systems be $E_1, E_2, \ldots, E_n$ respectively.

The probability that the phase point for the system $S_1$ will be in the element of volume $d\,\Gamma_1=\rho_1\,(E_1,N_1)\,d\Gamma_1$.

The probability that the phase point for the system $S_2$ will lie in the element of volume $d\Gamma_2=\rho_2\,(E_2,N_2)\,d\,\Gamma_2$.

In general, the probability that the phase point for the system $S_i$ will lie in the element of volume $d\,\Gamma_i=\rho_i\,(E_i,N_i)\,d\,\Gamma_i$.

The probability that the phase points for the ensemble (*n* systems together) lie in the element of volume $d\,\Gamma$ is

$$\rho\,(E,N)\,d\,\Gamma=\rho_1\,(E_1,N_1)\,d\,\Gamma_1\rho_2\,(E_2,N_2)\,d\,\Gamma_2\ldots\rho_n\,(E_n,N_n)\;d\,\Gamma_n$$

where $d\,\Gamma=d\,\Gamma_1\,d\,\Gamma_2\,d\,\Gamma_n$.

and
$$\rho\,(E,N)=\rho_1\,(E_1,N_1)\,\rho_2\,(E_2,N_2)\ldots\rho_n\,(E_n,N_n). \qquad \ldots(2)$$

The general solution of eqn. (2) can be written as

$$\log\rho\,(E,N)=a+bE+cN. \qquad \ldots(3)$$

Where *a*; *b* and *c* are some constants independent of *E* and *N*. Let us now consider the following three cases.

**(i) When both *E* and *N* are constants :** This is the case of *microcanonical ensemble.* In this case eqn. (3) takes the form

$$\log\rho=\text{constant } i.e.,\ \rho=\text{constant}. \qquad \ldots(4)$$

As *E* is constant in the case, the phase points can move in a hypervolume of constant energy in such a way that the density of phase points in this hypervolume remains constant.

**(ii) When *N* is constant :** This the case of a *canonical ensemble.* In this case eqn. (3) can be written as

$$\log\rho=bE+\text{constant}.$$

This equation yields

$$\rho=e^{(C_1-E)/C_2}. \qquad \ldots(5)$$

where $C_1$ and $C_2$ are constants for the ensemble, $C_1$ is equivalent to Gibb's free energy $F$ and $C_2$ is equivalent to $kT$ where $k$ is Boltzmann's constant and $T$ is the absolute temperature of the ensemble. Here $E$ is chosen to be negative because $\rho$ decreases as $E$ increases.

**(iii) When both $E$ and $N$ are variables :** This is the case of a *grand canonical ensemble.* In this case eqn. (3) yields

$$\rho = e^{(C_1 + C_2 N - E)/C_3} \qquad \ldots(6)$$

where $C_1$, $C_2$ and $C_3$ are constants for the ensemble. $C_1$ is equivalent to grand potential $(-pV)$, $C_2$ is equivalent to $kT$ and $C_3$ is equivalent to the chemical potential.

## 6.11 Statistical Equilibrium

*An ensemble is said to be in statistical equilibrium if the probabilities of finding the phase points in the various regions of the phase space and the average values of the properties of its systems are independent of time.*

Mathematically the condition of an ensemble in statistical equilibrium may be expressed as

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = 0 \text{ for all values of } q \text{ and } p. \qquad \ldots(1)$$

This means that for an ensemble to be in statistical equilibrium, the density $\rho$ must be independent of time at all points in phase space.

Now the problem is to find what function $\rho$ will satisfy equation (1)

Several different functions, corresponding to various types of ensembles, are possible. For conservative system $\rho$ is taken as the function of energy which in turn can be expressed as a function of $p$'s and $q$'s being representable by the Hamiltonian function. In general for any ensemble, $\rho$ is a function of some property which in turn can be expressed as a function of $p$'s and $q$'s. Let this property be represented by $\varepsilon$, then we may write

$$\rho = \rho(\varepsilon). \qquad \ldots(2)$$

This gives

and

$$\left.\begin{aligned} \frac{\partial \rho}{\partial q_i} &= \frac{\partial \rho}{\partial \varepsilon}\frac{\partial \varepsilon}{\partial q_i} \\ \frac{\partial \rho}{\partial p_i} &= \frac{\partial \rho}{\partial \varepsilon}\frac{\partial \varepsilon}{\partial p_i} \end{aligned}\right\} \qquad \ldots(3)$$

From expression (13) for Liouville's theorem (6.9), we have

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} + \sum_{i=1}^{f} \frac{\partial \rho}{\partial q_i}\dot{q}_i + \sum_{i=1}^{f} \frac{\partial \rho}{\partial p_i}\dot{p}_i = 1.$$

Substituting values from equation (3), we get

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} + \sum_{i=1}^{f} \frac{\partial \rho}{\partial \varepsilon}\frac{\partial \varepsilon}{\partial q_i}\dot{q}_i + \sum_{i=1}^{f} \frac{\partial \rho}{\partial \varepsilon}\frac{\partial \varepsilon}{\partial p_i}\dot{p}_i = 0.$$

or

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = -\frac{\partial \rho}{\partial \varepsilon}\sum_{i=1}^{f}\left(\frac{\partial \varepsilon}{\partial q_i}\dot{q}_i + \frac{\partial \varepsilon}{\partial p_i}\dot{p}_i\right) \qquad \ldots(4)$$

As $\varepsilon$ is assumed to be the function of $q$'s and $p$'s such that is value for any given system in statistical equilibrium does not change with time, we may write

$$\frac{d\varepsilon}{dt} = \sum_{i=1}^{f}\left(\frac{\partial \varepsilon}{\partial q_i}\dot{q}_i + \frac{\partial \varepsilon}{\partial p_i}\dot{p}_i\right) = 0. \qquad \ldots(5)$$

Using equation (5), equation (4) yields

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = 0. \qquad \ldots(6)$$

As the values of $q$ and $p$ have not been specified, this result holds for any point in the phase space. Hence we conclude that an ensemble of systems will be in statistical equilibrium if.

(i) the density $\rho$ is independent of time at all points in the phase space and

(ii) the density $\rho$ is a function of some property (energy for conservative systems) of the ensemble which depends only on $q$'s and $p$'s and is independent of time.

## 6.12 Postulate of Equal a Priori Probability

Let us now introduce a postulate which enables us to meet this situations of actual interest. According to this postulate.

"*The probability of finding the phase point for a given system in any one region of phase space is identical with that for any other region of equal extension or volume.* This postulate is known as *the postulate of equal a priori probability.*"

The necessity of this postulate does not arise due to any inadequacy in the principles of classical mechanics : but is arises due to incompleteness of our knowledge concerning the system of interest. This postulate, through incapable of direct proof, appears to be resonable in character with the principles of statistical mechanics derived from Liouville's theorem.

According to the principle of conservation of density in the phase space, the density of a group of phase points remains constant along their trajectories in the phase space. If at any time the phase points are distributed uniformly in the phase space, they (phase points) move in such a way that they will have uniform density of phase points at all times. Thus there is no crowding together of phase points in any particular region of phase space. Further according to the principle of conservation of extension in the phase space; any arbitrary element of volume in the phase space bounded by a moving surface, and containing a definite number of phase points does not change with time despite the displacements and distortions. The property of no crowding of phase points in any particular region of phase space and the constancy of volume element of phase space with time indicate the validity of the postulate that *probability of finding a phase point in any particular region of phase space is directly proportional to the volume of that region,* provided the region under consideration satisfies the conditions holding good for the system of interest. The postulate replaces the postulate of equal a priori probability stated above, when instead of equal extensions, different extensions in the phase space are considered.

## 6.13 Microstates and Macrostates

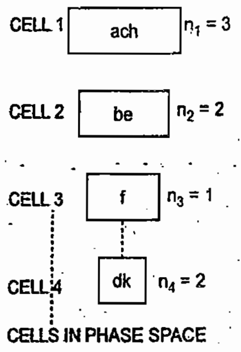
Let us consider an ensemble consisting of a large number of independent systems or a gas consisting of a large number of molecules, in the phase space. Each system or molecule may be represented by point known as phase point or representative point in the phase space. Let the phase space be divided into cells numbered 1, 2, 3, ... $i$ ... etc. adjoining one another and having a volume equal to

$$\delta q_1\, \delta q_2 \ldots \delta q_f\, \delta p_1\, \delta p_2 \ldots \delta p_f.$$

A phase point for any system or molecule may be supposed to lie inside one of these cells. ***In order to define the microstate of the ensemble we must specify the individual position of phase points for each system or molecule of the ensemble.*** In other words, we must state to which cell each system or molecule belongs temporarily. Such a deep analysis is quite unnecessary to determine the observable properties of any ensemble (or gas). For example, the density is same if the number of molecules in each volume element of ordinary space is the same regardless of which particular molecule lie in any volume element.

***A macrostate of the ensemble may be defined by the specification of the number of phase points*** (*i.e.*, **system or molecules) in each cell of phase space** such as $n_1$ phase points are in cell 1, $n_2$ phase points are in cell 2, $n_3$ phase points are in cell 3 and so on.

*Many different microstates may correspond to the same macrostate.* For example let us identify the phase points as $a, b, c$ ... etc. Let a particular microstate be specified by stating that the phase points *ach* are in cell 1, *be* are in cell, 2, $f$ is in cell 3 and so on as shown in fig. 6.5. The corresponding macrostate is specified be merely giving the number of phase points $n_1$ (= 3) in cell 1, the number $n_2$ (= 2) in cell 2, $n_3$ (= 1) in cell 3 and so on. If we interchange any two phase points from different cells, say $a$ and $b$, we shall have the different microstates, but the same macrostate. On the other hand if we interchange the two phase points in the same cell, say $a$ and $c$, we shall have the same microstate as well as the same macrostate. If the systems of ensemble are in constant motion just like the molecules of a gas, the ensemble is continuously and spontaneously changing from one microstate to another and almost as frequently from one macrostate to the other.



(Fig. 6.5)

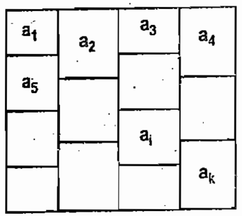
The microstate which are allowed under given restriction are called *accessible microstates*. For example in the case of 3 molecules $a, b, c$ to be distributed between two halves of a box, if none can be outside the box, then $(ab, c)$, $(a, bc)$, $(ac, b)$ are accessible microstates while $(a, b)$, $(a, c)$, $(b, c)$ etc. are inaccessible microstates. One of the most fundamental postulate of statistical mechanics is that *all accessible microstates corresponding to possible macrostates are equally probable.* In other words this states that the probability of finding the phase point in any one region is identical with that for any other region of equal volume provided the regions correspond equally well with the given conditions. Thus this postulate if 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 correspond to that macrostate. The number of microstates corresponding to a given macrostate is called the *thermodynamic probability* of the macrostate. Thus the probability that the ensemble will possess energy $E$ is proportional to $\Omega(E)$ *i.e.*,

$$P(E) = C\Omega(E)$$

where C is constant of proportionality and $\Omega(E)$ is thermodynamic probability.

## 6.14 General Expression for Probability

In order to obtain a general expression for the total probability of a distribution, consider a large box divided into $k$ cells of areas $a_1, a_2, a_3 \dots a_k$ as shown in fig. 6.6. Let us throw $N$ balls into the box in a completely random manner, so that no part of the box is favoured. We note down the number of balls falling in each cell and then repeat the experiment a large number of times. After a large number of observations of the distribution of balls among the various cells, we note that a certain distribution occurs more often than any other, we call this the *most probable distribution.* While the most probable distribution may or may not be found actually; it is the one most likely to be found. Clearly the most probable distribution is one in which the number of balls in each cell is proportional to the size of the cell; a large cell has greater probability to be hit than a small cell.



(Fig. 6.6)

The probability $P$ that the balls be distributed in a certain way among the cells depends upon two factors :

1. *The a priori probability* G or the distribution which is based upon the properties of each cell.
2. *The thermodynamic probability* $\Omega$ of the distribution which is the number of different accessible sequence is which the balls may be distributed among the cell without changing the number in each cells. Thus the balls are explicity assumed to be identical but distinguishable.

The a priori probability $g_i$ that a balls falls into the $i$th cell is the ratio of the area $a_i$ to the total area $A$ of the entire box, *i.e.*,

$$g_i = \frac{a_i}{A} \qquad \dots(1)$$

Obviously greater is the area of the cell, greater is the probability of the ball falling into it and the cells of equal area have equal probability of getting the ball.

We have
$$A = a_1 + a_2 + \dots + a_k. \qquad \dots(2)$$

Since by hypothesis the ball falls into the box somewhere, it follows than the sum of the a priori probabilities of all the cells must be 1, *i.e.*,

$$\Sigma g_i = g_1 + g_2 + \dots + g_k = 1. \qquad \dots(3)$$

Since the probability of a composite event is equal to the product of the probability of the individual and independent events, it follows that the probability that *two balls* fall simultaneously in the $i$th cell is $g_i \times g_i = g_i^2$. Therefore the a priori probability that $n_i$ balls simultaneously in the $i$th cell is $(g_i)^{n_i}$.

The a priori probability of any particular distribution of $N$ balls among the $k$ cells such that $n_1$ ball fall in first cell, $n_2$ balls fall in second cell etc. is the product of $k$ probabilities of the form $(g_i)^{n_i}$ *i.e.*,

$$G = (g_i)^{n_1}(g_2)^{n_2} \dots (g_i)^{n_i} \dots (g_k)^{n_k}. \qquad \dots(4)$$

Subject to the conditions that the total number of balls is $N$,

*i.e.*,
$$N = n_1 + n_2 + \dots + n_i + \dots + n_k = \sum_i n_i \qquad \dots(5)$$

If all the cells are of equal size, they all have the same a prior probability $g$, so that

$$G = g^N. \qquad \dots(6)$$

Since all the distributions of balls among the cells are not equally probable, we have to introduce the concept of *thermodynamic probability*. We have $n_1$ balls in first cell, $n_2$ balls in second cell ... $n_i$ balls in $i$th cell, ... and $n_k$ balls in $k$th cell. There can be a number of ways in which this configuration can be obtained. This number is called the thermodynamic probability for this configuration.

The number of ways in which any $n_1$ ball out of total $N$ balls may fall in the first cell are

$$^N C_{n_1} = \frac{N!}{n!(N - n_1)!}.$$

The number of ways in which any $n_2$ balls but of remaining $(N - n_1)$ balls may fall in the second cell are

$$^{N-n_1} C_{n_2} = \frac{(N - n_1)!}{n_3!(N - n_1 - n_2)!}.$$

The number of ways in which any $n_3$ balls out of remaining $(N - n_1 - n_2)$ balls may fall in the third cell are

$$^{N-n_1-n_2}C_{n_3} = \frac{(N-n_1-n_2)!}{n_2!\,(N-n_1-n_2-n_3)!}$$

and so on upto $n_k$ balls for $k$ th cell.

The total number of ways in which $n_1$ balls fall in cell 1, $n_2$ balls fall in cell 2 ... $n_k$ balls fall in cell $k$ are

$$\Omega = \frac{N!}{n_1!\,(N-n_1)!} \times \frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)!} \times \frac{(N-n_2-n_2)!}{n_3!\,(N-n_1-n_2-n_3)!} \times \ldots \times \frac{(N-n_1-n_2\ldots-n_{k-1})!}{n_k!\,(N-n_1-n_2\ldots-n_k)!}$$

$$= \frac{N!}{n_1!\,n_2!\ldots n_k!}.$$

This expression represents the thermodynamic probability of the distribution.

The total probability $P$ of the distribution is the product of the a priori probability $G$ and the thermodynamic probability $W$

*i.e.,*
$$P = G\Omega = \frac{N!}{(n_1!\,n_2!\ldots n_k)!}(g_1)^{n_1}(g_2)^{n_2}\ldots(g_i)^{n_i}\ldots(g_k)^{n_k}$$

$$= N!\prod_{i=1}^{k}\frac{(g_i)^{n_i}}{n_i!} \qquad \ldots(7)$$

To prove the correctness of equation. (7) we use the fact that the sum of the probabilities of all possible distribution must be equal to 1.

For the purpose, adding probabilities of all possible distributions, *i.e.,*

$$\Sigma P = \Sigma N!\prod_{i=1}^{k}\frac{(g)^{n_i}}{n_i!}$$

Using multinomial theorem (a generalization of the binomial theorem), we get

$$\Sigma P = (g_1 + g_2 + \ldots + g_k)^N.$$

Since from equation (3), $g_1 + g_2 + \ldots + g_k = 1$, we get

$$\Sigma P = g^N = 1$$

which means that all $N$ balls are certain to fall in the box somewhere. This confirms the correctness of equation (7).

## 6.15 Stirling's Formula

For a very large values of $n$, the calculation of $n!$ becomes very troublesome. Stirling's formula gives a suitable analytic approximation of $\log n!$ for large values of $n$.

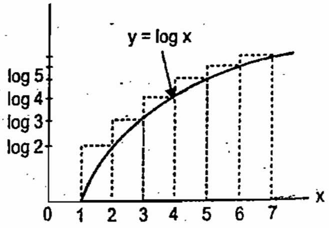
We note that

$$n! = n(n-1)(n-2)\ldots 4\times3\times2\times1.$$

Thus
$$\log n! = \log n + \log(n-1) + \log(n-2) + \ldots$$
$$+ \log 4 + \log 3 + \log 2 + \log 1$$

$$= \sum_{x=2}^{n}\log x \qquad (\text{since } \log 1 = 0) \qquad \ldots(1)$$

Let us now plot $\log x$ versus $x$ for values of $x = 2, 3 \ldots n$ as shown in fig. 6.7.



(Fig. 6.7)

The area under the stepped curve is

$$= \sum_{x=2}^{n}\log x = \log(n)!.$$

For large values of $x$, the stepped curve and the smooth curve of $\log x$ become indistinguishable. So we can approximate $\log n!$ by integration of $\log x$ for $x = 1$ to $n$. This approximation is quite satisfactory for large values of $n$ since $\log x$ in the range of large values of $x$ varies only slightly when $x$ is increased by unity. Thus for large values of $n$.

$$\log n! = \int_1^n \log x\,dx$$

$$= \int x\log x\Big]_1^n - \int_1^n \frac{1}{x}\cdot x\,dx$$

$$= n\log n - n + 1.$$

As $n$ is very large, we may neglect 1 in the above result, so we obtain

$$\log n! = n\log n - n. \qquad \ldots(2)$$

This equation is known as *Stirling's formula.*

## 6.16 The Most Probable Distribution

Let us now see which distribution of the balls is most probable, *i.e.,* which distribution has the largest probability $P$. The total probability $P$ of a distribution ($n_1$ phase points in cell 1, $n_2$ phase points in cell 2, ..., $n_k$ phase points in cell $k$) is given by (equation (7) of 6.14)

$$P = \frac{N!}{n_1!\,n_2!\ldots n_k!}(g_1)^{n_1}(g_2)^{n_2}\ldots(g_i)^{n_i}\ldots(g_k)^{n_k} \qquad \ldots(1)$$

Taking natural logarithm of above equation, we get

$$\log P = \log(N)! - \sum_i \log(n_i)! + \sum_i n_i \log g_i \qquad \ldots(2)$$

Using Stirling's formula we may write equation (2) as

$$\log P = N\log N - N - \sum_i n_i \log n_i + \sum_i n_i + \sum_i n_i \log g_i.$$

But $\sum_i n_i = N$, therefore,

$$\log P = N\log N - \sum_i n_i \log n_i + \sum_i n_i \log g_i. \qquad \ldots(3)$$

For *most probable distribution,* small changes $\delta n_i$ in any of the $n_i$'s do not affect the value of $P$ *i.e.,*

$$\frac{\partial P_{\max}}{\partial n_i} = 0 = \frac{\partial(\log P_{\max})}{\partial n_i} \qquad \ldots(4)$$

for most probable distribution.

As $N$ is constant, therefore, for most probable distribution equation (3), yields.

$$\delta \log P_{\max} = -\sum_i n_i\,\delta(\log n_i) - \sum_i \log n_i\,\delta n_i + \sum_i \log g_i\,\delta n_i = 0. \qquad \ldots(5)$$

Now $\delta \log n_i = \dfrac{1}{n_i}\,\delta n_i$

Therefore,
$$\sum_i n_i \,\delta (\log n_i) = \sum_i \delta n_i, \qquad \ldots(6)$$
$$-\sum_i \delta n_i - \sum_i \log n_i \delta n_i + \sum_i \log g_i \,\delta n_i = 0 \qquad \ldots(7)$$

Since total number of balls is constant *i.e.*,
$$N = \sum_i n_i$$
$$\sum_i \delta n_i = 0. \qquad \ldots(8)$$

Using equation (8), equation (7) becomes
$$-\sum_i \log n_i \,\delta n_i + \sum_i \log g_i \,\delta n_i = 0. \qquad \ldots(9)$$

Now we shall use the method of Lagrangian undermined multipliers. For the purpose multiplying equation (8) by undetermined multiplier α which does not depend upon any of the $n_i$'s,

*i.e.*,
$$\sum_i \alpha \delta n_i = 0. \qquad \ldots(10)$$

Adding equations (9) and (10) we obtain
$$-\sum_i \log n_i \,\delta n_i + \sum_i \log g_i \,\delta n_i + \sum_i \alpha \,\delta n_i = 0.$$

*i.e.*,
$$\sum (-\log n_i + \log g_i + \alpha)\, \delta n_i = 0 \qquad \ldots(11)$$

As $\delta n_i$'s are independent variables, therefore for the validity of equation (11), the quantity in parentheses must always be zero regardless of the value of $i$.

Thus we, have
$$-\log n_i + \log g_i + \alpha = 0,$$

*i.e.*,
$$n_i = g_i e^{\alpha}. \qquad \ldots(12)$$

Since α does not depend upon $i$, we have
$$\sum_i n_i = e^{\alpha} \sum_i g_i.$$

Remembring that $g_i$ is the priori probability that a ball falls into the $i$th cell, so from equation (3) of 6.14, we have
$$\sum_i g_i = 1$$

Therefore
$$e^{\alpha} = \sum n_i = N.$$

Hence equation (12) becomes
$$n_i = N g_i. \qquad \ldots(13)$$

*Thus, for most probable distribution the number of balls in any cells is proportional both to the total number of balls N and to the a priori probability $g_i$ which is equal to the relative size of the cell i.e., $g_i = \frac{a_i}{A}$ and, therefore,*
$$n_i = \frac{N}{A} a_i. \qquad \ldots(14)$$

*Thus, for most probable distribution the number of balls in any cell is equal to the product of the average density $\left(\frac{N}{A}\right)$ and the area of the cell.*

## SOLVED EXAMPLES

**Ex. 10.** *Four distinguishable coins are tossed for a large number of times. Write down the different microstates which may be observed and the macrostate into which they would fall. Write down the probability of the most probable macrostate.*

**Solution.** Let us denote the coins by $a, b, c, d$. If they are tossed for a large number of times we shall have the microstates and macrostates as shown in table.

| Microstate | | Macrostate |
|---|---|---|
| Coins having head up | Coins having tail up | $n_1$ = number of heads up<br>$n_2$ = number of tails up |
| *abcd* | — | $n_1 = 4, n_2 = 0$ |
| *abc* | *d* | $n_1 = 3, n_2 = 1$ |
| *abd* | *c* | $n_1 = 3, n_2 = 1$ |
| *acd* | *b* | $n_1 = 3, n_2 = 1$ |
| *bcd* | *a* | $n_1 = 3, n_2 = 1$ |
| *ab* | *cd* | $n_1 = 2, n_2 = 2$ |
| *ac* | *bd* | $n_1 = 2, n_2 = 2$ |
| *ad* | *bc* | $n_1 = 2, n_2 = 2$ |
| *bc* | *ad* | $n_1 = 2, n_2 = 2$ |
| *bd* | *ac* | $n_1 = 2, n_2 = 2$ |
| *cd* | *ab* | $n_1 = 2, n_2 = 2$ |
| *a* | *bcd* | $n_1 = 1, n_2 = 3$ |
| *b* | *acd* | $n_1 = 1, n_2 = 3$ |
| *c* | *abd* | $n_1 = 1, n_2 = 3$ |
| *d* | *abc* | $n_1 = 1, n_2 = 3$ |
| — | *abcd* | $n_1 = 0, n_2 = 4$ |

Clearly the number of microstates is 16 while that of macrostates is 5.

The most probable macrostate is $n_1 = 2, n_2 = 2$ whose probability is $6/16 = 3/8$.

**Ex. 11.** *In a random distribution of 10 particles between two boxes with equal probability, calculate the following :*

*(i) Probability of distribution (3, 7).*

*(ii) Ratio of probability of this distribution with the distribution of the largest probability.*

*(iii) The total number of microstates and the number of macrostates.*

*(iv) The number of microstates in macrostates (3, 7).*

**Solution.** The probability of the distribution $(r, s)$ is
$$P(r, s) = \frac{n!}{r!\,s!} \cdot \frac{1}{2^n} \qquad \text{where } s = n - r.$$

(i) Here $r = 3$, $s = 7$, $n = 10$; therefore, the probability of distribution (3, 7) is given by
$$P(3, 7) = \frac{10!}{3!\,7!} \cdot \frac{1}{2^{10}}$$
$$= 120 \times 2^{-10}.$$

(ii) For the distribution of largest probability,

$$r = \frac{n}{2} = \frac{10}{2} = 5 \text{ (since } n = 10)$$

and

$$s = n - r = 10 - 5 = 5.$$

∴ Largest probability

$$P(5, 5) = \frac{10\,!}{5\,!\,5\,!} \cdot \frac{1}{2^{10}}$$

$$= 252 \times 2^{-10}.$$

∴ Ratio of probability of distribution (3, 7) to that of largest probability.

$$= \frac{P(3, 7)}{P(5, 5)} = \frac{120 \times 2^{-10}}{252 \times 10^{-10}}$$

$$= \frac{10}{21}.$$

(iii) Total number of microstates $= 2^n = 2^{10}$.

Total number of microstates = number of terms in binomial expansion.

$$(a+b)^n = \text{number of binomial terms in } (a+b)^{10}$$

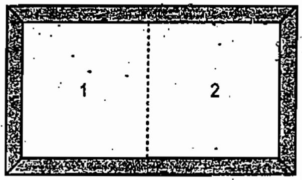
$$= 11.$$

The number of microstates in macrostate (3, 7)

$$= \frac{n\,!}{r\,!\,n-r\,!} = \frac{10\,!}{3\,!\,7\,!} = 120.$$

## 6.17 Fluctuations and their dependence on *N*.

Consider *N* molecules of an ideal gas confined within a container or a box. Let us now consider the positions of these molecules and their distribution in space. For the purpose, consider the box to be divided by some imaginary partition into two equal parts. Let *n* and *n′* be the number of molecules in the left and right halves of the box respectively then



(Fig. 6.8)

$$n + n' = N$$

If *N* is large, it would ordinarily be found that $n \approx n'$ *i.e.*, approximately half of the molecules are in each half of the box.

Due to intermolecular interactions, the molecules collide with each other or with the walls; as a result some of the molecules enter left half of the box while some leave it. Thus the number *n* of the molecules actually located in the left half fluctuates constantly in time. For large *N* these fluctuations are so small that *n* does not differ too much from $\frac{N}{2}$. The state $\left(\frac{N}{2}, \frac{N}{2}\right)$ is the state of maximum probability and is called **equilibrium state.** Actually the different states are repeated in proportion to their probabilities. Thus all the *N* molecules may be in the left half of the box (*i.e.*, $n = N$, $n' = 0$); but the probability of occurrence of such a state is appreciably small.

If $N = 40$ the most probable distribution is (20, 20). The probability of this distribution is

$$P_{\max} = P(20, 20) = \frac{40\,!}{20\,!\,20\,!} \cdot \frac{1}{2^{40}}.$$

The probability of distribution (15, 25), *i.e.*, a distribution 25% off most probable distribution is

$$P(15, 25) = \frac{40\,!}{15\,!\,25\,!} \cdot \frac{1}{2^{40}}.$$

The ratio *R* of these two probabilities is

$$R\,(25\%\text{ off}) = \frac{P(15, 25)}{P(20, 20)}$$

$$= \frac{20\,!\,20\,!}{15\,!\,25\,!} \approx 0{\cdot}3.$$

If $N = 400$ the probability of most probable distribution (200, 200) is

$$P(200, 200) = \frac{400\,!}{200\,!\,200\,!} \cdot \frac{1}{2^{400}}.$$

The probabiliy of a distribution 25% off from this

*i.e.*,

$$P(150, 250) = \frac{400\,!}{150\,!\,250\,!} \cdot \frac{1}{2^{400}}.$$

∴ The relative probability, $R\,(25\%\text{ off}) = \dfrac{P(150, 250)}{P(200, 200)}$

$$\approx 10^{-5}.$$

This it is obvious tht as *N increases the probability of distributions appreciably far from the most probable distribution becomes appreciably small.*

Let us now consider $2n$ particles randomly distributed in two halves of a box. The most probable distribution will be $(n, n)$. The probability of the most probable distribution,

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

The probability of the distribution $(n+s, n-s)\left(\frac{s}{n} \ll 1\right)$ is,

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

∴ Relative probability $(n+s, n-s)$ will be,

$$R = \frac{P(n+s, n-s)}{P(n, n)}$$

$$= \frac{n\,!\,n\,!}{n+s\,!\,n-s\,!}$$

$$= \frac{(n-s+1)(n-s+2)\ldots n}{(n+1)(n+2)\ldots(n+s)}$$

$$= \left\{\frac{(n+1)-s}{n+1}\right\}\left\{\frac{(n+2)-s}{n+2}\right\}\ldots\left\{\frac{n}{n+s}\right\}$$

$$= \left(1 - \frac{s}{n+1}\right)\left(1 - \frac{s}{n+2}\right)\ldots\left(1 - \frac{1}{1+s/n}\right)$$

$$\approx \left(1 - \frac{s}{n}\right)\left(1 - \frac{s}{n}\right)\ldots\left(1 - \frac{s}{n}\right) (s \text{ times})$$

$$= \left(1 - \frac{s}{n}\right)^s$$

$$\therefore \quad \log_e R = s \log_e\left(1 - \frac{s}{n}\right)$$

$$= s\left[-\frac{s}{n} - \frac{s^2}{n^2} - \frac{s^3}{n^3} - \frac{s^4}{n^4} \ldots\right]$$

$$= s\left(-\frac{s}{n}\right) \text{for } s << n$$

$$= -\frac{s^2}{n} = -\frac{s^2}{n^2} n$$

$$= -f^2 . n$$

where $f = \frac{s}{n}$ is the fractional deviation from the most probable distribution

$$\therefore \qquad R = e^{-f^2 n} = \exp(-f^2 n)$$

$\therefore$ The probability of distribution corresponding to fractional deviation $f$ will be

$$P(f) = Ce^{-f^2 n}$$

$$= C \exp(-f^2 n)$$

where $C$ is any constant.

We have

$$\int_{-1}^{+1} P(f)\, df = 1$$

$$\int_{-1}^{+1} Ce^{-f^2 n}\, df = 1$$

This gives $C = \sqrt{\left(\frac{n}{\pi}\right)}$

$$\therefore \qquad P(f) = \sqrt{\left(\frac{n}{\pi}\right)}\, e^{-f^2 n}$$

$$= \sqrt{\frac{n}{\pi}} \exp(-f^2 n)$$

It is obvious that as the fractional deviation $f$ from the most probable distribution increases, the probability $P(f)$ decreases exponentially.

This result may also be derived as follows :

For the distribution of $N$ molecules of a gas in two equal halves of a box, the most probable distribution is $\left(\frac{N}{2}, \frac{N}{2}\right)$ or $(n, n')$ with $n = n' = \frac{N}{2}$.

If the distribution $(n, n')$ is such that $n = \frac{N}{2} + x$, where $N$ is very large, we have $N - n = \frac{N}{2} - x$; so that the probability of the distribution is given by

$$P(n, n') = \frac{N!}{n!\,n'!} \cdot \frac{1}{2^N} = \frac{N!}{\left(\frac{1}{2}N + x\right)!\left(\frac{1}{2}N - x\right)!} \cdot \frac{1}{2^N}$$

$$= \frac{N!}{\left[\left(\frac{N}{2}\right)\right]^2} \cdot \frac{1}{2^N} \cdot \frac{\left[\left(\frac{N}{2}\right)!\right]^2}{\left(\frac{1}{2}N + x\right)!\left(\frac{1}{2}N - x\right)!}$$

$$= P_{\max} \cdot \frac{\left[\left(\frac{N}{2}\right)!\right]^2}{\left(\frac{1}{2}N + x\right)!\left(\frac{1}{2}N - x\right)!} \qquad \ldots(3)$$

According to Stirling theorem for large values of $N$,

$$\log N! = N \log N - N = N(\log N - 1)$$

therefore equation (3) becomes

$$\log P(n, n') = \log P_{\max} + 2\left(\frac{N}{2}\right)\left[\log\left(\frac{N}{2} - 1\right) - \left(\frac{N}{2} + x\right)\left[\log\left(\frac{N}{2} + x\right) - 1\right]\right.$$
$$\left. - \left(\frac{N}{2} - x\right)\left[\log\left(\frac{N}{2} - x\right) - 1\right]\right]$$

If $\frac{x}{N} << 1$, then $\log\left(1 + \frac{2x}{N}\right) = \frac{2x}{N} - \frac{2x^2}{N^2}$.

$$\log P(n, n') = \log P_{\max} - \frac{2x^2}{N}$$

$$\therefore \qquad P(n, n') = P_{\max} \cdot \exp\left(\frac{-2x^2}{N}\right) = \frac{N!}{\left(\frac{N}{2}\right)^2 !} \cdot \frac{1}{2^N} \exp\left(\frac{-2x^2}{N}\right)$$

$\therefore$ Thus obviously the probability of the distribution for large values of $N$, *i.e.*, for a large deviation from most probable distribution is vanishingly small and decreases exponentially with increase of $x$.

## 6.18 Time and Ensemble Averages

An ensemble consists of a large number of independent systems, each of which may be represented by a particular point in the phase space. For example, a gas containing a large number of molecules forming a system. The gas molecules move constantly and hence they change their position and momentum with time. The entire gas, however, shows a time independent property *e.g.*, temperature, energy, etc. which may be considered as the average of the specified property of the constituent gas molecules Our aim is to discuss this type of average property of the ensemble.

Let the state of the ensemble changes with time due to the motion of the phase points corresponding to its systems.

Let $u$ be the property of the ensemble which takes values of $u_1, u_2, u_3, \ldots, u_i, \ldots, u_m$ in the states of the ensemble having probabilities $P_1, P_2, P_3, \ldots, P_i, \ldots, P_m$, respectively, then the average values of $u$, denoted by $\bar{u}$ is defined as

$$\bar{u} = \frac{P_1 u_1 + P_2 u_2 + P_3 u_3 + \ldots + P_i u_i + \ldots + P_m u_m}{P_1 + P_2 + P_3 + \ldots + P_m}$$

$$= \frac{\sum_{i=1}^{m} P_i u_i}{\sum_{i=1}^{m} P_i} \qquad \dots(1)$$

Since the ensemble has be to be found in any of the possible states, the sum of the probabilities of all possible stats must be equal to 1 *i.e.,*

$$P_1 + P_2 + P_3 + \dots + P_i + \dots + P_m = \sum_{i=1}^{m} P_i = 1. \qquad \dots(2)$$

This is called the *normalisation condition.*

Using equation (2), equation (1) becomes

$$\bar{u} = \sum_{i=1}^{m} P_i u_i \qquad \dots(3)$$

If the ensemble consists of $N$ systems, the property $u$ can be expressed as the function of all position and momentum coordinates of the systems of the ensemble. If the probability distribution function is continuous function in all position and momentum co-ordinates, then equation (1) may be expressed as

$$\bar{u} = \frac{\int u(q,p)\, P(q,p)\, d\Gamma}{\int P(q,p)\, d\Gamma} \qquad \dots(4)$$

where $d\Gamma = dq_1 \dots dq_f dp_1 \dots dp_f$

But according to the normalization condition.

$$\int P(q,p)\, d\Gamma = 1.$$

Therefore, the ensemble average of any quantity $u$, is given by

$$\bar{u} = \int u(q,p)\, P(q,p)\, d\Gamma. \qquad \dots(5)$$

## 6.19 Division of Phase Space into Cells

Consider a $2f$ dimensional phase space defined by position coordinates $q_1, q_2, q_f$ and momentum co-ordinates $p_1, p_2, \dots, p_f$.

An element of volume in this phase space will be represented by

$$\delta q_1 . \delta q_2 \dots \delta q_f . \delta p_1 . \delta p_2 \dots \delta p_f \qquad \dots(1)$$

The dimensions of this volume element are those of (length × momentum)$^f$. Therefore the unit of this volume element is (joule-second)$^f$.

Let us now divide any finite volume of phase space into a large number of cells. Let the size of each cell be $h^f$. Here $h$ is any arbitrary constant and has the dimensions of joule-second,

*i.e.,*

$$h = \delta q_i \, \delta p_i \qquad \dots(2)$$

As $p_i$ and $q_i$ can take all possible continuously variable values there may be infinite representative points and hence possible microstates in any finite volume of phase space.

The number of phase cells in this volume is

$$\frac{\delta q_i \, \delta q_2 \dots \delta q_f . \delta p_1 \, \delta p_2 \dots \delta p_f}{h^f} \qquad \dots(3)$$

## 6.20 Number of Microstates in the Energy Range $E$ to $E + \delta E$.

For a single particle we have six dimensional phase space. Three position co-ordinates $(x, y, z)$ and three momentum co-ordinates $p_x, p_y, p_z$ specify the microstate of a particle in the phase space. An element of volume in the phase space is

$$\delta x \, \delta y \, \delta z \, \delta p_x \, \delta p_y \, \delta p_z = h^3 \qquad (\text{since } h = \delta p_i \, \delta q_i)$$

The total volume of the phase space is

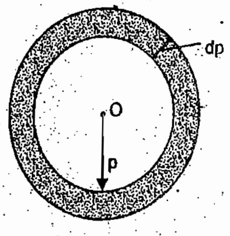
$$\iiiiiint dx\, dy\, dz\, dp_x\, dp_y\, dp_z$$

where the limits of integration are to be specified.

We have $\iiint dx\, dy\, dz =$ given volume $V$

So the volume of phase space $= V \iiint dp_x\, dp_y\, dp_z$

Volume of momentum space containing momentum between $p$ and $p + dp$ will be given by the volume of a spherical shell of radius $p$ and thickness $dp$.



(Fig. 6.9)

Therefore $\iiint dp_x\, dp_y\, dp_z = 4\pi p^2 \, dp$

If energy corresponding to momentum $p$ is ε, then

$$p^2 = 2m\varepsilon \quad \text{or} \quad p = \sqrt{(2m\varepsilon)}$$

$$\therefore \quad dp = \sqrt{(2m)} \cdot \frac{1}{2} \varepsilon^{-1/2} \, d\varepsilon$$

$$= \sqrt{\left(\frac{m}{2\varepsilon}\right)} \, d\varepsilon$$

Therefore volume of phase space

$$= V . 4\pi (2m\varepsilon) \sqrt{(m/2\varepsilon)} . d\varepsilon$$

$$= 4 \sqrt{2} \, \pi V \, m^{3/2} \, \varepsilon^{1/2} \, d\varepsilon$$

$\because$ The number of cells in the phase space

$$\Omega(\varepsilon)\, d\varepsilon = \frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \, \varepsilon^{1/2} \, d\varepsilon .$$

For a single particle the number of accessible microstates will be equal to the number of cells in the phase space. Therefore, the number of microstates in this energy range ε to ε + δε is given by

$$\Omega(\epsilon)\, d\varepsilon = \frac{\sqrt{2}\pi V}{h^3} m^{3/2} \, \varepsilon^{1/2} \, d\varepsilon$$

## 6.21 Maxwell Boltzmann Distribution Law

The assemblies consist of, in general, three kinds of particles :

1. Identical but distinguishable particles of any spin. The molecules of a gas are the particles of this kind.

2. Identical and indistinguishable particles of zero or integral spin. The helium atoms at low temperature and the photons are the particles of this kind. These particles are called *Bose particles* and do not obey the Pauli's exclusion principle.

3. Identical and indistinguishable particles of spin $\frac{1}{2}$. These particles obey Pauli's exclusion principle and are called the *Fermi particles*. The examples of this kind of particles are electrons, protons, neutrons etc.

The particles of first kind obey the *Maxwell-Boltzmann distribution law* which tells us how a total fixed amount of energy is distributed among the various members of an assembly of identical particles in the most probable distribution.

Consider a system of $N$ similar; but distinguishable molecules of a gas. We know that the instantaneous state of a molecule is represented by a phase point in the phase space. Let the phase space be divided into a large number of cells 1, 2, 3, ... $i$, ... $k$. Let $n_1, n_2, n_3, \ldots n_i \ldots n_k$ be the number of gas molecules whose phase points lie in cell $1, 2, 3, \ldots i, \ldots k$ respectively in the equilibrium state. As the gas molecules are moving continuously; therefore, $n_i$'s will change continuously in many different ways; but will always keep values close to those for the state of equilibrium *i.e.*, the most probable state. Let us suppose $n_i$'s change obeying the fundamental postulate of statistical mechanics;

(1) The total number of molecules is constant *i.e.*,

$$N = n_1 + n_2 + n_3 + \ldots + n_i + \ldots n_k = \text{constant}. \qquad \ldots(1a)$$

or

$$\delta N = \delta n_1 + \delta n_2 + \delta n_3 + \ldots + \delta n_i + \ldots + \delta n_k = 0$$

*i.e.*,

$$\sum_i \delta n_i = 0. \qquad \ldots(1b)$$

(2) The total energy of the system is constant, *i.e.*,

$$E = \varepsilon_1 n_1 + \varepsilon_2 n_2 + \varepsilon_3 n_3 + \ldots + \varepsilon_i n_i + \ldots + \varepsilon_k \varepsilon_k = \text{constant}, \qquad \ldots(2a)$$

or

$$\delta E = \varepsilon_1\, \delta n_1 + \varepsilon_2\, \delta n_2 + \varepsilon_3\, \delta n_3 + \ldots + \varepsilon_i\, \delta n_i + \ldots + \varepsilon_k\, \delta n_k = 0$$

*i.e.*,

$$\Sigma\, \varepsilon_i\, \delta n_i = 0. \qquad \ldots(2b)$$

(3) When gas is in equilibrium, the probability is maximum,

*i.e.*,

$$\delta P = 0.$$

When $P$ is maximum, $\log P$ is maximum,

*i.e.*,

$$\delta (\log P) = 0. \qquad \ldots(3)$$

But

$$P = \frac{N\,!}{n_1\,!\, n_2 \ldots n_i\,! \ldots n_k\,!} (g_1)^{n_1} (g_2)^{n_2} \ldots (g_i)^{n_i} \ldots (g_k)^{n_k}$$

where $g_i$ is the a priori probability for a molecule to have the energy $\varepsilon_i$.

Taking natural logarithm of above equation, we get

$$\log P = \log N\,! - \sum_i \log n_i\,! + \sum_t n_i \log g_i$$

Using Stirling's formula, we get

$$\log P = N \log N - N - \sum_i n_i \log n_i + \sum_t n_i + \sum_i n_i \log g_i$$

But $\sum_t n_i = N$, therefore

$$\log P = N \log N - \sum_i n_i \log n_i + \sum_t n_i \log g_t$$

Therefore, according to equation (3), we get

$$\delta (\log P) = 0 - \sum_i n_i\, \delta (\log n_i) - \sum_i \log n_i\, \delta n_i + \sum_t \log g_i\, \delta n_i = 0 \qquad \ldots(4)$$

(since $N \log N$ is constant).

But

$$n_i\, \delta (\log n_i) = n_i \times \frac{1}{n_i}\, \delta n_i = \delta n_i$$

or

$$\sum_i n_i\, \delta (\log n_i) = \sum_i \delta n_i = 0 \qquad \text{[using (1)]}$$

Therefore, equation (4) gives

$$\sum_i \log n_i\, \delta n_i - \sum_t \log g_i\, \delta n_i = 0. \qquad \ldots(5)$$

Let us now use the method of Lagrangian undetermined multipliers. For the purpose multiplying equations [1 (b)] and [2 (b)] by $\alpha$ and $\beta$ respectively, where $\alpha$ and $\beta$ are undermined quantities independent of $n_i$'s and then adding the resulting expression to equation (5), we get

$$\sum_i \log n_i\, \delta n_i - \sum_i \log g_i\, \delta n_i + \sum_i \alpha \delta n_i + \sum_i \beta \varepsilon_i\, \delta n_i = 0$$

*i.e.*,

$$\sum_i [\log n_i - \log g_i + \alpha + \beta \varepsilon_i]\, \delta n_i = 0. \qquad \ldots(6)$$

As $\delta n_i$'s are independent variables, therefore for the validity of equation (6), the quantity within brackets must always be zero regardless of the value of $i$. Thus, we have

$$\log n_i - \log g_i + \alpha + \beta \varepsilon_t = 0,$$

*i.e.*,

$$n_i = g_i e^{-\alpha} e^{-\beta \varepsilon_i}$$

or

$$n_i = A g_i\, e^{-\beta \epsilon_i} \qquad \ldots(7)$$

where $A = e^{-\alpha}$ is a new constant

This result determines the most probable distribution of molecules among the various possible individual states and is known as *Maxwell-Boltzmann distribution law*.

**Evaluation of constants $A$ and $\beta$.**

For evaluating $A$ and $\beta$ it is convenient to consider continuous distribution of molecular energies rather than discrete energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_k$.

Then equation (7) becomes

$$n (\varepsilon)\, d\varepsilon = A g (\varepsilon)\, e^{-\beta \varepsilon}\, d\varepsilon. \qquad \ldots(8)$$

Here $n$ ($\varepsilon$) represents the number of molecules having energies between $\varepsilon$ and $\varepsilon + d\varepsilon$. If $p$ is the molecular momentum, then

$$\varepsilon = \frac{p^2}{2m}.$$

So that equation (8) may be written as

$$n (p)\, dp = A g (p)\, e^{-\beta p^2/2m}\, dp. \qquad \ldots(9)$$

Here $n (p)\, dp$ represents the number of molecules having momentum between $p$ and $p + dp$. The a priori probability $g (p)$ that a molecule have momentum between $p$ and $p + dp$ is equal to the number of cells in the phase space within which such a molecule may exist. If each cell has infinitesimal volume $h^3$, then

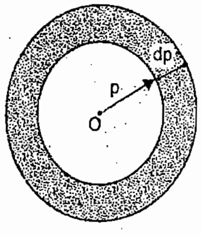
$$g (p)\, dp = \frac{\int\int\int\int\int\int dx\, dy\, dz\, dp_x\, dp_y\, dp_z}{h^3} \qquad \ldots(10)$$

where the number represents the volume of the phase space occupied by the particles with the specified momenta.

If $V$ is the volume occupied by the gas in ordinary position space, then

$$\iiint dx\,dy\,dz = V. \qquad \ldots(11)$$

Now we have to integrate with respect to $p_x, p_y, p_z$. If we care only about the resultant momentum components, we can find $\iiint dp_x\,dp_y\,dp_z$ as follows :



(Fig. 6.10)

Let us imagine that $p_x, p_y$ and $p_z$ are along three mutually perpendicular axes and draw a sphere of radius $p$ about the origin. Then the surface of the sphere drawn will contain all the points for which $p_x^2 + p_y^2 + p_z^2 = p^2$. Now let us draw another sphere of radius $p + dp$ concentric with the first. The volume between two spheres of radii $p$ and $p + dp$ will contain all the molecules in the momentum having momentum between $p$ and $p + dp$.

The volume between two spheres is given by

$$\iiint dp_x\,dp_y\,dp_z = \frac{4}{3}\pi\,(p+dp)^3 - \frac{4}{3}\pi p^3.$$

$$= \frac{4}{3}\pi\,[p^3 + 3p^2\,dp + 3p\,dp^2 + dp^3] - \frac{1}{3}\pi p^3$$

$$= \frac{4}{3}\pi\,.\,3p^2 dp \text{ neglecting terms containing } dp^2 \text{ and } dp^3$$

$$= 4\pi p^2\,dp. \qquad \ldots(12)$$

Substituting values from equations (11) and (12) in equation (10), we get

$$g\,(p)\,dp = \frac{V\,4\pi p^2\,dp}{h^3} \qquad \ldots(13)$$

Therefore,

$$n\,(p)\,dp = \frac{V\,.\,4\pi p^2\,A\,e^{-\beta p^2/2m}\,dp}{h^3} \qquad \ldots(14)$$

Since total number of molecules is $N$, *i.e.*,

$$\int_0^\infty n\,(p)\,dp = N \qquad \ldots(15)$$

the integral of equation (14) yields

$$N = \frac{4\pi\,VA}{h^3}\int_0^\infty p^2 e^{-\beta p^2/2m}\,dp. \qquad \ldots(16)$$

Since standard definite integral

$$\int_0^\infty x^2\,e^{-ax^2}\,dx = \frac{1}{4}\sqrt{\left(\frac{\pi}{a^3}\right)},$$

$$\therefore \quad \int_0^\infty p^2\,e^{-\beta p^2/2m}\,dp = \frac{1}{4}\left[\frac{\pi}{(\beta/2m)^3}\right]^{1/2} = \frac{1}{4}\left[\frac{8m^3\pi}{\beta^3}\right]^{1/2} \qquad \ldots(17)$$

Substituting the value of the integral (17) in (16), we get

$$N = \frac{4\pi\,VA}{h^3}\cdot\frac{1}{4}\left[\frac{8m^2\,\pi}{\beta^3}\right]^{1/2} = \frac{AV}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}$$

*i.e.*,

$$A = \frac{Nh^3}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2} \qquad \ldots(18)$$

Substituting this value in (14), we get

$$\therefore \quad n\,(p)\,dp = 4\pi N\left(\frac{\beta}{2\pi m}\right)^{3/2}.\,e^{-\beta p^2/2m}\,p^2 dp. \qquad \ldots(19)$$

In order to calculate the value of $\beta$, we compute the total energy $E$ of the system of molecules. Remembering that

$$p^2 = 2m\varepsilon \text{ and } dp = \frac{m\,d\varepsilon}{\sqrt{(2m\varepsilon)}}, \text{ we may write equation (19) as}$$

$$n\,(\varepsilon)\,d\varepsilon = 4\pi N\left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta\varepsilon}\,2m\varepsilon\,\frac{m\,d\varepsilon}{\sqrt{(2m\varepsilon)}}$$

$$\therefore \quad = 2\pi N\left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta\varepsilon}\,\varepsilon^{1/2}\,d\varepsilon. \qquad \ldots(20)$$

The total energy $E$ is given by

$$E = \int_0^\infty \varepsilon n\,(\varepsilon)\,d\varepsilon = \int_0^\infty 2\pi N\left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta\varepsilon}\,\varepsilon^{3/2}\,d\varepsilon$$

Using standard definite integral $\int_0^\infty e^{-\beta\varepsilon}\,e^{3/2}\,d\varepsilon = \frac{3}{4}\sqrt{\left(\frac{\pi}{\beta^5}\right)}$.

We get

$$E = 2\pi N.\left(\frac{\beta}{\pi}\right)^{3/2}\cdot\frac{3}{4}\sqrt{\left(\frac{\pi}{\beta^5}\right)} = \frac{3}{2}\frac{N}{\beta} \qquad \ldots(21)$$

As we are considering the non-interacting (ideal) gas molecules, according to kinetic theory of gases the total energy $E$ of $N$ molecules of an ideal gas at absolute temperature $T$ is

$$E = \frac{3}{2}NkT, \qquad \ldots(22)$$

where $k$ is Boltzmann's constant and its value is $1{\cdot}380 \times 10^{-23}$ joule/kelvin.

Comparing equations (21) and (22), we get

$$\frac{3}{2}\frac{N}{\beta} = \frac{3}{2}NkT$$

*i.e.*,

$$\beta = \frac{1}{kT} \qquad \ldots(23)$$

Substituting this value in equation (19) and (20), we get

$$n\,(p)\,dp = 4\pi N\left(\frac{1}{2\pi\,mkT}\right)^{3/2} e^{-p^2/2mkT}\,p^2 dp \qquad \ldots(24)$$

and

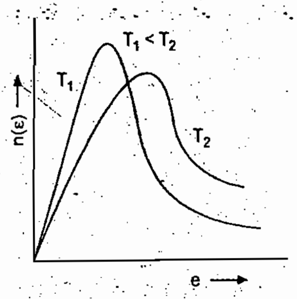
$$n\,(\varepsilon)\,d\varepsilon = 2\pi N\left(\frac{1}{\pi kT}\right)^{3/2} e^{-\varepsilon/kT}\,\varepsilon^{1/2}\,d\varepsilon. \qquad \ldots(25)$$

Equation (24) represents the number of molecules with momenta between $p$ and $p + dp$ in an assembly of an ideal gas containing $N$ molecules at absolute temperature $T$ and is called the *Maxwell-Boltzmann distribution law of momenta.*

Equation (25) represents the number of molecules with energies between $\varepsilon$ and $\varepsilon + d\varepsilon$ in the same assembly of ideal gas and is called the *Maxwell-Boltzmann distribution law of energies.* For small values of

$\varepsilon$ the term $e^{-\varepsilon/kT}$ is nearly unity and hence $n(\varepsilon)$, *i.e.*, the number of molecules with energy $\varepsilon$ is proportional to $\varepsilon^{1/2}$ and so for $\varepsilon = 0$, $n(\varepsilon) = 0$.

For large values of $\varepsilon$ the term $e^{-\varepsilon/kT}$ dominates over $\varepsilon^{1/2}$ therefore $n(\varepsilon)$ is proportional to $e^{-\varepsilon/kT}$. Thus, if $n(\varepsilon)$ is plotted against $\varepsilon$, the energy distribution curve first rises due to term $\varepsilon^{1/2}$, reaches a maximum and then falls according to $e^{-\varepsilon/kT}$. The Maxwell-Boltzmann energy distribution at two different temperatures $T_1$ and $T_2$ $(T_1 < T_2)$ is shown in fig. 6.11.



(Fig. 6.11)

## 6.22 Maxwell's Distribution Law of Velocities; the Function $F(v_x)$

Let us consider an ideal gas in a vessel of volume $V$. If the gas is in equilibrium, then according to Maxwell-Boltzmann's canonical distribution law, the number of molecules in cell of energy $\varepsilon_i$ will be

$$n_i = Ae^{-\beta\varepsilon_i}$$

Clearly, the number of molecules having position co-ordinates in the range $x$ to $x+dx$, $y$ to $y+dy$, $z$ to $z+dz$ and the velocity components in ranges $v_x$ to $v_x+dv_x$, $v_y$ to $v_y+dv_y$, $v_z$ to $v_z+dv_z$, wil be proportional to the volume element $dx\,dy\,dz\,dv_x\,dv_y\,dv_z$ of phase space.

Therefore, the number of molecules having energy $\varepsilon_i$ and having position co-ordinates between $x$ and $x+dx$, $y$ and $y+dy$, $z$ and $z+dz$ and velocity components between $v_x$ and $v_x+dv_x$, $v_y$ and $v_y+dv_y$, $v_z$ and $v_z+dv_z$ is given by

$$n_i\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z = Ae^{-\beta\varepsilon_i}\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z$$

But $\varepsilon_i$ = energy of a particle $= \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2+v_y^2+v_z^2)$

Which yields

$$n_i\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z = Ae^{-m\beta\left[\frac{1}{2}(v_x^2+v_y^2+v_z^2)\right]}dx\,dy\,dz\,dv_x\,dv_y\,dv_z \qquad ...(1)$$

The constant $A$ can be determined by the fact that the total number of molecules is constant, equal to $N$, which will be obtained by integrating eqn. (1) over all available volume and all ranges of velocities *i.e.*,

$$N = \iiiint\!\!\iint Ae^{-m\beta\left[\frac{1}{2}(v_x^2+v_y^2+v_z^2)\right]}dx\,dy\,dz\,dv_x\,dv_y\,dv_z$$

But $\iiint dx\,dy\,dz = V$ = volume of the vessel containing gas.

$$\therefore \qquad N = AV\iiint e^{-\frac{m\beta}{2}[(v_x^2+v_y^2+v_z^2)]}dv_x\,dv_y\,dv_z$$

$$= AV\int_{-\infty}^{+\infty} e^{-\frac{\beta mv_x^2}{2}}dv_x \int_{-\infty}^{+\infty} e^{-\frac{\beta mv_y^2}{2}}dv_y \int_{-\infty}^{+\infty} e^{-\frac{\beta mv_z^2}{2}}dv_z \qquad ...(2)$$

We have

$$\int_{-\infty}^{+\infty} e^{-\frac{\beta mv_x^2}{2}}dv_x = \sqrt{\left(\frac{2\pi}{m\beta}\right)}$$

$$\int_{-\infty}^{+\infty} e^{-\frac{\beta mv_y^2}{2}}dv_y = \sqrt{\left(\frac{2\pi}{m\beta}\right)}$$

and

$$\int_{-\infty}^{+\infty} e^{-\frac{\beta mv_z^2}{2}}dv_z = \sqrt{\left(\frac{2\pi}{m\beta}\right)}$$

Substituting these values in eqn. (2), we get

$$N = AV\left(\frac{2\pi}{m\beta}\right)^{3/2}$$

or

$$A = \frac{N}{V}\left(\frac{2\pi}{m\beta}\right)^{-3/2}$$

But we know $\beta = \frac{1}{kT}$

$$\therefore \qquad A = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2}$$

Substituting values of $A$ nad $\beta$ in eqn. (1), we get

$$n_i\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2kT}dx\,dy\,dz\,dv_x\,dv_y\,dv_z \qquad ...(3)$$

The number of molecules having velocity co-ordinates in the range $v_x$ to $v_x+dv_x$, $v_y$ to $v_y+dv_y$, $v_z$ to $v_z+dv_z$ irrespective of the position co-ordinates, can be found by integrating eqn. (3) with respect to position co-ordinates, which gives

$$n_i\,dv_x\,dv_y\,dv_z = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2kT}dv_x\,dv_y\,dv_z\,V.$$

$$= N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2kT}dv_x\,dv_y\,dv_z \qquad ...(4)$$

Fimally let us find the number of molecules having velocity components in the range $v_x$ to $v_x+dv_x$ irrespective of $v_y$, $v_z$, $x$, $y$, $z$. This will be obtained by integrating eqn. (4) with respect to $v_y$ and $v_z$, *i.e.*,

$$n_i\,dv_x = N\left(\frac{m}{2\pi kT}\right)^{3/2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-m(v_x^2+v_y^2+v_z^2)/2kT}dv_x\,dv_y\,dv_z$$

$$= N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-(mv_x^2/2kT)}dv_x\int_{-\infty}^{+\infty} e^{-mv_y^2/2kT}dv_y\int_{-\infty}^{+\infty} e^{-mv_z^2/2kT}dv_z$$

$$= N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv_x^2/2kT}dv_x\left[\sqrt{\frac{2\pi kT}{m}}\right]\times\left[\sqrt{\frac{2\pi kT}{m}}\right]$$

$$= N\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}dv_x. \qquad ...(5)$$

The probability that a molecule will have $x$-component of velocity in the range $v_x$ to $v_x+dv_x$ is given by

$$P(v_x)\,dv_x = \frac{n_i}{N}dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}dv_x \qquad ...(6)$$

Equations (5) and (6) represent Maxwell's distribution of velocities.

The probability function

$$f(v_x) \text{ or } P(v_x) \text{ is given by } \frac{P(v_x)\,dv_x}{dv_x}$$

$$\therefore \qquad f(v_x) = P(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} \qquad \ldots(7)$$

Equation (7) can also be expressed in terms of momentum component $p_x$. Substituting $mv_x = p_x$ and $m\,dv_x = dp_x$ on R.H.S. of equation (6), we get

$$P(p_x)\,dp_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-p_x^2/2mkT}\,\frac{dp_x}{m}$$

$$= \left(\frac{1}{2\pi mkT}\right)^{1/2} e^{-p_x^2/2mkT}\,.\,dp_x$$

$$\therefore \qquad P(p_x) = \left(\frac{1}{2\pi mkT}\right)^{1/2} e^{-p_x^2/2mkT} \qquad \ldots(8)$$

**Discussion of Maxwell's velocity distribution formula :** The probability that a molecule will have velocity component between $v_x$ and $v_x + dv_x$ is given by equation (6)

$$P(v_x)\,dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\,dv_x \qquad \ldots(9)$$

(i) From this equation it is obvious that the function $P(v_x)$ is symmetrically distributed about the value $v_x = 0$ since average value of $v_x$ for Maxwellian distribution is zero, *i.e.*,

$$\overline{v_x} = \int_{-\infty}^{+\infty} v_x\,P(v_x)\,dv_x$$

$$= \int_{-\infty}^{+\infty} \left(\frac{m}{2\pi kT}\right)^{1/2} v_x\,e^{-mv_x^2/2kT}\,dv_x$$

$$= 0 \qquad \left[\text{since} \int_{-\infty}^{+\infty} v_x\,e^{-mv_x^2/2kT}\,dv_x = 0\right]$$

Also from equation (9) it is clear that

$$P(-v_x) = P(v_x).$$

This again indicates that $P(v_x)$ is symmetrical about $v_x = 0$.

(ii) The probability distribution function is maximum for that value of $v_x$ for which

$$\frac{\partial P(v_x)}{\partial v_x} = 0$$

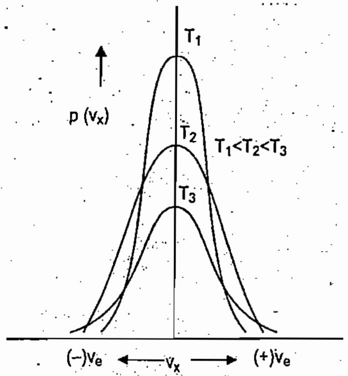
or $$\frac{\partial}{\partial v_x}\left[\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\right] = 0$$

or $$\left(\frac{m}{2\pi kT}\right)^{1/2} .\,e^{mv_x^2/2kT}\left(-\frac{m}{2kT}\right) 2v_x = 0$$

This gives $v_x = 0$ and the maximum value is

$$P_{\max}{}^{(v_x)} = \left(\frac{m}{2\pi kT}\right)^{1/2} \qquad \ldots(10)$$

This shows that $P_{\max}(v_x)$ increases as $m$ increases and $T$ decreases.



(Fig. 6.12)

The probability function $P(v_x)$ is plotted against $v_x$ for three different temperatures in fig. 6.12. As $T$ increases, the peak at $v_x = 0$ becomes lower and the distribution spreads out. The area under the curve is always unity.

## SOLVED EXAMPLES

**Example 12.** *Find the values of $v_x$ for which the probalitity falls to (i) $\frac{1}{e}$ times (ii) $\frac{1}{10}$ times, the maximum value.* ***(Kumaun 1998, Rohilkhand 2004, 2000)***

**Solution :** The probability of a molecule having $x$ component of velocity $v_x$ is.

$$P(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} \qquad \ldots(1)$$

The probability will be maximum when $v_x = 0$, *i.e.*,

$$P_{\max}(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2}$$

(i) Given $P(v_x) = \frac{1}{e}(P_{\max}) = \frac{1}{e}\left(\frac{m}{2\pi kT}\right)^{1/2}$

$\therefore$ Substituting this value of $P(v_x)$ in (1), we get

$$\frac{1}{e}\left(\frac{m}{2\pi kT}\right)^{1/2} = \left(\frac{m}{2\pi kT}\right)^{1/2} .\,e^{-mv_x^2/2kT}$$

or $$\frac{1}{e} = e^{-mv_x^2/2kT}$$

or $$-1 = -\frac{mv_x^2}{2kT}$$

$$\therefore \qquad v_x = \sqrt{\left(\frac{2kT}{m}\right)}$$

(ii) Given $P(v_x) = \frac{1}{10} P_{\max} = \frac{1}{10}\left(\frac{m}{2\pi kT}\right)^{1/2}$

or $$\frac{1}{10}\left(\frac{m}{2\pi kT}\right)^{1/2} = \left(\frac{m}{2\pi kT}\right)^{1/2} .\,e^{-mv_x^2/2kT}$$

or $$\frac{1}{10} = e^{-mv_x^2/2kT}$$

Taking log, we get

$$-\log_e 10 = \frac{-mv_x^2}{2kT}$$

or $$v_x = \sqrt{\left(\frac{2kT}{m}\log_e 10\right)} = \sqrt{\left(\frac{2kT}{m} \times 2{\cdot}3\right)}$$

$$\therefore \qquad v_x = \sqrt{\left(\frac{4{\cdot}6\,kT}{m}\right)}.$$

**Example 4.** *Let $v_x, v_y, v_z$ represent the three Cartesian components of velocity of a molecule in a gas. Using symmetry considerations and equipartition theorem, deduce, expressions for the following mean values in terms of k, T and m :*

*(i) $< v_x >$, (ii) $< v_x^2 >$,*

*(iii) $< v_x v_z >$, (iv) $< (v_x + bv_y)^2 >$*

*where b is a constant.* ***(Purvanchal 2002)***

**Solution :** (i) We have

$$\overline{v_x} = \langle v_x \rangle = \int_{-\infty}^{+\infty} v_x . P(v_x)\, dv_x$$

$$= \int_{-\infty}^{+\infty} v_x \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\, dv_x$$

$$= \left(\frac{m}{2\pi kT}\right)^{1/2} \int_{-\infty}^{+\infty} v_x\, e^{-mv_x^2/2kT}\, dv_x$$

$$= 0 \qquad \left(\text{since} \int_{-\infty}^{+\infty} v_x\, e^{-mv_x^2/2kT}\, dv_x = 0\right)$$

(ii) $\overline{v_x^2} = \langle v_x^2 \rangle = \int_{-\infty}^{+\infty} v_x^2\, P(v_x)\, dv_x$

$$= \int_{-\infty}^{+\infty} \left(\frac{m}{2\pi kT}\right)^{1/2} v_x^2\, e^{-mv_x^2/2kT}\, dv_x$$

$$= \left(\frac{m}{2\pi kT}\right)^{1/2} \int_{-\infty}^{+\infty} v_x^2\, e^{-mv_x^2/2kT}\, dv_x$$

$$= \left(\frac{m}{2\pi kT}\right)^{1/2} . \frac{1}{2} \sqrt{\left\{\frac{\pi}{(m/2kT)^3}\right\}} \qquad \left[\text{since} \int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2}\, dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}}\right]$$

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

(iii) $\overline{v_x \cdot v_z} = \langle v_x\, v_z \rangle$

$$= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} v_x v_z\, P(v_x\, v_z)\, dv_x\, dv_z$$

$$= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} v_x\, v_z\, P(v_x)\, P(v_z)\, dv_x\, dv_z$$

$$= \int_{-\infty}^{+\infty} v_x\, P(v_x)\, dv_x \int_{-\infty}^{+\infty} v_z\, P(v_z)\, dv_z$$

$$= \int_{-\infty}^{+\infty} v_x \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\, dv_x \int_{-\infty}^{+\infty} v_z \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_z^2/2kT}\, dv_z$$

$$= \left(\frac{m}{2\pi kT}\right) \int_{-\infty}^{+\infty} v_x\, e^{-mv_x^2/2kT}\, dv_x \int_{-\infty}^{+\infty} v_z\, e^{-mv_z^2/2kT}\, dv_z$$

$$= 0.$$

(iv) $\overline{(v_x + bv_y)^2} = \langle (v_x + bv_y)^2 \rangle$

$$= \langle (v_x^2 + 2b\, v_x v_y + b^2 v_y^2) \rangle = \langle v_x^2 \rangle + 2b \langle v_x\, v_y \rangle + b^2 \langle v_y^2 \rangle$$

$$= \frac{kT}{m} + 0 + b^2 \left(\frac{kT}{m}\right)$$

$$= (1 + b^2)\, \frac{kT}{m}.$$

### 6.23. Maxwell's Distribution Law of Speeds : The Function f (v).

Let us find an expression for the number of molecules of a gas whose speeds lie between $v$ and $v + dv$.

Let us consider a zone of cells, *i.e.*, a group of cells in the phase space corresponding to the range in speed from $v$ to $v + dv$. If $g_i$ represents the number of cells in the zone, then the number of particles in $i$th zone, each having an energy close to $\varepsilon_i = \frac{1}{2} mv^2$, is given by Maxwell-Boltzmann law :

$$N_i = A g_i\, e^{-\beta \varepsilon_i} \qquad \ldots(1)$$

where

$$\beta = \frac{1}{kT} \qquad \ldots(2)$$

As the number of molecules with speeds lying between $v$ and $v + dv$ will be proportional to $dv$, we may write $N_i = N_v\, dv$ where $N_v$ is known as the **distribution function** with regard to speeds, so that equation (1) takes the form

$$N_v\, dv = a g_i\, e^{-\beta \varepsilon_i} \qquad \ldots(3)$$

Let us now express $g_i$ in terms of $v$ and $dv$.

We have $g_i$ = Number of cells in the zone under consideration

$$= \frac{\text{Volume of the zone in the phase space}}{\text{Volume of one cell}}$$

To find the volume of the zone in the phase-space, we must integrate $dx\, dy\, dz\, dp_x\, dp_y\, dp_z$ of the zone, *i.e.*,

Volume of the zone in the phase space $= \iiiint\!\!\iint dx\, dy\, dz\, dp_x\, dp_y\, dp_z$

If $h^3$ is the volume of one cell, we must have

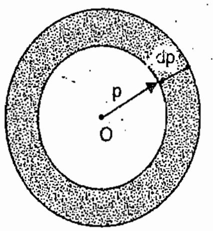
$$g_i = \frac{\iiiint\!\!\iint dx\, dy\, dz\, dp_x\, dp_y\, dp_z}{h^3} \qquad \ldots(4)$$

If $V$ is the volume occupied by the gas, we must have

$$V = \iiint dx\, dy\, dz. \qquad \ldots(5)$$

Now we have to integrate with respect to $p_x, p_y$ and $p_z$. If we care only about the resultant momentum $p$ and not about the momentum components, we can find integration with respect to $p_x, p_y, p_z$ as follows :

Let us imagine that $p_x, p_y$ and $p_z$ are along three mutually perpendicular axes and draw a sphere of radius $p$ about the origin. Then the surface of the sphere drawn will contain all the points for which $p_x^2 + p_y^2 + p_z^2 = p^2$. Now draw another sphere of radius $p + dp$, concentric with the first. The volume between two spheres of radii $p$ and $p + dp$ will contain all the molecules in the momentum space having momentum between $p$ and $p + dp$.



(Fig. 6.13)

The volume between two spheres is given by

$$\iiint dp_x\, dp_y\, dp_z = \frac{4}{3}\, \pi (p + dp)^3 - \left(\frac{4}{3}\right) \pi p^3$$

$$= \frac{4}{3}\pi[(p+dp)^3 - p^3]$$

$$= \frac{4}{3}\pi[p^3 + 3p^2\,dp + 3p\,(dp)^2 + (dp)^3 - p^3]$$

$$= \frac{4}{3}\pi(3p^2\,dp) \quad \text{neglecting terms containing } dp^2 \text{ and } dp^3$$

$$= 4\pi p^2\,dp. \qquad \dots(6)$$

Substituting values from eqns. (5) and (6) in (4), we get

$$g_i = V\frac{(4\pi p^2\,dp)}{h^3} = \frac{4\pi V p^2\,dp}{h^3}. \qquad \dots(7)$$

Substituting value of $g_i$ from eqn. (7) in eqn. (3) and using the fact that $\varepsilon_i = \frac{1}{2}mv^2$, me get

$$N_v\,dv = \frac{4\pi AV}{h^3}p^2 e^{-\beta mv^2/2}\,dp$$

$$= \frac{4\pi AVm^3}{h^3}v^2 e^{-\beta mv^2/2}\,dv \quad [\text{snce } p = mv \text{ and } dp = mdv]$$

Substituting $\frac{4\pi AVm^3}{h^3} = B$, where $B$ is any constant, we get

$$N_v\,dv = Bv^2 e^{-\beta mv^2/2}\,dv$$

Since $\beta = \frac{1}{kT}$

$$N_v\,dv = Bv^2 e^{-mv^2/2kT}\,dv \qquad \dots(8)$$

**Discussion**

(i) If $v = 0$, then from eq. (8) $N_v = 0$ *i.e., no molecule has a zero speed.*

(ii) **For small values of $v$**

$$\frac{mv^2}{2kT} << 1$$

and $e^{-mv^2/2kT} = 1$

$\therefore$ $N_v \propto v^2$

Thus value of $N_v$ *increases parabolically with increase of value of $v$* and attains a maximum value for a particular value of $v$.

(iii) **For large value of $v$**

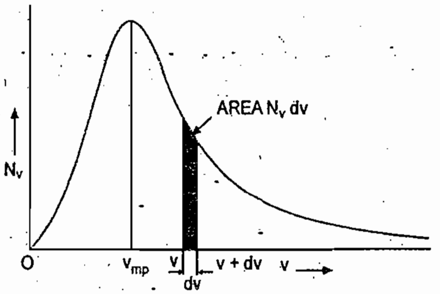
$$\frac{mv^2}{2kT} >> 1$$

Here exponential term $e^{-mv^2/2kT}$ dominates over $v^2$. Hence

$$N_v \propto e^{-mv^2/2kT}$$

Thus with increase in the value of $v$, $N_v$ decreases exponentially.

Thus if we plot $N_v$ against $v$ the curve first rises parabolically, reaches a maximum and then falls exponentially to zero as shown in fig. 6.14. The maximum corresponds to the most probable speed $v_{mp}$. As the area under the curve towards right of maximum is greater that to the left, this indicates that the mean speed $v$ is greater than $v_{mp}$. The area of the shaded curve gives the number of molecules lying in the speed range $v$ and $v + dv$.



(Fig. 6.14)

**Evaluation of Constant B**

In eqn. (8), $N_v\,dv$ denotes the number of molecules having speed in the range $v$ and $v + dv$. As the molecules may have speed 0 to ∞, we may write

$$\int_0^\infty N_v\,dv = N$$

where $N$ is the total number of molecules in the given state

or $$B\int_0^\infty v^2 e^{-\beta mv^2/2}\,dv = N$$

or $$B\left[\frac{1}{4}\sqrt{\left(\frac{8\pi}{\beta^3 m^3}\right)}\right] = N$$

or $$\beta = 4N\sqrt{\left(\frac{\beta^3 m^3}{8\pi}\right)} \dots\dots$$

But we have $\beta = \frac{1}{kT}$

$$\therefore \quad B = 4N\sqrt{\left[\left(\frac{1}{kT}\right)^3 \frac{m^3}{8\pi}\right]}$$

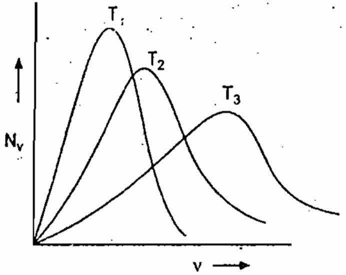
$$= \frac{4N}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2} = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2}$$

Substituting the value of $B$ and $\beta$ in equ. (8), **Maxwell's distribution law of speed of** molecules may be expressed as

$$N_v\,dv = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\,dv \qquad \dots(10)$$

or $$N_v = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} \qquad \dots(11)$$

This equation represents the effect of temperature on the speed distribution of a given number of molecules. The graphs of $N_v$ against $v$ according to eqn (11) at different temperatures $T_1$, $T_2$ and $T_3$ such that $T_1 < T_2 < T_3$, are drawn in fig. 6.15. We see that higher is the temperature, higher is the speed possessed by the molecules. However the area under all the three curves is same.



(Fig. 6.15)

The fraction of molecules having speed between $v$ and $v + dv$ is given by

$$\frac{N_v\,dv}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\,dv.$$

According to definition of probability, this is the probability of molecules to possess the speed between $v$ and $v + dv$ *i.e.*,

$$P_v\,dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\,dv. \qquad \ldots(12)$$

The probability function $f(v)$ or $P(v)$ represents the probability of a molecule having speed $v$ is given by

$$f(v) = P(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} \qquad \ldots(13)$$

## SOLVED EXAMPLES

**Ex. 13.** *Calculate the probability that the speed for oxygen molecule lies between 100 and 101 metre/second at 200 K.* **(Rohilkhand 2005, 03, Purvanchal 2005, 2001, Meerut 2006, 1989)**

**Solution.** The probability that a molecule posssses speed between $v$ and $v + dv$.

$$P(v)\,dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\,v^2 dv.$$

Here $m = 32 \text{ amu} = \frac{32}{6\times 10^{23}}\text{ g} = \frac{32}{6\times 10^{26}}\text{ kg}$.

$v = 100$ metre/second, $dv = 101 - 100 = 1$ metre/second

$k = 1{\cdot}38\times 10^{-23}$ joule/kelvin, $T = 200$ K.

$$\therefore\; P(v)\,dv = 4\times 3{\cdot}14\times\left[\frac{\{(32/6)\times 10^{26}\}}{2\times 3{\cdot}14\times 1{\cdot}38\times 10^{-23}\times 200}\right]^{3/2}\times\exp\left[-\frac{\{(32/6)\times 10^{26}\}\,(100)^2\}}{2\times 1{\cdot}38\times 10^{-23}\times 200}\right]\times(100)^2$$

$$= 6{\cdot}11\times 10^{-4}.$$

## 6.24 Most Probable speed, Average speed and Root mean square speed

The probability that a molecule possessing speed $v$ is given by

$$P(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} \qquad \ldots(1)$$

**Most Probable Speed :** For most probable speed, the probability $P(v)$ must be maximum. Therefore, for obtaining most probable speed $v_{mp}$, let us differentiate equation (1) with respect to $v$ and equate to zero, *i.e.*,

$$\frac{\partial P(v)}{\partial v} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left[2ve^{-mv^2/2kT} - \frac{m}{kT}v^3 e^{-mv^2/2kT}\right] = 0.$$

$$\Rightarrow \qquad 4\pi\left(\frac{m}{2\pi\,kT}\right)^{3/2} e^{-mv^2/2kT}\,.\,(2v)\left[1 - \frac{m}{2kT}v^2\right] = 0$$

This gives either $v = 0$ or $v\,\infty$ *or* $v = \sqrt{\frac{2kT}{m}}$

But $v = 0$ and $v = \infty$ correspond to least probable speeds, so

Most probable speed, $\quad v_{mp}\,(= v) = \sqrt{\left(\frac{2kT}{m}\right)}. \qquad \ldots(2)$

**Average Speed :** If there are $n_1, n_2, \ldots, n_i \ldots$ particles having speeds $v_1, v_2, \ldots, v_i, \ldots$ respectively, the average speed $\bar{v}$ is defined

$$\bar{v} = \frac{\sum_i n_i v_i}{\sum_i n_i} = \frac{\sum_i n_i v_i}{N}.$$

As the speeds of the molecules are approximately continuous, we may write average speed $\bar{v}$ as

$$\bar{v} = \frac{1}{N}\int_0^\infty v\,n(v)\,dv = \int_0^\infty v\,P(v)\,dv.$$

Substituting value of $P(v)$ from equation (1), we get

$$\bar{v} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2kT}\,dv \qquad \ldots(3)$$

But standard definite integral $\int_0^\infty v^3 e^{-av^2}\,.\,dv = \frac{1}{2a^2}$ therefore

$$\int_0^\infty v^3 e^{-mv^2/2kT}\,dv = \frac{1}{2}\cdot\left(\frac{1}{m/2kT}\right)^2 = \frac{1}{2}\cdot\left(\frac{2kT}{m}\right)^2.$$

Substituting this in equation (3), we get

$$\bar{v} = 4\pi\cdot\left(\frac{m}{2\pi kT}\right)^{3/2}\cdot\frac{1}{2}\cdot\left(\frac{2kT}{m}\right)^2.$$

Thus, *average speed*, $\quad \bar{v} = \sqrt{\left(\frac{8kT}{m\pi}\right)} \qquad \ldots(4)$

**Root Mean Square Speed :** The mean square speed $\overline{v^2}$ or $< v^2 >$ is defined as

$$\overline{v^2} = \frac{\int_0^\infty v^2\,n(v)\,dv}{N} = \int_0^\infty v^2\,P(v)\,dv$$

$$= \int_0^\infty v^2\,.\,4\pi\,.\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\,dv$$

$$= 4\pi\left(\frac{m}{2\pi\,kT}\right)^{3/2}\int_0^\infty v^4 e^{-mv^2/2kT}\,dv$$

By standard definite integral

$$\int_0^\infty v^4 e^{\alpha v^2}\,dv = \frac{3}{4}\sqrt{\frac{\pi}{\alpha^5}}\,;\ \text{Here } \alpha = \frac{m}{2kT}$$

$$\therefore\quad \overline{v^2} = 4\pi\left(\frac{m}{2\pi kT}\right)^{2/3}\cdot\frac{3}{8}\sqrt{\left[\frac{\pi}{(m/2kT)^5}\right]} = \frac{3kT}{m}. \qquad \ldots(5)$$

Therefore *root mean square speed* $v_{rms}$ is given by

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} \qquad \ldots(6)$$

From equations (2), (4) and (6) it is obvious that

$$v_{rms} > v_{av} > v_{mp}.$$

## SOLVED EXAMPLES

**Ex. 14.** *Calculate the fraction of oxygen molecules within 1% of the most probable velocity at N.T.P. What is the effect of changing (i) the gas to hydrogen (ii) the temperature to 500°C.*

**Solution.** The fraction of molecules having speeds between $v$ and $v + dv$ is given by

$$P(v)\,dv = \frac{n(v)\,dv}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\,dv \qquad \ldots(1)$$

The most probable speed is given by

$$v_{mp} = \sqrt{\left(\frac{2kT}{m}\right)}$$

Substituting this is equation (1), we get

$$\frac{n(v)\,dv}{N} = \frac{4}{\sqrt{\pi}} \cdot \frac{1}{v_{mp}^3} v^2 e^{-v^2/v_{mp}^2}\,dv \qquad \ldots(2)$$

Given that $v$ varies within 1% of the most probable velocity, *i.e.*, from $0{\cdot}99\, v_{mp}$ to $1{\cdot}01\, v_{mp}$,

$\therefore$ $$dv = 1{\cdot}01\, v_{mp} - 0{\cdot}99\, v_{mp} = 0{\cdot}02\, v_{mp}.$$

and $$v \approx v_{mp}.$$

Therefore equation (2) is written as

$$\frac{n(v)\,dv}{N} = \frac{4}{\sqrt{\pi}\,.\,v_{mp}} e^{-1}\,(0{\cdot}02\, v_{mp})$$

$$= \frac{0{\cdot}08}{\sqrt{\pi}} e^{-1} = 0{\cdot}045\, e^{-1}.$$

$\therefore$ The required fraction $= 0{\cdot}405\, e^{-1}$.

It is obvious that the fraction of oxygen molecules lying between given velocities is independent of the molecular weight and temperature. Hence there would be no effect of either changing the gas or the temperature.

**Ex. 15** *At what temperature, pressure remaining unchanged, will the molecular velocity (root mean square velocity) of hydrogen will be double of its value at N.T.P.*

**Solution.** Let $v_{r.m.s.}$ be the value of velocity of hydrogen molecules at N.T.P. and $2v_{r.m.s.}$ at $T$K.

According to eqn. (3) we see that

$$v_{r.m.s.} = \sqrt{\left(\frac{3kT}{m}\right)}$$

At N.T.P. we have $T = 0^\circ\text{C} = 273$ K

$\therefore$ $$v_{r.m.s.} = \sqrt{\left(\frac{3k \times 273}{m}\right)} \qquad \ldots(1)$$

At $T$K, we have

$$2v_{r.m.s.} = \sqrt{\left(\frac{3kT}{m}\right)} \qquad \ldots(2)$$

Dividing (2) by (1), we get

$$2 = \sqrt{\left(\frac{T}{273}\right)}$$

$$4 = \frac{T}{273}$$

$$T = 273 \times 4 = 1092 \text{ K}$$

$$= (1092 - 273)^\circ\text{C} = 819^\circ\text{C}.$$

**Ex. 16.** *If the root mean square value of the molecules of hydrogen at N.T.P. is 1·84 kilometre/second., calculate the root mean square velocity of the oxygen molecules at N.T.P. Molecular weight of hydrogen and oxygen are 2 and 32 respectively.* **(Mumbai 2003)**

**Solution.** If $v'_{r.m.s.}$ and $v''_{r.m.s.}$ are the root mean square values of velocity of hydrogen and oxygen molecules respectively, we have

$$v'_{r.m.s.} = \sqrt{\left(\frac{3kT}{m'}\right)} \qquad \ldots(1)$$

$\therefore$ $$v''_{r.m.s.} = \sqrt{\left(\frac{3kT}{m''}\right)} \qquad \ldots(2)$$

where $m'$ and $m''$ are the masses of hydrogen and oxygen molecules respectively.

Dividing eqn. (2) by (1) we get

$$\frac{v'_{r.m.s.}}{v''_{r.m.s.}} = \sqrt{\left(\frac{m'}{m''}\right)}$$

Given $$\frac{m'}{m''} = \frac{2}{32} = \frac{1}{16}$$

and $$v'_{r.m.s.} = 1{\cdot}84 \text{ km/s}$$

$\therefore$ $$v''_{r.m.s.} = \sqrt{\left(\frac{m'}{m''}\right)} v'_{r.m.s.}$$

$$= \sqrt{\left(\frac{1}{16}\right)} \times 1{\cdot}84 \text{ km/s}$$

$$= \frac{1{\cdot}84}{4} \text{ km/s} = 0{\cdot}46 \text{ km/s}$$

**Ex. 17.** *At what temperature the root mean square velocity is equal to the escape velocity from the surface of the earth for hydrogen and for oxygen.*

**Solution.** K.E. of a molecule of mass $m$ and mean square speed $\overline{v^2}$

$$= \frac{1}{2} m\overline{v^2}$$

But $$\overline{v^2} = \frac{3kT}{m}$$

$\therefore$ $$\frac{1}{2} m\overline{v^2} = \frac{3}{2} kT$$

Escape velocity, $v_e = \sqrt{(2gR)}$, where $R$ is the radius of the earth

Given $$v_{r.m.s.} = v_e$$

$\therefore$ K.E. of molecule $= \dfrac{3kT}{2} = \frac{1}{2} m.\, 2gR = mgR$

or $$T = \frac{2}{3} \frac{mgR}{k}$$

Temperature for hydrogen.

$$T_H = \frac{2}{3}\frac{m_H gR}{k} \left( m_H = \frac{(2a\ m.u.)}{N} kg = \frac{2}{6 \times 10^{26}} \text{kg} \right)$$

$$= \frac{2}{3} \frac{(2/6 \times 10^{26}) \times 9{\cdot}8 \times 6{\cdot}4 \times 10^6}{1{\cdot}38 \times 10^{-23}} = (1{\cdot}0 \times 10^4) \textbf{ kelvin.}$$

Temperature for oxygen.

$$T_0 = \frac{2}{3}\frac{m_0 gR}{k}$$

$$= \frac{2}{3} \times \left( \frac{32}{6 \times 10^{26}} \right) \times \frac{9{\cdot}8 \times 6{\cdot}4 \times 10^6}{1{\cdot}38 \times 10^{-23}}$$

$$= 16 \times 10^4 \textbf{ kelvin.}$$

**Ex. 18.** *The first excited state of hydrogen atom is 10·2 eV above its ground state. What temperature is needed to excite hydrogen atoms to the first excited level?*

**Solution.** According to kinetic interpretation of temperature, the average kinetic energy per molecule at absolute temperature $T$ is given by

$$\tfrac{1}{2} mv^2 = \tfrac{3}{2} kT$$

Given $\tfrac{1}{2} mv^2 = 10{\cdot}2 \text{ eV} = 10{\cdot}2 \times 1{\cdot}6 \times 10^{-19}$ joule.

∴ ~~$\tfrac{3}{2} kT = 10{\cdot}2 \times 1{\cdot}6 \times 10^{-19}$ joule~~

or $$T = \frac{2}{3} \times \frac{10{\cdot}2 \times 1{\cdot}6 \times 10^{-19}}{3 \times 1{\cdot}38 \times 10^{-23}}$$

(since $k = 1{\cdot}38 \times 10^{-23}$ joule/K)

$$= 7{\cdot}88 \times 10^4 \textbf{ kelvin.}$$

**Ex. 19.** *Calculate the root mean square speed and most probable speed of a gas whose density is 1·4 g/litre at a pressure of $10^5$ N/m².*

**Solution.** We have $P = 10^5 \text{ N/m}^2$

$$\rho = 1{\cdot}4 \text{ gm./litre} = 1{\cdot}4 \text{ kg/m}^3.$$

$$v_{r.m.s.} = \sqrt{\left(\frac{3P}{\rho}\right)} = \sqrt{\left(\frac{3 \times 10^5}{1{\cdot}4}\right)}$$

$$= 4{\cdot}6 \times 10^2 \text{ m/s.}$$

and most probable speed, $v_{mp} = \sqrt{(2/3)}\, v_{rms} = \sqrt{(2/3)} \times 4{\cdot}6 \times 10^2$

$$= 3{\cdot}77 \times 10^2 \textbf{ m/s.}$$

**Ex. 20.** *At what temperature will the average speed of hydrogen molecules be the same as that of nitrogen molecules kept at 35°C. Molecular weight of nitrogen and hydrogen are 28 and 2 atomic mass units respectively. Also calculate the most probable speed of nitrogen molecules at this temperature. Given Boltzmann's constant $k = 1{\cdot}38 \times 10^{-23}$ joule per degree.*

**Solution.** If $\bar{v}_1$ and $\bar{v}_2$ are the average speeds of hydrogen and nitrogen molecules at temperatures $T_1 K$ and $T_2 K$ respectively, we have

$$\bar{v}_1 = \sqrt{\left(\frac{8kT_1}{m_1 \pi}\right)} \quad \text{...(1)}$$

$$\bar{v}_2 = \sqrt{\left(\frac{8kT_2}{m_2 \pi}\right)} \quad \text{...(2)}$$

where $m_1$ and $m_2$ are the masses of hydrogen and nitrogen molecules respectively.

Dividing eqn. (1) by (2) we get

$$\frac{\bar{v}_1}{\bar{v}_2} = \sqrt{\left(\frac{T_1/m_1}{T_2/m_2}\right)} = \sqrt{\left(\frac{T_1 m_2}{T_2 m_1}\right)} \quad \text{...(3)}$$

Given when $T_2 = 35°\text{C} = (273 + 35) \text{ K} = 308 \text{ K}, \bar{v}_1 = \bar{v}_2$

and $$\frac{m_2}{m_1} = \frac{28}{2} = 14.$$

Substituting these values in (3), we get

$$1 = \sqrt{\left(\frac{T_1 \times 14}{308}\right)}$$

or $$T_1 = \frac{308}{14} = \mathbf{22\ K.}$$

The most probable speed of nitrogen at temp. $T$ is given by

$$v_{mp} = \sqrt{\left(\frac{2kT}{m}\right)}.$$

Here $k = 1{\cdot}38 \times 10^{-23}$ joule per degree, $T = 22$ K

and $$m = 28 \ a.m.u. = \frac{28}{6 \times 10^{26}} \text{ kg.}$$

$$\therefore \quad v_{mp} = \sqrt{\left(\frac{2 \times 1{\cdot}38 \times 10^{-23} \times 22}{28/6 \times 10^{26}}\right)}$$

$$= \sqrt{\left(\frac{2 \times 1{\cdot}38 \times 10^{-23} \times 24 \times 6 \times 10^{26}}{28}\right)}$$

$$= 1{\cdot}44 \times 10^2 \textbf{ m/s.}$$

**Ex. 21.** *The number of molecules in energy range ε and ε + dε is given by*

$$n(\varepsilon)\, d\varepsilon = 2\pi N \left(\frac{1}{\pi kT}\right)^{3/2} \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon$$

*Deduce the expression for (i) the most probable energy, (ii) the number of molecules containing most probable energy, (iii) the probability at the most probable energy, (iv) the mean energy.*

***(Mumbai 2003, Rohilkhand 2004, 1992; Meerut 1999)***

**Solution.** The number of molecules in the energy range ε and ε + $d\varepsilon$ is given by

$$P(\varepsilon)\, d\varepsilon = \frac{n(\varepsilon)\, d\varepsilon}{N} = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon \quad \text{...(1)}$$

The probability that a molecule will have energy $\varepsilon$ is given by

$$P(\varepsilon) = \frac{n(\varepsilon)}{N} = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2} \varepsilon^{1/2} e^{-\varepsilon/kT}.$$

(i) For the most probable energy $P(\varepsilon)$ must be maximum, *i.e.*, $\frac{dP(\varepsilon)}{d\varepsilon}$ must be equal to zero which gives

$$\frac{dP(\varepsilon)}{d\varepsilon} = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\left[\frac{1}{2}\varepsilon^{-1/2}e^{-\varepsilon/kT} + \varepsilon^{1/2}.\left(-\frac{1}{kT}\right).e^{-\varepsilon/kT}\right] = 0$$

$$\Rightarrow \qquad 2\pi\left(\frac{1}{\pi kT}\right)^{3/2} e^{-\varepsilon/kT}\varepsilon^{-1/2}\left[\frac{1}{2} - \frac{\varepsilon}{kT}\right] = 0$$

$$\Rightarrow \qquad \varepsilon = \infty \text{ or } \varepsilon = \frac{1}{2}kT$$

But $\varepsilon = \infty$ is least probable energy.

Most probable energy, $\qquad \varepsilon_{mp} = \frac{1}{2}kT.$

(ii) The number of molecules containing most probable energy is

$$n(\varepsilon_{mp}) = 2\pi N\left(\frac{1}{\pi kT}\right)^{3/2}\left(\frac{1}{2}kT\right)^{1/2} e^{-1/2}$$

$$= \left(\frac{2}{\pi e}\right)^{1/2}.\left(\frac{1}{kT}\right).N. \qquad \ldots(2)$$

(iii) The probability at the most probable energy is given by

$$P(\varepsilon_{mp}) = \frac{n(\varepsilon_{mp})}{N} = \left(\frac{2}{\pi e}\right)^{1/2}\frac{1}{kT} \qquad \ldots(3)$$

(iv) The mean energy is given by

$$<\varepsilon> = \frac{\int_0^\infty \varepsilon.n(\varepsilon)\,d\varepsilon}{N} = \int_0^\infty \varepsilon P(\varepsilon)\,d\varepsilon$$

$$= 2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\int \varepsilon^{3/2}e^{-\varepsilon/kT}\,d\varepsilon$$

Substituting $\varepsilon^{1/2} = x$, we get

$$<\varepsilon> = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\int_0^\infty x^3 e^{-x^2/kT}.2x\,dx$$

$$= 4\pi.\left(\frac{1}{\pi kT}\right)^{3/2}\int_0^\infty x^4 e^{-x^2/kT}\,dx \qquad \ldots(4)$$

As standard definite integral $\int_0^\infty x^4 e^{-ax^2}dx = \frac{3}{8}\sqrt{\left(\frac{\pi}{a^5}\right)}$

Therefore, $\qquad \int_0^\infty x^4 e^{-x^2/kT}dx = \frac{3}{8}\sqrt{\left(\frac{\pi}{(1/kT)^5}\right)} = \frac{3}{8}\sqrt{\pi}.(kT)^{5/2}$

Substituting this value of the integral in equation (4) we get

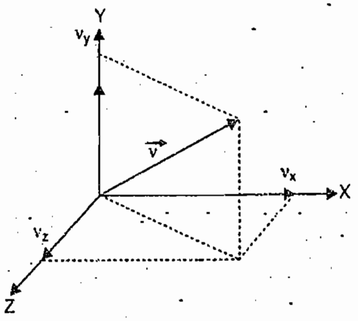
$$\text{Mean energy} <\varepsilon> = 4\pi\left(\frac{1}{\pi kT}\right)^{3/2}\frac{3}{8}.\sqrt{\pi}.(kT)^{5/2} = \frac{3}{2}kT. \qquad \ldots(5)$$

## 6.25 Degrees of Freedom

*The degrees of freedom of a dynamical system may be defined as the total number of independent coordinates required to specify completely its position and configuration. Thus degree of freedom indicates the number of independent motions which the particle can undergo.*

For example, the **translatory motion of a particle** can take place in any direction in space and can be resolved parallel to three axes $X$, $Y$ and $Z$ of the cartesian co-ordinate system. Thus it requires three co-ordinates to definite its position and hence possesses **three degrees of freedom.**

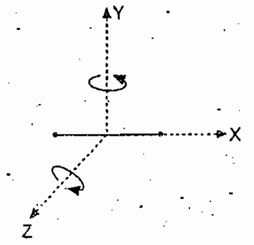
The velocity v of the molecule of a **monoatomic gas** (such as He, $A$) can be resolved along three coordinate axes $X$, $Y$ and $Z$ (Fig. 6.16) and hence it possesses **three degrees of freedom,** all translational. The molecule of a monoatimic gas can also rotate but its kinetic energy of rotation is insignificant because its moment of inertia is negligible about axis of rotation.



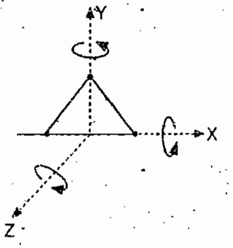
(Fig. 6.16)

The **molecules of a diatomic gas** (such as $H_2$, $O_2$, $N_2$ etc.) are made up of two atoms joined rigidly through a bond. It can not only move but also rotate about three coordinate axes $X$, $Y$, $Z$. But its moment of inertia about the axis joining the two atoms (X-axis) is negligible (Fig. 6.17) and hence it can have only two rotational motions. Thus it has only **five degrees of freedom** (three translational and two rotational).

The **molecules of a polyatomic gas** (such as $CO_2$, $O_3$, $CH_4$ etc.) can rotate about any of the three coordinate axes (Fig. 6.18) and hence it has **six degrees of freedom** (three translational and three rotational).



(Fig. 6.17)



(Fig. 6.18)

At high temperatures, the atoms of diatomic and polyatomic gas molecules vibrate with respect to each other and then possess a number of degrees of freedom with respect to vibration also.

## 6.26 Law of Equipartition of Energy

The law states that *the total kinetic energy of a dynamical system consisting of a large number of particles in thermal equilibrium is equally divided among its all the degrees of freedom and the average energy associated with each degree of freedom is* $\frac{1}{2}kT$, where $k$ is Boltzmann's constant and $T$ is the absolute temperature of the system.

For the proof of this theorem, let us consider a dynamical system with $f$ degrees of freedom. Classically this system is described by $f$ position co-ordinates $(q_1, q_2, \ldots, q_f)$ and the corresponding $f$ momenta co-ordinates $(p_1, p_2, \ldots, p_f)$. The total energy $E$ of the system can then be written as function of these position and momenta co-ordinates,

*i.e.,* $$E = E(q_1, q_2, \ldots, q_f ; p_1, p_2, \ldots, p_f). \qquad \ldots(1)$$

Let $p_i$ be any particular momentum, then the total energy can be expressed as

$$E = \varepsilon_i(p_i) + E'(q_1, q_2, \ldots, q_f, p_1, p_2, \ldots, p_f). \qquad \ldots(2)$$

where $\varepsilon_i(p_i)$ is the function of momentum $p_i$ alone and the second term $E'(q_1, q_2, \ldots, q_f, p_1, p_2, \ldots, p_f)$ is the function of all the position and momenta co-ordinates excluding the momentum $p_i$.

Classically the mean energy $\bar{\varepsilon}_i$ is defined as

$$\bar{\varepsilon}_i = \frac{E}{N} = \frac{\int \varepsilon_i e^{-E/kT} dq_1 dq_2 \ldots dq_f dp_1 dp_2 \ldots dp_f}{\int e^{-E/kT} dq_1 dq_2 \ldots dq_f dp_1 dp_2 \ldots dp_f} \qquad \ldots(3)$$

Since $E = \varepsilon_i + E'$, therefore,

$$\bar{\varepsilon}_i = \frac{\int \varepsilon_i e^{-(\varepsilon_i + E')/kT} dq_1 dq_2 \ldots dq_f dp_1 dp_2 \ldots dp_f}{\int e^{-(\varepsilon_i + E')/kT} dq_1 dq_2 \ldots dq_f dp_1 dp_2 \ldots dp_f}$$

$$= \frac{\int_{-\infty}^{+\infty} \varepsilon_i e^{-\varepsilon_i/kT} dp_i}{\int_{-\infty}^{+\infty} e^{-\varepsilon_i/kT} dp_i} \cdot \frac{\int e^{-E'/kT} dq_1 dq_2 \ldots dq_f dp_1 dp_2 \ldots dp_f}{\int e^{-E'/kT} dq_1 dq_2 \ldots dq_f dp_1 dp_2 \ldots dp_f}$$

where the integrals containing $e^{-E'/kT}$ extend over all the $q$'s and $p$'s except $p_i$. Such a separation of integrals is possible because $E'$ is independent of $p_i$. It is obvious that the integrals containing $e^{-E'/kT}$ are equal and hence cancel out. Thus, we have

$$\bar{\varepsilon}_i = \frac{\int_{-\infty}^{\infty} \varepsilon_i e^{-\varepsilon_i/kT} dp_i}{\int_{-\infty}^{\infty} e^{-\varepsilon_i/kT} dp_i} \qquad \ldots(4)$$

Since $\varepsilon_i$ is quadratic in $p_i$ and expressed as

$$\varepsilon_i = \frac{p_i^2}{2m} \qquad \ldots(5)$$

$$\therefore \quad \bar{\varepsilon}_i = \frac{\int_{-\infty}^{+\infty} \left(\frac{p_i^2}{2m}\right) e^{-p_i^2/2mkT} dp_i}{\int_{-\infty}^{+\infty} e^{-p_i^2/2mkT} dp_i}$$

---

$$= \frac{1}{2m} \cdot \frac{\frac{1}{2}\sqrt{\left(\frac{\pi}{1/(2mkT)^3}\right)}}{\sqrt{\left(\frac{\pi}{1/2mkT}\right)}} \qquad \left\{ \begin{array}{l} \text{since } \int_{-\infty}^{+\infty} x^2 e^{-ax^2} dx = \frac{1}{2}\sqrt{\left(\frac{\pi}{a^3}\right)} \\ \text{and } \int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\left(\frac{\pi}{a}\right)} \end{array} \right.$$

$$= \frac{1}{2} kT$$

This equation states that the mean value of energy expressible as independent quadratic term (*i.e.*, associated with each degree of freedom) is equal to $\frac{1}{2} kT$. This equation (5) represents the law of equiparitition of energy of classical statistical mechanics.

## SOLVED EXAMPLES

**Ex. 22.** *Calculate the mean energy for one dimensional harmonic oscillator.*

**Solution.** The total energy of one dimensional harmonic oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2} Cq^2. \qquad \ldots(1)$$

where C is force constant. Obviously this equation involves two quadratic terms.

The mean energy of one dimensional harmonic oscillator is given by

$$< E > = \frac{\int_{-\infty}^{\infty} \frac{p^2}{2m} e^{-p^2/2mkT} dp}{\int_{-\infty}^{\infty} e^{-p^2/2mkT} dp} + \frac{\int_{-\infty}^{\infty} \frac{1}{2} Cq^2 e^{-Cq^2/2kT} dq}{\int_{-\infty}^{\infty} e^{-Cq^2/2kT} dq}$$

$$= \frac{1}{2} kT + \frac{1}{2} kT = kT.$$

which is also obvious from equation (5) of above section, since in this case there are two quadratic terms, each of them would contribute $\frac{1}{2} kT$ to the average energy.

## 6.27. Atomicity of Gases

Let us consider a one gram mole of a perfect gas at absolute temperature $T$. The internal energy $U$ of this gas is the total kinetic energy of its molecules. As one mole contains $N$ (Avogadro's number) Now, if each molecule of the gas possesses $n$ degree of freedom, the average total K.E. per mole is

$$U = N \cdot n \cdot \frac{1}{2} kT = \frac{n}{2} RT \qquad \ldots(1)$$

where $R = Nk$ = universal gas constant.

Now the molar specific heat of a gas at constant volume is defined as the increase in internal energy of 1 g-mole of a gas per degree rise of temperature, *i.e.,*

Molar specific heat, $C_V = \frac{dU}{dT} = \frac{d}{dT}\left(\frac{n}{2} \cdot RT\right) = \frac{n}{2} R.$

Also according to Mayer's relation

$$C_P - C_V = R$$

or $$C_P = C_V + R = \frac{n}{2}R + R = \left(\frac{n}{2}+1\right)R.$$

Hence ratio of two specific heats of a gas

$$\gamma = \frac{\left(\frac{n}{2}+1\right)R}{\frac{n}{2}\cdot R} = 1+\frac{2}{n}.$$

**Particular Cases:**

(i) **Monoatomic gas :** Each molecule of an ideal gas have only translatory motion and hence only 3 degrees of freedom, *i.e.*, $n = 3$.

$$\therefore \quad C_V = \frac{n}{2}R = \frac{3}{2}R; \; C_P = \left(\frac{n}{2}+1\right)R = \frac{5}{2}R$$

and $$\gamma = 1+\frac{2}{n} = 1+\frac{2}{3} = \frac{5}{3} = 1{\cdot}67$$

(ii) **Diatomic gas :** Each molecule of a diatomic gas has two atoms. Such a molecule has three degrees of freedom of translation and two degrees of freedom of rotation. Thus total number of degrees of freedom associated with each molecule of a diatomic gas is 5, *i.e.*, $n = 5$. Therefore

$$C_V = \frac{n}{2}R = \frac{5}{2}R$$

$$C_P = \left(\frac{n}{2}+1\right)R = \frac{7}{2}R$$

and $$\gamma = \left(1+\frac{2}{n}\right) = \left(1+\frac{2}{5}\right) = \frac{7}{5} = 1{\cdot}40.$$

(iii) **Triatomic gas :** Each molecule of a triatomic gas possesses 6 degrees of freedom, *i.e.*, $n = 6$. Therefore

$$C_V = \frac{n}{2}R = 3R$$

$$C_P = \left(\frac{n}{2}+1\right)R = 4R$$

and $$\gamma = \left(1+\frac{2}{n}\right) = \left(1+\frac{2}{6}\right) = \frac{4}{3} = 1{\cdot}33.$$

## SOLVED EXAMPLES

**Ex. 23.** *Calculate the kinetic energy of each of the molecules of an ideal monoatomic gas at N.T.P. (Boltzmann's constant $1{\cdot}38 \times 10^{-23}$ joule per degree).*

**Solution.** Each molecule of an ideal monoatomic gas can have only translatory motion and hence only three degrees of freedom. From the law of equipartition of energy, the energy associated with three degrees of freedom.

$$= 3 \times \frac{1}{2}kT = \frac{3}{2}kT$$

$\therefore$ The kinetic energy of each molecule of an ideal monoatomic gas, $= \frac{3}{2}kT$

Given $k = 1{\cdot}38 \times 10^{-23}$ joule per degree K, and $T = 27$ K

$\therefore$ Kinetic energy of each molecule

$$= \frac{3}{2} \times 1{\cdot}38 \times 10^{-23} \times 273 \text{ joule} = 5{\cdot}65 \times 10^{-21} \textbf{ joule.}$$

### 6.28 Interpretation of Temperature

If $E$ is the total energy of the system of $N$ molecules of a monoatomic gas, then some of the energy will be in the form of translational energy, while the rest may be in the form of rotational, vibrational, potential energies of the molecules. Let $E_t$ be the translational energy, then according to law of equipartition of energy

$$\frac{E_t}{N} = \frac{3}{2}kT \qquad \ldots(1)$$

where $T$ is the temperature (in kelvin of the system and $k$ is the Boltzmann's constant.)

But $\frac{E_t}{N} = \bar{\varepsilon}_t$ = average translational energy per molecule.

Therefore equation (1) becomes

$$\bar{\varepsilon}_t = \frac{3}{2}\cdot kT \qquad \ldots(2)$$

or $$\bar{\varepsilon}_t \propto T \qquad \ldots(3)$$

***i.e.*, the average kinetic energy of translation per molecule of an ideal monoatomic gas in a given mass in directly proportional to absolute temperature of the gas.**

Clearly, if average kinetic energy of translation of each molecule of the gas is zero, then $T = 0$.

**Thus *the absolute zero temperature is that temperature at which the average kinetic energy of translation of each molecule of the gas is zero, i.e.*, the temperature at which the molecular translational velocities of a gas are reduced to zero.**

### 6.29 The Condition of Equilibrium between two Systems in Thermal Contact-The β Parameter

The two systems which are capable of exchanging heat between one other, are said to be in *thermal contact*. Let there be two systems $A$ and $B$ having specified volumes $V_A$ and $V_B$ and specified total energy $E^*$. Let $E$ and $E'$ be the energies of systems $A$ and $B$ in equilibrium state. Obviously,

$$E' = E^* - E \qquad \ldots(1)$$

When systems $A$ and $B$ are in equilibrium, the probability of system $A$ and $B$ possessing energies $E$ and $E'$ respectively will be maximum.

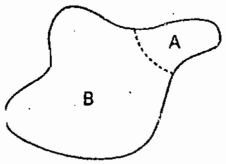
The probability of $A$ possessing energy $E$ is given by

$$P(E) = C\Omega(E)$$

where $C$ is a constant and $\Omega(E)$ the number of microstates in the energy range $E$ range $E$ and $E + \delta E_0$ ($\delta E_0$ is very small quantity). Similarly the probability of $B$ possessing energy $E'$ will be

$$P(E') = C'\Omega'(E')$$

The composite probability that the systems $A$ and $B$ will have energies $E$ and $E' (= E^* - E)$ respectively at the same time will be the



(Fig. 6.19)

product of these two separate probabilities. [As the probability of a composite event is equal to the product of the probabilities of individual and independent events]. Hence

$$P(E, E') = C\Omega(E)\, C'\Omega'(E')$$
$$= CC'\,\Omega(E)\,\Omega'(E'). \qquad \ldots(2)$$

For equilibrium state this probability should be maximum. To use this fact taking logarithms of both the sides, we get

$$\log P(E, E') = \log C + \log C' + \log \Omega(E) + \log \Omega'(E').$$

Differentiating this with respect to $E$ and equating to zero, we get

$$\frac{\partial \log \{P(E, E')\}}{\partial E} = \frac{\partial}{\partial E} \log \Omega(E) + \frac{\partial}{\partial E'} \log \Omega'(E) \frac{\partial E'}{\partial E} = 0 \qquad \ldots(3)$$

But $\frac{\partial E'}{\partial E} = -1$ from equation (1)

∴ Equation (3) gives

$$\frac{\partial}{\partial E} \log \Omega(E) - \frac{\partial}{\partial E'} \log \Omega'(E) = 0$$

or

$$\frac{\partial}{\partial E} \log \Omega(E) = \frac{\partial}{\partial E'} \log \Omega'(E'). \qquad \ldots(4)$$

This is the required condition of equilibrium between two given systems in thermal contact.

*Thus according to statistical mechanics the two systems in thermal contact will be in equilibrium if their functions* $\left[\frac{\partial}{\partial E} \log \Omega\right]$ *are equal.*

The functions $\frac{\partial}{\partial E} \log \Omega$ is generally represented by β, so that

$$\beta(E) = \frac{\partial \log \Omega}{\partial E} = \frac{1}{\Omega}\frac{\partial \Omega}{\partial E} \qquad \ldots(5)$$

and

$$\beta(E') = \frac{\partial \log' \Omega}{\partial E'} = \frac{1}{\Omega}\frac{\partial \Omega'}{\partial E'} \qquad \ldots(6)$$

β has the dimensions of reciprocal energy and for thermal equilibrium we have

$$\beta = \beta'. \qquad \ldots(7)$$

Thermal equilibrium in terms of temperature is specified as

$$T = T'$$

Thus according to statistical mechanics equality of temperature means equality of β parameters. We may now write

$$\frac{1}{\beta} = kT, \frac{1}{\beta'} = kT' \qquad \ldots(8)$$

where $k$ is a constant. The dimensions of $k$ are joule deg$^{-1}$ and we shall see later that this constant $k$ is Boltzmann's constant defined by $k = \frac{R}{N}$ where $R$ is gas constant for 1 mol and $N$ is Avogadro number.

## 6.30 Entropy and Probability

In 1896, Boltzmann discovered a relation between entropy (a thermodynamical quantity) and probability (a statistical quantity). Boltzmann started from a simple idea that the equilibrium state of the system is the state of maximum probability, *i.e.*, the probability of the system in equilibrium state is maximum. But from thermodynamic point of view the equilibrium state of the system is the state of maximum entropy. If the system is not in equilibrium, then changes take place within the system so that equilibrium state (or the state of maximum entropy) is reached. Thus in equilibrium state both the entropy and thermodynamical probabilities have their maximum values.

This led Boltzmann to expect some correlation between them.

According to thermodynamics entropy $S$ of a system is related with temperature by the relation,

$$\frac{1}{T} = \frac{\partial S}{\partial E} \qquad \ldots(1)$$

According to Statistical mechanics, we have

$$\frac{1}{T} = k\beta = k\frac{\partial}{\partial E} \log \Omega. \qquad \ldots(2)$$

From equation (1) and (2) we have

$$\frac{\partial S}{\partial E} = k\frac{\partial}{\partial E} \log \Omega.$$

Integrating we get

$$S = k \log \Omega. \qquad \ldots(3)$$

This is the required relation between entropy and probability and is called **Boltzmann's Statistical definition (or relation)** for entropy.

**Aliter :** As entropy and thermodynamical probability have their maximum values in equilibrium position, Boltzman concluded from this that entropy is a function of probability, *i.e.*,

$$S = f(\Omega) \qquad \ldots(4)$$

where $S$ is entropy and Ω is the thermodynamical probability of the state.

To find out the nature of the function let us consider two completely independent systems $A$ and $B$ having entropies $S_1$ and $S_2$ respectively. An entropy is an extensive (additive) quantity; the entropy $S$ of two systems together must be equal to the sum of their separate entropies.

*i.e.,*

$$S = S_1 + S_2 \qquad \ldots(5)$$

If the probability of $A$ is $\Omega_1$ and that of $B$ is $\Omega_2$, then probability Ω of finding both the systems at the respective given conditions will be the product of these two probabilities [As the probabilities of a composite event is equal to the product of the probabilities of the individual and independent events]. Hence

$$\Omega = \Omega_1 . \Omega_2 \qquad \ldots(6)$$

Thus, we have

$$S = f(\Omega) = f(\Omega_1\Omega_2) \qquad \ldots(7)$$
$$S_1 = f(\Omega_1) \qquad \ldots(8)$$
$$S_2 = f(\Omega_2). \qquad \ldots(9)$$

Using equation (7), (8) and (9), equation (5) takes the form

$$f(\Omega_1\Omega_2) = f(\Omega_1) + f(\Omega_2) \qquad \ldots(10)$$

Differentiating partially above equation with respect to $\Omega_1$ and $\Omega_2$, we get

$$\Omega_2 f'(\Omega_1\Omega_2) = f'(\Omega_1) \qquad \ldots(11)$$

and

$$\Omega_1 f'(\Omega_1\Omega_2) = f'(\Omega_2). \qquad \ldots(12)$$

Equation (11) and (12), give

$$\frac{f'(\Omega_1)}{f'(\Omega_2)} = \frac{\Omega_2}{\Omega_1}$$

*i.e.,* $$\Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2) = \ldots k.$$

where $k$ is any constant.

This gives,

$$f'(\Omega_1) = \frac{k}{\Omega_1} \text{ and } f'(\Omega_2) = \frac{k}{\Omega_2}$$

Integrating, we get

$$f(\Omega_1) = k \log \Omega_1 + C_1$$

and $$f(\Omega_2) = k \log \Omega_2 + C_2.$$

In general we may write

$$f(\Omega) = k \log \Omega + C$$

*i.e.,* $$S = k \log \Omega + C. \qquad \ldots(13)$$

The constant of integration C in above equation is chosen in accordance with the *third law of thermodynamics* also known is *Nernst heat theorem.*

According to this theorem the entropy of a thermodynamical system tends to zero as its temperature tends to absolute zero. The temperatures approaching absolute zero are generally attained by the process of adiabatic demagnetization. The process requires to subject the paramagnetic salts to high magnetic field so that the spins of the electrons align themselves parallel to the direction of the applied field. At absolute zero all the electron spins are aligned parallel to the direction of the field since at absolute zero there is no thermal energy to disturb their alignment. Thus at absolute zero there is only one configuration where all the electron spins are ordered in a particular direction, *i.e.,* at absolute zero, the thermodynamical probability (or weight of configuration) is 1.

Hence for a thermodynamical system at absolute zero $\Omega = 1$ and $S = 0$.

So that equation (13) yields $C = 0$.

Hence $$S = k \log \Omega \qquad \ldots(14)$$

This is the well known relation between entropy and probability.

**Identification of constant $k$ :** The constant $k$ appearing in relation (14) can be identified by considering an equivalent situation in thermodynamics. For this, consider the expansion of one mole of an ideal gas originally at pressure $p_1$ and volume $V_1$ into an evacuated chamber of volume $V_2$. The final pressure is $p_2$ and the final volume is $V_1 + V_2$. The problem is to find the isothermal change in the entropy of this gas.

When the containers of volumes $V_1$ and $V_2$ are connected, the probability of finding one molecule in the first container of volume $V_1$ is $\dfrac{V_1}{V_1 + V_2}$.

As one mole of an ideal gas contains $N$ (= Avogadro number) molecules and the probability of a composite event is equal to the product of the probabilities of individual and independent events, therefore, the probability of finding one mole of the gas in the container of volume $V$.

$$= \left(\frac{V_1}{V_1 + V_2}\right)^N.$$

The probability of finding one mole (= $N$ molecules of an ideal gas in the final volume $(V_1 + V_2)$) is

$$\left(\frac{V_1 + V_2}{V_1 + V_2}\right)^N = (1)^N.$$

Hence from Boltzmann's relation

$$\Delta S = S_2 - S_1 = k \log \Omega_2 - k \log \Omega_1 = k \log (\Omega_2/\Omega_1).$$

$$= k \log \left[\frac{1}{V_1/(V_1 + V_2)}\right]^N = k \log \left(\frac{V_1 + V_2}{V_1}\right)^N$$

$$= Nk \log_e \frac{V_1 + V_2}{V_1} \qquad \ldots(15)$$

But the change in entropy when the gas changes from one state (volume $V_1$ temperature $T_1$) to another state (volume $V_1 + V_2$, temperature $T_2$) is given by

$$\Delta S = C_V \log_e \frac{T_2}{T_1} + R \log_e \frac{V_1 + V_2}{V_1}.$$

As the change in isothermal entropy is given by

$$\Delta S = R \log_e \left(\frac{V_1 + V_2}{V_1}\right) \qquad \ldots(16)$$

Comparing equation (15) and (16), we get

$$Nk = R$$

*i.e.,* $$k = \frac{R}{N}$$

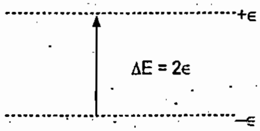
which is obviously Boltzmann's constant

$$k = (1.38 \times 10^{-23} \text{ joule/K}).$$

Hence the constant $k$ occuring in Boltzmann's entropy relation (14) is identified as *Boltzmann's constant.*

## 6.31 Probability Distribution and Entropy of a two level system

Consider a system of $N$-independent particles, each of magnetic moment $\mu$ that can be parallel or anti parallel to an external magnetic field $H$. Let $+\varepsilon$ be the energy associated with one orientation and $-\varepsilon$, that associated with another orientation, where $|\varepsilon| = \mu B$. If $N_+$ and $N_-$ be the number of particles of energy $+\varepsilon$ and $-\varepsilon$ respectively, then total energy of an isolated system is



(Fig. 6.20)

$$E = N_+ \varepsilon - N_- \varepsilon = (N_+ - N_-)\, \varepsilon = n\varepsilon \qquad \ldots(1)$$

where $$n = N_+ - N_- \qquad \ldots(2)$$

If total number of particles is $N$, then

$$N = N_+ + N_- \qquad \ldots(3)$$

Solving (2) and (3), we get

$$N_+ = \frac{1}{2}(N + n) \text{ and } N_- = \frac{1}{2}(N - n) \qquad \ldots(4)$$

Now we wish to calculate the number of accessible microstates of isolated system having constant energy $E$.

The **accessible microstates,** according to formula, are given by

$$\Omega(n) = \frac{N!}{N_+!\, N_-!} \qquad \ldots(5)$$

$$\log \Omega = \log N! - \log N_+! - \log N_-!$$
$$= N \log_e N - N - (N_+ \log N_+ - N_+) - (N_- \log N_- - N_-)$$

As $N = N_+ + N_-$, we have

$$\log \Omega = (N_+ + N_-) \log N - N_+ \log N_+ - N_- \log N_-$$
$$= -\left[ N_+ \log\left(\frac{N_+}{N}\right) + N_- \log\left(\frac{N_-}{N}\right) \right]$$

Using (4), we get

$$\log \Omega = -\left[ N_+ \log\left(\frac{\frac{1}{2}(N+n)}{N}\right) + N_- \log\left(\frac{\frac{1}{2}(N-n)}{N}\right) \right]$$
$$= -\left[ N_+ \log \frac{1}{2}\left(1 + \frac{n}{N}\right) + N_- \log \frac{1}{2}\left(1 - \frac{n}{N}\right) \right] \qquad \ldots(6)$$

Using

$$\log\left(1 \pm \frac{n}{N}\right) = \pm \frac{n}{N} - \frac{n^2}{2N^2} \pm \ldots \qquad \ldots(7)$$

we get

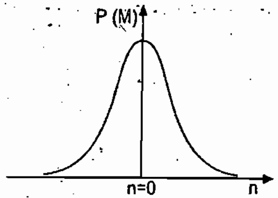
$$\log \Omega = -N_+\left[\log \frac{1}{2} + \left(\frac{n}{N} - \frac{n^2}{2N^2}\right)\right] - N_-\left[\log \frac{1}{2} + \left(-\frac{n}{N} - \frac{n^2}{2N^2}\right)\right]$$
$$= -(N_+ + N_-) \log \frac{1}{2} - (N_+ + N_-) \frac{n^2}{2N^2}$$
$$= -N \log \frac{1}{2} - \frac{n^2}{2N}. \qquad \ldots(8)$$

As there are only two possible orientations, the probability of each orientation is $\frac{1}{2}$. As the total number of particles is $N$ and then all are independent, therefore the probability of a given sequence of particle is $\left(\frac{1}{2}\right)^N$.

The net magnetic moment $= (N_+ - N_-)\,\mu = n\mu$

The probability $P(M)$ of the system to possess the net magnetic moment $M = n\mu$ is given by

$$P(M) = \left(\frac{1}{2}\right)^N . \, \Omega(n)$$
$$= \left(\frac{1}{2}\right)^N \exp\,[\log_e \Omega(n)]$$
$$= \left(\frac{1}{2}\right)^N \exp\left(-N \log_e \frac{1}{2} - \frac{n^2}{2N}\right)$$
$$= \left(\frac{1}{2}\right)^N . \exp \log_e \left(\frac{1}{2}\right)^{-N} . \exp\left(-\frac{n^2}{2N}\right)$$
$$= \left(\frac{1}{2}\right)^N . \left(\frac{1}{2}\right)^{-N} \exp\left(-\frac{n^2}{2N}\right) = e^{-n^2/2N} \qquad \ldots(9)$$



(Fig. 6.21)

This represents Gaussian distribution, which is symmetrical about the value $n = 0$ (fig. 6.21). As expected the average value of magnetization in the absence of an external magnetic field is zero. The most probable value is same as the average value. The entropy is given by

$$S = k \log \Omega$$
$$= -k\left[ N_+ \log_e \frac{N_+}{N} + N_- \log_e \frac{N_-}{N} \right] \qquad \ldots(10)$$

If we use to approximation (8), we get

$$S = k \log \Omega = -k\left[ N \log_e \frac{1}{2} + \frac{n^2}{2N} \right]$$
$$= -Nk\left[ -\log_e 2 + \frac{n^2}{2N^2} \right] \qquad \ldots(11)$$

using equation (1) for $n$, we get

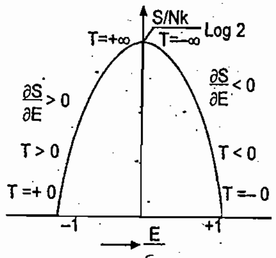
$$S = -Nk\left[ -\log_e 2 + \left(\frac{(E/\varepsilon)^2}{2N^2}\right) \right]$$
$$= -Nk\left[ -\log_e 2 + \frac{1}{2}\left(\frac{E}{\varepsilon N}\right)^2 \right] \qquad \ldots(12)$$

or

$$\frac{S}{Nk} = \log_e 2 - \frac{1}{2}\left(\frac{E}{\varepsilon N}\right)^2 \qquad \ldots(13)$$

If we plot a graph of $\left(\frac{S}{Nk}\right)$ versus $\left(\frac{E}{\varepsilon_N}\right)$ we get, parabola as shown in fig. 6.22.

When magnetic moment $\mu = 0, n = 0$, then from (11), the entropy $S = kN \log_e 2$ in the stirling approximation. This is just the entropy of all possible arrangements $2^N$, because each particle can have two possibilities, parallel or antiparallel moment, regardless of the presence of other particles. Thus we *conclude that the entire accessible phase space has the properties of the most probable condition of the system with large number of particles (N).*



(Fig. 6.22)

## 6.32 Negative Temperature

The temperature ($T$) is defined as the reciprocal of slope of $S$ versus $E$ curve

i.e.,
$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$$

But $E = n\varepsilon$,
$$\therefore \; \frac{1}{T} = \frac{1}{\varepsilon} \frac{\partial S}{\partial n}$$

using equation (10), of above section we get

$$\frac{1}{T} = -\frac{k}{\varepsilon} \frac{\partial}{\partial n}\left[ N_+ \log_e \frac{N_+}{N} + N_- \log_e \frac{N_-}{N} \right]$$

Using (4) for $N_+$ and $N_-$, we get

$$\frac{1}{T}=\frac{-k}{\varepsilon}\frac{\partial}{\partial n}\left[\frac{1}{2}(N+n)\log_e\left\{\frac{1}{2}\frac{(N+n)}{N}\right\}+\frac{1}{2}(N-n)\log_e\left\{\frac{1}{2}\frac{N-n}{N}\right\}\right]$$

Simplifying, we get

$$\frac{1}{T}=\frac{1}{2}\frac{k}{\varepsilon}\log_e\frac{N-n}{N+n}=\frac{1}{2}\frac{k}{\varepsilon}\log_e\frac{N_-}{N_+}$$

At the *conventional absolute zero temperature* all the particles are in lower energy state $-\varepsilon$.

$\therefore$ $$n=N_+-N_-=0-N=-N\leq 0,\text{ giving}$$

$$T=+0\text{ and }S=0\text{ (an energy state of complete order) at }E=-N\varepsilon.$$

As the temperature is raised, the energy is supplied to system and particles jump from energy state $\varepsilon_-$ to energy state $\varepsilon_+$, so the upper level ($\varepsilon_+$) grows at $T>0$, till we have $n=0$, giving probability $S'=Nk\log_e 2$, a state of maximum disorder and $T=+\infty$. If more energy is supplied to system, the upper level becomes more populated than the lower level *i.e.*, $N_+>N_-$, and so $n\geq 0$ and we get a decrease in entropy $S$ (more ordered state) and $T<0$ (negative temperature). Thus the system loses its normal behaviour. Thus the negative temperature $T_-$ corresponds to higher energies than positive temperature $T_+$.

If $T_-$ and $T_+$ systems are brought into thermal contact, the energy will flow from $T_-$ state to $T_+$ state. Thus according to concept of temperature $T_-$ is hotter than $T_+$. A laser is a device based on such a $T_-$ system. As energy is continuously given to system we get $n=N_+-N_-=N-0=N>0$. This means that all the particles are in the upper state giving $S=0$ (a complete ordered state) at $T=-0$ (fig. 6.22). The difference between $+0$ and $-0$ is that $+0$ is aproached from the side of positive temperature and $-0$ is approached from the side of negative temperature. The possible temperature ranges being $+0$ through $+\infty$, $-\infty$ to $-0$, $+\infty$ and $-\infty$ coinciding with each other.

For a system to have a negative temperature, the following conditions must be satisfied.

(i) It must have a finite upper limit to the energy spectrum.

(ii) It must be in thermal equilibrium.

(iii) It must have the negative temperature states isolated from positive temperature states.

## SOLVED EXAMPLES

**Ex. 23.** *If the energy in a magnetic field is $E=-n\mu B$, then show that for $n<<N$, the Helmholtz free energy $F(n)$ is given by*

$$F(n)\approx -n\mu B+\frac{n^2kT}{2N},$$

*and* $$[F(n)]_{\min}=-\frac{n\mu B}{2}$$

**Solution.** Helmholtz free energy $F(n)$ is given by

$$F(n)=E-TS=E-T\,.\,k\log\Omega(M)\qquad[\text{since }S=k\log\Omega(M)]$$

Substituting the value of $\log\Omega(M)$ from $\Omega(M)=e^{-n^2/2N}$ and given value of $E$ in above equation we get

$$F(n)=-n\mu B+\frac{n^2kT}{2N}\qquad\ldots(1)$$

For minimum value of $F(n)$, $\dfrac{\partial F(n)}{\partial n}=0$ and $\dfrac{\partial^2 F(n)}{\partial n^2}$ should be positive. Thus,

$$\frac{\partial}{\partial n}F(n)=-\mu B+\frac{nkT}{N}=0,\quad i.e.,\quad \frac{nkT}{N}=\mu B.\qquad\ldots(2)$$

and $\dfrac{\partial^2F(n)}{\partial n^2}=\dfrac{kT}{N}$ which is positive.

Substituting volume from (2) in (1), we get

$$[F(n)]_{\min}=-n\mu B+\frac{n\mu B}{2}=-\frac{n\mu B}{2}\qquad\ldots(3)$$

**Ex. 24.** *Two states with energy difference $4{\cdot}83\times 10^{-21}$ joule occur with relative probability $e^2$. Calculate the temperature.*

*Given $k=1{\cdot}38\times 10^{-23}$* joule/K. *(Agra 2003)*

**Solution.** Let the energy of two states be $\varepsilon_1$ and $\varepsilon_2$. The probability $P_1$ and $P_2$ of the states of energies $\varepsilon_1$ and $\varepsilon_2$ are given by

$$P_1=Ce^{-\varepsilon_1/kT}$$

$$P_2=Ce^{-\varepsilon_2/kT}$$

$$\frac{P_1}{P_2}=\frac{Ce^{-\varepsilon_1/kT}}{Ce^{-\varepsilon_2/kT}}=e^{(\varepsilon_2-\varepsilon_1)/kT}$$

or $$\log_e\frac{P_1}{P_2}=\frac{\varepsilon_2-\varepsilon_1}{kT}$$

$\therefore$ $$T=\frac{\varepsilon_2-\varepsilon_1}{k\log_e\dfrac{P_1}{P_2}}$$

Here $\varepsilon_2-\varepsilon_1=4{\cdot}83\times 10^{-21}$ joule, $\dfrac{P_1}{P_2}=e^2$

$\therefore$ $$T=\frac{4{\cdot}83\times 10^{-21}}{k\log_e(e^2)}=\frac{4{\cdot}83\times 10^{-21}}{k\times 2}$$

$$=\frac{4{\cdot}83\times 10^{-21}}{2\times 1{\cdot}38\times 10^{-23}}=\mathbf{175\ K.}$$

**Ex. 25.** *A system can take only three different energy states $\varepsilon_1=0$, $\varepsilon_2=1{\cdot}38\times 10^{-21}$ joule, $\varepsilon_3=2{\cdot}76\times 10^{-21}$ joule. These three states can occur in 2, 5 and 4 different ways respectively. Find the probability that at temperature 100 K the system may be (i) in one of the microstate of energy $\varepsilon_3$ (ii) in the ground state $\varepsilon_1$.*

**Solution.** The probabilities with which the microstates can occur in three energy values $\varepsilon_1$, $\varepsilon_2$ and $\varepsilon_2$ are given by

$$p_1=Ce^{-\varepsilon_1/kT}=Ce^0=C$$

$$p_2=Ce^{-\varepsilon/kT}=C\exp\left[\frac{-1{\cdot}38\times 10^{-21}}{1{\cdot}38\times 10^{-23}\times 100}\right]=Ce^{-1}\qquad\ldots(2)$$

and $$p_3 = Ce^{-\varepsilon_3/kT} = C\exp\left[\frac{-2.76\times10^{-21}}{1.38\times10^{-23}\times100}\right] = Ce^{-2}.$$

Keeping in mind that 2, 5, 4 microstates can occur in the three energy states, the probabilities are

$$P_1 = 2C, P_2 = 5\,Ce^{-1}, P_3 = 4Ce^{-2}$$

But $\Sigma P = 1.$

∴ $$P_1 + P_2 + P_3 = 1$$

or $$2C + 5Ce^{-1} + 4Ce^{-2} = 1$$

or $$C\,(2 + 5e^{-1} + 4e^{-2}) = 1$$

or $$C = \frac{1}{2 + 5e^{-1} + 4e^{-2}} = \frac{1}{2 + 1.84 + 0.54} \quad \text{(since, } e = 2.72)$$

$$= \frac{1}{4.38}$$

(i) The probability for the system to be in one of the microstates of energy $\varepsilon_3$ is $p_3 = 4Ce^{-2}$

$$= \frac{4C}{e^2} = \frac{4}{4.38\times(1.72)^2} = 0.12.$$

(ii) This probability for the system to be in ground state is $P_1 = 2C = \frac{2}{4.38} = 0.45.$

## EXERCISES

### SHORT ANSWER QUESTIONS

1. Define probability. Under what condition the probability is (i) maximum (ii) minimum?
2. Prove that the probability of a composite event is equal to the product of probabilities of the individual and independent events. *(Rohilkhand 2001)*
3. The probability of distribution of $n$ particles in two boxes is equal. What will be the probabilities of maximum and minimum distribution. *(Kumaun 2003)*
4. When three unlike coins $a, b$ and $c$ are tossed, find the number of possible events and the probability for each event. How will this distribution change if one considers them alike? *(Garhwal 1991)*
5. Define the terms with examples :
   (i) Macrostate
   (ii) Microstates
   (iii) Ensemble
   (iv) Accessible microstates. *(Garhwal 1992, Meerut 93)*
6. Differentiate between the following :
   (i) μ-space and τ-space
   (ii) Phase points, phase density and a cell. *(Meerut 2003)*
7. Define and explain the most probable macrostates. *(Rohilkhand 2002 Improvement)*
8. Define thermodynamical probability. *(Rohilkhand 2001)*

9. State and prove Boltzmann's theorem connecting entropy and probability. *(Rohilkhand 2001)*
10. What do you mean by statistical equilibrium?
11. What do you mean by phase space? How will you divide the phase space into cells? *(Rohilkhand 2003, Gorakhpur 1993)*
12. What are the fundamental postulates of statistical mechanics. *(Agra 2005)*
13. Explain the postulate of equal a priori probability and obtain the condition of statistical equilibrium. *(Avadh 2003, 1994)*
14. Explain the statistical meaning of entropy. *(Avadh 2002,1994)*
15. Differentiate between microstate and macrostate. How does probability depend upon the number of microstates? *(Rohilkhand 2004, 98)*
16. What do you mean by canonical ensemble? For what type of system is it suitable? *(Lucknow 2000, 1993)*
17. Differentiate between microcanonical and canonical ensembles. *(Lucknow 2005,1994)*
18. Define ensemble. Differentiate between canonical, microcanonical and grand canonical ensembles? *(Meerut 2002)*
19. What do you understand by a priori probability and thermodynamical probability of distribution. *(Meerut 2000)*
20. State Liouville's theorem.
21. State Maxwell's Boltzmann's distribution law of molecular speeds.
22. State the law of equipartition of energy.
23. Explain the concept of negative temperature.

### LONG ANSWER QUESTIONS

1. Define probability and prove that the probability of a composite event is equal to the product of the probabilities of the individual and independent events, *(Rohtak 2005)*
2. $n$ similar coins are tossed simultaneously for a large number of times. Prove that the probability of getting $r$ heads uppermost is
$$P\,(r, n-r) = \frac{n!}{r!\,n-r!}\cdot\frac{1}{2^n}.$$
Hence find the probability of (i) most probable and (ii) the least probable combination. *(Rohilkhand 2002)*
$$\left[\text{Ans. (i) } r = \frac{n}{2}, P = \frac{n!}{[n/2!]^2}\cdot\frac{1}{2^n}, \text{ (ii) } r = 0 \text{ or } n, P = \frac{1}{2^n}\right]$$
3. There are $2n$ particles which are distributed between two similar boxes. Calculate the probability for a distribution $(n+s, n-s)$ where $\frac{s}{n} < 1$. Plot this probability versus $\frac{s}{n}$. *(Kumaun 1988, Rohilkhand 2002)*
4. What do you understand by the term phase space? Classify different types of phase space. Derive an expression for the number of states in the energy range $E$ and $E + dE$. *(Rohilkhand 1999)*

5. Define thermodynamical probability. Derive an expression for the thermodynamical probability when $N$ identical molecules are distributed in $K$ cells. *(Rohilkhand 1997, 98, 2002)*
6. Define entropy and probability and establish a relation between them. *(Meerut 2006, 1998; Lucknow 1994, 90; Kanpur 94, 92; Garhwal 92; Rohilkhand 2001, 99, Agra 2002, 94)*
7. Deduce Boltzmann's entropy probability relation
$$S = k \log_e \Omega(E)$$
where $S$ is entropy, $\Omega(E)$ is the number of microstates in the energy interval between $E$ and $E + \delta E$ and $k$ is a constant. *(Meerut 2000, Rohilkhand 2003)*
8. Define entropy and probability. Show that the entropy of the system is proportional to the logarithm of probability of that system. *(Rohilkhand 2001 imp.)*
9. Derive the number of phase cells in a given energy range for free particles. *(Meerut 1996; Agra 2002)*
10. Show that when two systems are placed in thermal contact
$$\beta(E) = \beta'(E') = \frac{1}{kT} = \frac{1}{\Omega} \cdot \frac{\partial \Omega}{\partial E}.$$
*(Meerut 1999, 1994)*
11. Determine the condition of statistical equilibrium between two systems when the systems are in thermal contact. *(Kumaun 1989; Agra 86, 92, 93)*
12. Deduce an expression for the number of molecules in a cell of energy $\varepsilon_i$ in thermal equilibrium at temperature $T$. *(Gorakhpur 1993)*
13. Give statistical definition of entropy and use it to show that the difference in entropy between a state of volume $V_f$ and state of volume $V_i$ (temperature and number of molecules remaining constant) is equal to $R \log_e \frac{V_f}{V_i}$. *(Rohilkhand 2004, 1977)*
14. Show that the number of molecules in a cell of energy $\varepsilon_i$ in the equilibrium state is given by
$$n_i = A e^{-\varepsilon_i kT}$$
where $A$ is any constant. *(Rohilkhand 2004, 81)*
15. (a) State the postulate of equal a priori probability. *(Rohilkhand 2006, Agra 2007)*
    (b) State and prove Boltzmann's Canonical distribution theorem. *(Rohilkhand 2002)*
16. Show that the probability that a system in equilibrium with a heat reservoir at temperature $T$ may exist in a microstate of energy $\varepsilon_r$ is proportional to exp. $\left(-\frac{\varepsilon_r}{kT}\right)$ where $k$ is Boltzmann's constant. *(Rohilkhand 1999; Agra 1998)*
17. Derive Maxwell Boltzmann distribution law. Hence show that the number of molecules between energy $U$ and $U + dU$ at temperature $T$ in equilibrium is given by
$$n(U)\, dU = 2\pi N \left(\frac{1}{\pi kT}\right)^{3/2} U^{1/2} e^{-U/kT} dU$$
*(Mumbai 2004)*
18. The number of microstates accessible to any system in energy range $E$ and $E + dE$ may be denoted by $\Omega(E)$. Show that the probability for this system to be found in a particular state of energy $E_r$ is proportional to exp. $(-\beta E_r)$, where $\beta$ is defined by
$$\beta = \frac{\partial}{\partial E}[\log \Omega(E)] \equiv \frac{1}{kT}.$$
$T$ being the temperature, defined through this relation for the reservior with which the system is in thermal equilibrium. *(Mumbai 2004; Rohilkhand 2002; Agra 2004)*

19. Derive Liovilles's theorem for the change of density of distribution with time and show that the density of phase points is conserved. *(Meerut 2003)*
20. State and prove Liouville's theorem. Mention its use in the study of ensembles. *(Delhi 2004; Mumbai 2006; Meerut 1989; Rohilkhand 2005)*
21. What are the principles of conservation of density and the conservation of extension in the phase space ? Explain how these pronciples together lead to the postulate of equal a priori probabilities.
22. What do you mean by the statistical equilibrium of an ensemble ? Derive the necessary condition.
23. Describe how an expression for the entropy is set up in statistical mechanics. Show how it has the same properties as the thermodynamic entropy.
24. (a) State the fundamental assumption of statistical mechanics regarding an assembly of particles.
    (b) Deduce an expression for the nunber of 6-dimensional phase cells in the range of energy $E$ and $E + \delta E$. *(Agra 2006)*
25. What do you mean by the terms phase space and ensembles ? For the phase space representing a single particle in the volume $V$, calculate the number of phase cells in the energy range 0 to $E$. Given that volume of each phase cells is $h^3$. What will be the number of microstates in this energy range $E$ to $E + \delta E$. *(Kanpur 2005; Meerut 2004)*
26. Derive distribution function for Maxwell-Boltzmann statistics. Hence calculate the number of gas molecules within the velocity range $v$ and $v + dv$. *(Meerut 2006, 2001)*
27. Deduce Maxwell's-Boltzmann's law for the distribution of molecules in a gas. Use the law to prove the theorem of equipartition of energy among various degrees of freedom of the molecules.
28. (a) Using Maxwell-Boltzmann's law, show that the fraction of molecules within the momentum range $p$ and $p + dp$ is given by
$$f(p)\, dp = 4\pi \left(\frac{1}{2\pi mkT}\right)^{3/2} e^{-p^2/2mkT} p^2\, dp$$
    (b) The fraction of molecules within the energy range $\varepsilon$ and $\varepsilon + d\varepsilon$ is
$$f(\varepsilon)\, d\epsilon = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} e^{-\varepsilon/kT} \varepsilon^{1/2}\, d\varepsilon$$
*(Meerut 2003, 1999)*
29. (a) Show that in an assembly of particles the number of molecules having energy $\epsilon$ is given by
$$n(\varepsilon) = 2\pi N \left(\frac{1}{\pi kT}\right)^{3/2} \varepsilon^{1/2} e^{-\varepsilon/kT}$$
where $N$ is the total number of particles.
    (b) Show that the most probable velocity $v_{mp}$ of the moiecuies of a Maxwellian gas is given by the relation,
$$v_{mp}^2 = 2/3\, v_{rms}^2$$
where $v_{rmp}$ is the root mean square velocity of the molecules.

30. Deduce Maxwell-Boltzmann distribution law of molecules in a gas. Evaluate the constants α and β. *(Meerut 2004)*

31. Show that for an assembly of $N$ molecules of an ideal gas at absolute temperature $T$, the number of molecules in energy range $\varepsilon$ and $\varepsilon + d\,\varepsilon$ is

$$n(\varepsilon)\, d\varepsilon = 2\pi N \left(\frac{1}{\pi kT}\right)^{3/2} \varepsilon^{1/2} e^{-\varepsilon/T} d\varepsilon .$$

Hence obtain expression for most probable energy. *(Meerut 1998; Agra 2003)*

32. Derive Maxwell's law of **distribution** of velocities of molecules of a gas and obtain expression for (i) average velocity; **(ii)** root mean square velocity; and (iii) most Probable velocity. *(Kanpur 2004; Agra 2002)*

33. Derive the Maxwell-Boltzmann distribution law and obtain expressions for the most probable energy and most probable speed of a gas molecule. *(Rohilkhand 1996)*

34. Show that the probability function is given by

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

Hence derive expressions for most probable speed, average speed and root mean square speed.

35. Deduce Maxwell-Boltzmann law for the distribution of molecules in a gas. Hence prove the theorem of equipartition of energy amomg various degrees of freedom of molecules. *(Meerut 1995)*

36. Show that mean speed $(v)$, the most probable speed $(v_{mp})$ and the root mean square speed $\sqrt{v^2}$ of the molecules are given by

$$\bar{v} = \sqrt{\left(\frac{8kT}{m}\pi\right)}, \quad v_{mp} = \sqrt{\left(\frac{2kT}{m}\right)} \quad \sqrt{\bar{v}^2} = \sqrt{\left(\frac{3kT}{m}\right)}$$

37. State the law of equipartition of energy. Use the classical distribution law to prove that the average energy for each degree of freedom of a perfect gas molecule is $\frac{1}{2}kT$. *(Meerut 2005)*

38. Establish the law of equipartition of energy in classical statistical mechanics. How does this law agree with observations for diatomic gases ? Give a detailed description of the expected and observed behaviour for a particular gas at various temperatures. *(Rohilkhand 2006; Meerut 2004)*

39. Discuss and prove the law of equipartition of energy in statistical mechanics. *(Agra 2004; Meerut 2005)*

40. Write a detailed note on 'Nernst third law of thermodynamics,' *(Rohilkhand 1998)*

41. (a) Derive Liouville's theorem for the change of density of distribution with time and show that the density of phase points is conserved.
    (b) Explain probability. Give the physical imerpretations for probability of a system as a function of its entropy. *(Rohilkhand 1998)*

42. Deduce Boltzmann's canonical distribution law $n_i = Ae^{-\beta\varepsilon_i}$ and determine the expression for probability for molecule having energy $\varepsilon_i$

$$P(\varepsilon_i) = \frac{e^{-\varepsilon_i/kT}}{\Sigma e^{-\varepsilon_i/kT}}$$

*(Agra 1991)*

43. Give the concept of ensemble and phase space. Calculate the number of states per unit volume of the phase space. *(Rohilkhand 2000)*

44. State and prove Boltzmann's canonical distribution law and give some of its applications. *(Meerut 1997, 2000; Agra 2002)*

45. State and briefly comment on :
    (i) Liouville's theorem. *(Rohilkhand 2005)*
    (ii) Principles of equal a priori probabilities. *(Agra 2004)*
    (iii) Maxwell- Boltzmann's distribution law. *(Rohilkhand 2003)*
    (iv) Entropy is statistical mechanics. *(Meerut 2001)*
    (v) Law of equipartition of energy. *(Kanpur 2004; Tohtak 2003)*
    (iv) Negative temperature. *(Rohtak 2003)*

## NUMERICAL QUESTIONS

1. Eight similar coins are tossed for a large number of times. Calculate :
    (i) the probability of getting the heads of five coins uppermost.
    (ii) the probability of most probable combination. *(Agra 1998)*

2. 10 similar coins are tossed simultaneously for a large number of times. Calculate (i) the probability of getting the heads of 7 coins uppermost, (ii) the probability of most probable combination and (iii) the probability of least probable combination.
[**Ans.** (i) $120 \times 2^{-10}$, (ii) $252 \times 2^{-10}$, (iii) $2^{-10}$]

3. Calculate the probability that in tossing a coin 10 times we get (i) all heads, (ii) 4 heads, 6 tails, (iii) 2 heads, 8 tails, (iv) 7 heads, 3 tails, (v) 1 head, 9 tails. *(Agra 2003)*
[**Ans.** 1/1024, 210/1024, 45/1024, 120/1024, 10/1024]

4. A dice having 6 equally likely faces marked as 1, 2, 3, 4, 5, 6 is thrown. Calculate the probability of getting number (i) 6 uppermost, (ii) either 3 or 6 uppermost (iii) either 2 or 3 or 4 uppermost. [**Ans.** (i) 1/6, (ii) 1/3 (iii) 1/2]

5. A six faced dice has its six faces marked from 1 to 6 and in a toss all the faces have equal probability of appearing up. If 8 such dice are tossed, calculate the probability for the following :
    (i) all dice showing up 3.
    (ii) None of 8 dice showing up 3.
    (iii) At least one dice showing up 3.
    (iv) Just two dice showing up 3. *(Rohilkhand 1983)*

$$\left[\textbf{Ans.}\ \text{(i)} \left(\frac{1}{6}\right)^8 \text{(ii)} \left(\frac{5}{6}\right)^8 \text{(iii)}\ 1 - \left(\frac{5}{6}\right)^8 \text{(iv)}\ 28 \times \left(\frac{1}{6}\right)^2 \left(\frac{5}{6}\right)^6\right]$$

6. Three similar dice $A$, $B$ and $C$ each having six equally likely faces marked as 1, 2, 3, 4, 5, 6 are thrown simultaneously. Calculate the probability of getting the faces of all the dice uppermost marked with same particular number. [**Ans.** 1/216]

7. In a random distribution of 6 particles between 2 boxes with equal probability, calculate the following :

(i) the probability of distribution (1, 5), (2, 4),

(ii) the probability of most probable distribution. *(Rohilkhand 2005)*

[**Ans.** (i) (3/32), (15/64) (ii) $P(3, 3) = (10/32)$]

8. (a) If two dice are thrown show that the probability of the sum of the number uppermost being 5 is 4/36.

(b) A six faced dice has its faces marked from 1 to 6 and in a toss all the faces have equal probability of appearing up. If 5 such dice are tossed, calculate the probability of the following : (i) all five dice showing up 6, (ii) none of the five dice showing up 6, (iii) just two dice showing up 6. *(Agra 2004)*

[**Ans.** (i) $(1/6)^5$, (ii) $(5/6)^5$, (iii) 0·16]

9. 14 particles are to be distributed in two boxes with weightages in the ratio 5 : 2. Determine the probabilities of distributions (10, 4), (14, 0), (7, 7). [**Ans.** 0·23, 0·009, 0·51]

10. A coin is so tossed that probability of getting head in a toss is 0·70. Deduce the probability that in 5 tosses, we get :

(i) all tails, (ii) 1 head, 4 tails, (iii) two heads, three tails, (iv) all heads. *(Agra 1980)*

[**Ans.** (i) $5C_0\,(0{\cdot}30)^5$, (ii) $5C_1\,(0{\cdot}30)^4.\,(0{\cdot}70)$, (iii) $5C_2\,(0{\cdot}70)^2\,(0{\cdot}30)^3$, (iv) $(0{\cdot}70)^5$]

11. Using Heisenberg's uncertainty relation $\Delta p\,\Delta q \geq \hbar\;/2$, show that the volume occupied by each energy state in Gamma space is $(\hbar\;/2)^{3N}$. *(Meerut 1993)*

[**Hint :** For $N$ particles, elementary volume of phase space

$$dq_1\,dq_2\,dq_3 \ldots dq_{3N}\,dp_1\,dp_2 \ldots dp_{3N}$$

$$= \prod_{i=1}^{3N} dq_i\,dp_i = \left(\frac{\hbar}{2}\right)^{3N}\Bigg]$$

12. Consider two cells, 1, 2 and four molecules $a, b, c, d$. Write down explicitly the different microstates which may be observed and macrostates into which the molecules may be distributed; Also find the thermodynamical probability of the most probable and least probable macrostates. [**Ans.** 6, 1]

13. Given 3 cells and 5 particles. Calculate the thermodynamical probability for

(i) $n_1 = 5, n_2 = 0, n_3 = 0$

(ii) $n_1 = 4, n_2 = 1, n_3 = 0$

(iii) $n_1 = 3, n_2 = 2, n_3 = 0$

(iv) $n_1 = 3, n_2 = 1, n_3 = 1$

(v) $n_1 = 1, n_2 = 2, n_3 = 2.$

[**Ans.** (i) 1, (ii) 5 (iii) 10, (iv) 20 (v) 30]

14. Consider a system of 3 cells such that $n_1 = 5, n_2 = 3, n_3 = 2\ \varepsilon_1 = 0,\ \varepsilon_2 = 2$ and $\varepsilon_2 = 4$ joules/molecule. If $\delta n_2 = 2$, find $\delta n_1$ and $\delta n_3$. Also find the initial and final thermodynamical probabilities. [**Ans.** $\delta n_1 = -1, \delta n_3 = -1, \Omega = 2520, \Omega = 2520$]

15. A system of $n$ particles has only two allowed states. $A$ and $B$, The probability for state $A$ is $p$ and for state $B$ is $(1 - p)$. What is the probability for system of be in the macrostate defined by the distributions $(r, n - r)$. $\left[\textbf{Ans. } P(r, n - r) = \dfrac{n\,!}{r\,!\,(n - r)\,!}\,p^r\,(1 - p)^{n - r}\right]$

16. The speed of 10 particles in m/s are 0, 1, 2, 3, 3, 3, 4, 4, 5 and 6. Calculate the average speed, the root mean square speed and the most probable speed. [**Ans.** 3·1, $5\sqrt{5}$, 3]

---

17. Show that the ratio between most probable speed, average speed and root mean square speed is 1 : 1·128 : 1·224. Also show that root mean square speed = 1·085 × average speed.

18. Calculate the root mean square speed of nitrogen molecules at 15°C and 76 cm. of mercury pressure. Use Boltzmann constant $= 1{\cdot}38 \times 10^{-23}$ J/k. [**Ans.** 500 m/s]

19. At what temperature, pressure remaining constant, the root mean square velocity of a gas be half of its value at 0°C. [**Ans.** – 204·75°C]

20. Calculate the root mean square velocity of hydrogen at 127°C. The Boltzmann constant is $1{\cdot}34 \times 10^{-23}$ J/K and the mass of hydrogen molecule is $3{\cdot}34 \times 10^{-27}$ kg. [**Ans.** $2{\cdot}2 \times 10^3$ m/s.]

21. Find the root mean square velocity of chlorine at 0°C. Given, molecular weight of chlorine = 71 and Avogadro numbers $N = 6{\cdot}02 \times 10^{23}$/g mole. [**Ans.** $3{\cdot}094 \times 10^2$ m/s.]

22. If Avogadro's Number is $6{\cdot}02 \times 10^{23}$/g-mole and Boltzmann's constant $1{\cdot}38 \times 10^{-23}$ J/K, what is the average velocity of a molecule of oxygen at 27°C ? Convert this into km per hour. [**Ans.** 483·50 m/s.; 1741 km./hour]

23. Calculate molecular kinetic energy of one gram of helium at N.T.P. [**Ans.** 1699·4 joule]

24. Find the temperature at which r.m.s. speed of hydrogen molecule is equal to that of nitrogen molecule at 77°C. [**Ans.** 25 K]

25. Calculate the number of accessible microstates for a molecule of nitrogen enclosed in a box of volume 1 litre at 100 K having energy less than $6 \times 10^7$ joule. Given $h = 6{\cdot}6 \times 10^{-34}$ joule-second. [**Ans.** $1{\cdot}9 \times 10^{29}$]

26. The first vibrational energy level of a particular diatomic molecule is 600 cm$^{-1}$ above the ground state. Calculate the relative propulation of the molecules in these levels at 127°C. [**Ans.** 0·1]

## MULTIPLE CHOICE QUESTIONS : SELECT THE RIGHT CHOICE

1. Three similar coins are tossed for a large number of times. The probability of getting two heads and one tail uppermost is :

(a) $\frac{2}{8}$ (b) $\frac{3}{8}$ (c) $\frac{2}{64}$ (d) $\frac{1}{64}$

2. $n$ similar coins are tossed for a large number of times. If '$a$' denotes that the heads fall uppermost while '$b$' denotes that the tails fall uppermost. Then the probability of the combincation $a^r b^{n-r}$ is :

(a) ${}^nC_r$ (b) ${}^nC_r\,.\,2^n$ (c) ${}^nC_r/2^n$ (d) $2^n/{}^nC_r$

3. In the above equation, the minimum probability of the combination $a^r b^{n-r}$ is :

(a) zero (b) 1 (c) $2^n$ (d) $\frac{1}{2^n}$

4. A bag contains 6 green balls, 8 white balls and 10 black balls. If a ball is drawn from the bag, what is the probability of its being either white or black ?

(a) $\frac{1}{3}$ (b) $\frac{5}{12}$ (c) $\frac{5}{36}$ (d) $\frac{3}{4}$

$\left[p = \frac{8}{24} + \frac{10}{24}\right]$

5. From a pack of 52 cards, two are drawn at random. What is the probability that one is a king and the other a queen ?

(a) $\frac{8}{663}$ (b) $\frac{1}{16}$ (c) $\frac{1}{8}$ (d) $\frac{1}{26}$

$\left[\textbf{Hint}: P = \frac{({}^4C_1 \times {}^4C_1)}{{}^{52}C_2}\right]$

6. The probability that from two dice the sum of either 7 or 11 is obtained is :

(a) $\frac{1}{6}$ (b) $\frac{1}{18}$ (c) $\frac{2}{9}$ (d) $\frac{1}{108}$

[**Hint :** Two dice have $6 \times 6 = 36$ alternatives.

Cases in which sum 7 is obtained → (1, 6), (2, 5), (3, 4), (4, 3), (5, 2), (6, 1) Here probability of sum being 7 → $P(7) = \frac{6}{36}$

Similarly $P(11) = \frac{2}{36}$

$$\therefore \quad P(7 \text{ or } 11) = P(7) + P(11) = \frac{6}{36} + \frac{2}{36} = \frac{2}{9}]$$

7. What is the probability that in tossing a coin 10 times, we get all heads ?

(a) zero (b) $\left(\frac{1}{2}\right)^{10}$ (c) $\left(\frac{1}{2}\right)^{0}$ (d) $252\left(\frac{1}{2}\right)^{0}$

8. $n$ six faced dice are tossed simultaneously. Then the probability that $r$ of the $n$ dice show the same number uppermost is :

(a) ${}^nC_r\left(\frac{1}{6}\right)^r$ (b) ${}^nC_r\left(\frac{1}{6}\right)^{n-r}$

(c) ${}^nC_r\left(\frac{1}{6}\right)^r\left(\frac{5}{6}\right)^n$ (d) ${}^nC_r\left(\frac{1}{6}\right)^r\left(\frac{5}{6}\right)^{n-r}$

9. Four distinguishable coins are tossed for a large number of times. Then the probability of most probable macrostate is :

(a) 1 (b) $\frac{5}{16}$ (c) $\frac{3}{8}$ (d) 4

10. In a random distribution of 10 particles between two boxes with equal probability, the number of microstates in macrostate (3, 7) is :

(a) 120 (b) 5 (c) $\frac{10}{21}$ (d) $120 \times 2^{-10}$

11. Five particles are distributed in two phase cells. Then number of macrostates is :

(a) 10 (b) 6 (c) $\frac{5}{2}$ (d) 32

12. In the above question, the number of microstates is :

(a) 10 (b) 6 (c) $\frac{5}{2}$ (d) 32

13. Four phase points are distributed in two cells ($i$ and $j$) in phase space. Then the thermodynamical probability for the macrostate $n_i = 3$, $n_j = 1$ is :

(a) 2 (b) 4 (c) 6 (d) 24

14. In the equilibrium state :
(a) probability is maximum
(b) $\beta$ parameters of two systems are equal
(c) both (a) and (b)
(d) number of particles is maximum

15. According to Boltzmann canonical distribution law, the number of molecules per cell :
(a) decreases linearly with energy associated with the cell
(b) decreases exponentially with energy associated with the cell
(c) increases linearly with energy associated with the cell
(d) increases exponentially with energy associated with the cell

16. According to Boltzmann canonical distribution law :
(a) low energy cells contain more particles
(b) high energy cells contain more particles
(c) number of molecules having zero energy is greater than any other energy
(d) zero energy molecules are zero

17. If twelve particles are distributed randomly between two boxes $A$ and $B$ with equal probability, what is the probability of the distribution (8, 4) ?

(a) $4{\cdot}95 \times 2^{-12}$ (b) $495 \times 2^{-12}$ (c) $49{\cdot}5 \times 2^{-12}$ (d) $495 \times 2^{-11}$

***(Rohilkhand 2003)***

18. The relative probability between two different energy states having difference $1{\cdot}1 \times 10^{-20}$ joules at 40 K temperature is :

(a) $e^{-1}$ (b) $e^{-2}$ (c) $e$ (d) $e^2$

***[Rohilkhand 2003 (Impr.)]***

19. The relation between entropy and probability is :

(a) $S = k \log \Omega$ (b) $S = \frac{k}{\log \Omega}$ (c) $\Omega = k \log S$ (d) $\Omega = \frac{k}{\log S}$

20. The statistical condition of equilibrium of two systems in thermal contact is :

(a) $T_1 = T_2$ (b) $S_1 = S_2$

(c) $\Omega_1 = \Omega_2$ (d) $\frac{\partial}{\partial E_1} \log \Omega(E_1) = \frac{\partial}{\partial E_2} \log \Omega_2(E_2)$

21. Which of the following speeds is most closely related to kinetic energy of molecules.

(a) most probable speed (b) mean speed

(c) root mean square speed (d) all are equally related

## ANSWERS

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. (b) | 2. (c) | 3. (d) | 4. (d) | 5. (a) | 6. (c) | 7. (b) | 8. (d) |
| 9. (c) | 10. (a) | 11. (b) | 12. (d) | 13. (b) | 14. (c) | 15. (b) | 16. (a) |
| 17. (c) | 18. (d) | 19. (a) | 20. (d) | 21. (c) | | | |

# 7

# METHOD OF ENSEMBLES : PARTITION FUNCTIONS

## 7.0 Introduction

In preceding chapter we have given a **brief** introduction of three types of ensembles namely *microcanonical, canonical,* and *grand canonical.* The method of ensembles helps us in arriving at the thermodynamical functions of a thermodynamical system. In this chapter we shall find the partition function for each of the above three types of ensembles and then evaluate the thermodynamical functions of the thermodynamical system.

## 7.1 Micro Canonical Ensemble

The ensemble in which system has the same fixed energy and also the same number of particles is called a *microcanonical ensemble.* If the energy of the system is prescribed in the range $\delta E$ at $E$, then we may form a satisfactory microcanonical ensemble by taking the density to be equal to zero except in the selected narrow range of energy $\delta E$ at $E$. Obviously the density distribution function $\rho(E)$ of a microcanonical ensemble is a function of energy alone and is independent of time. Thus a microcanonical ensemble is characterised by

$$\left.\begin{aligned}\rho(E) &= \text{constant for energy in the range } \delta E\\ &= 0, \text{ elsewhere}\end{aligned}\right\} \qquad \ldots(1)$$

The systems whose energies are constant are considered as isolated systems. Thus isolated system can appropriately form micro-canonical ensemble. The volume of the phase space with energy $\delta E$ at $E$, (*i.e.* the volume of the phase space where $\rho(E) =$ constant), is called the *accessible region* of the phase space. The other ensembles, namely the canonical and the grand-canonical, are more widely used : but the micro-canonical ensemble is of the fundamental value.

$$E = \sum_{i=1}^{3n}\left(\frac{p_i^2}{2m_i}\right) \qquad \ldots(2)$$

For a system of $n$ three-dimensional simple harmonic oscillators the energy is

$$E = \sum_{i=1}^{3n}\left(\frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 q_i^2\right)$$

For a system of $n$ electrons spinning in a magnetic field $B$, the energy associated with the spin system is

$$E_S = -(n_1 - n_2)\,\mu_B B \qquad \ldots(4)$$

where $n_1$ is the number of electrons having their magnetic moment parallel to the field $B$, while $n_2$ is the number of electrons having their magnetic moment antiparallel to the field $B$ : $\mu_B$ is the Bohr magneton $\frac{e\hbar}{2m}$ (S.I. system).

**Implication of the micro-canonical ensemble :** The consider the implications of the micro-canonical ensemble let us imagine an *isolated system* consisting of fixed number of particles $n$ and *constant energy* $E$ in a given volume $V$. At time $t_0$ each particle of the system will have definite values of the coordinates and the velocity components. The microscopic average physical properties of the system would be calculated by following the motion of the particles over a reasonable interval of time. Here we do not consider the time average, but instead an average over an ensemble of systems each at constant energy $E$ within $\delta E$ at a particular instant $t$. The ensemble is arranged according to equation (1) with constant density in phase space in the region of phase space accessible is the volume with energy $E$ within range $\delta E$. Each point in the accessible region represents a system with a particular values of coordinates and momentum components at time $t_0$. In taking the ensemble average of any physical quantity $A$ (**p, q**) over the distribution $\rho(E)$ we assume implicity that *every system of the ensemble is just as good*—that is just as likely—*as any other system of the ensemble.* This concept leads to the assumption of *equal a priori probabilities for different accessible regions of equal volume in phase space.* This statement is taken as a definite and accepted postulate because its consequences agree with experimental results. Without making this or an equivalent postulate it would be very difficult to develop the subject of statistical mechanics.

In the historical development much emphasis was laid on another postulate which states that the phase point for any isolated system passes in succession through every point compatible with the energy of the system before returning to its original position in the phase space. In other words this means that *any particular system in the motion moves through all possible energy eigen states of the system and spends on an average equal time in each.* This statement is known as the **ergodic hypothesis.** There are, however convincing reasons for preferring the hypothesis of equal a priori probabilities.

In a micro-canonical ensemble where all states in a given energy range are equally probable if a parameter $x$ takes the value $x_i$ in the state $i$, then the average value of $x$ is given by

$$\bar{x} = \frac{\sum_i x_i}{\rho(E)} \qquad \ldots(5)$$

with the restriction that summation is to performed only over those states for which the energy is $E$ within the range $\delta E$ *i.e.* $E < E < E + \delta E$ and $\rho(E)$ is the number of states in this particular range of energy.

Due to the constraint condition the operation of summation and calculation of $\rho(E)$ becomes difficult; because we have to sum for only those states for which the condition of constraint holds and this requires the calculation of microscopic states that have a specific energy which is not easy. Moreover due to the condition of complete isolation of the system, thermodynamics can not be applied to this ensemble; because in thermodynamics we deal with systems which are kept in contact with a heat reservoir at a given temperature and we do not know the exact value of energy $E$ but we know the temperature $T$ *i.e.,* the average energy is known.

Micro-canonical ensemble can be made of practical use if we can apply thermodynamics to it. This is only possible if the *average energy* $\bar{E}$ of the system is specified, with $E$ chosen to be equal to the given energy $E_1$. This case will be dealt later in canonical ensemble as an approximation to micro-canonical ensemble. In that case the probability of the system being in any one of its $\rho(E_1)$ states of energy between $E_1$ and $E_1 + \delta E_1$ will be given by

$$\omega(E_1) \propto \rho(E_1)\, e^{-\beta E_1}$$

$$\bar{x}=\frac{\sum_i x_i e^{-\beta E_1}}{\sum_i e^{-\beta E_i}} \qquad ...(6)$$

**Analytical nature of the microcanonical ensemble :** Let us consider a microcanonical ensemble representing a system of two independent particles each of mass $m$ and moving in one direction along a line segment of length $l$. Let $E$ be the energy of the system. The phase space corresponding to this system has four coordinates $q_1, q_2, p_1, p_2$. The $q$ coordinates are accessible within the square of sides $l$ as shown in fig. 7.1 (a). The $p$-coordinates must satisfy the relation

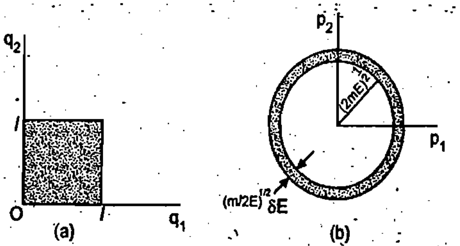
$$\frac{p_1^2}{2m}+\frac{p_2^2}{2m}=E. \qquad ...(7)$$

Thus the accessible region of $p$ space is a thin circular ring of radius $(2mE)^{1/2}$ as shown in fig. 7.1 (b).

If the energy is defined as $E$ within the range $\delta E$, then the width of the ring in momentum space is

$$(2m)^{1/2}(E+\delta E)^{1/2}-(2mE)^{1/2}\approx\left(\frac{m}{2E}\right)^{1/2}\delta E.$$

In this microcanonical ensemble the density $\rho$ is constant within the width of the ring and the $\Gamma$-space is the four dimensional space formed by combining the subspaces (a) and (b) of Fig. 7.1.



**(Fig. 7.1) Accessible regions of phase space for two independent free particles on a line segment of length $l$. The total energy of the system is $F$.**

## 7.2 Entropy in Statistical Mechanics

We have seen that thermodynamic entropy $S$ has the following important properties :

(i) $dS$ is an exact differential and is equal to $\frac{\Delta Q}{T}$ for a reversible process, where $\Delta$ is the quantity of heat given to the system.

(ii) The entropy is an additive quantity *i.e.* the entropy of a combined system is equal to the sum of the entropies of individual systems.

Mathematically, $S = S_1 + S_2$

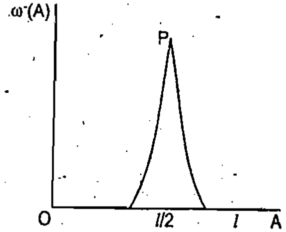
(iii) If the state of a closed system is given macroscopically at any instant, the most probable state at any other instant is one of equal or greater entropy *i.e.* $\Delta S \geq 0$.

These thermodynamic properties of entropy do not themselves give us real physical connection between the physical condition of the system and the value of entropy appropriate to the condition. The thermodynamics does not give the tools by which we may be able to understand the meaning of entropy in terms of the condition of the system. It only tells that entropy is a *state function* which depends explicity only on the actual state of the system; but not on the past history of the system. It is the statistical mechanics that gives up a physical picture of entropy.

Now consider a microcanonical ensemble and suppose that the observations are made of some physical quantity $A$ relating to the systems represented by the ensemble. If the system is composed of $N$ independent molecules, we might observe the physical quantity $A$ say, $x$ component of the centre of mass of the particles in the system. So that

$$A = x = \frac{\sum_{i=1}^{N} x}{N} \qquad ...(8)$$

where $x$ is the system average, not an ensemble average. If $N$ molecules are confined in a cube of side $l$, the distribution of observations follow the curve as shown in fig. 7.2. In the curve $\omega(A)\,dA$ is the probability that a given observation of $A$ will give a result at $A$ within the range $dA$. The probability curve for $A$ has a very sharp maximum at the mean value $\bar{A}$ where $\bar{A}$ is an ensemble average. The system under consideration spends the overwhelming proportion of its time in the region of phase space for which $A \approx \bar{A}$. This an important feature of statistical mechanics and central to the subject.



**(Fig. 7.2)**

The entropy $\sigma$ of a system in classical statistical mechanics in statistical equilibrium is defined as

$$\sigma = \log \Delta\Gamma. \qquad ...(9)$$

where $\Delta\Gamma$ is the volume of the phase space accessible to the system *i.e.* it is volume corresponding to energies between $E$ and $E+\delta E$.

In order to establish the connection between the statistical entropy $\sigma$ and the thermodynamic entropy $S$ let us now make a few preliminary observations about $\sigma$.

*The changes in entropy are independent of the system of units used to measure* $\Delta\Gamma$. As $\Delta\Gamma$ is the volume in the phase space of $N$ point particles, its dimensions are

$$:(\text{momentum} \times \text{length})^{3N} = (\text{Action})^{3N}.$$

If $h$ is the unit of action, then $\frac{\Delta\Gamma}{(h)^{3N}}$ is dimensionless.

If $\sigma$ were defined as

$$\sigma = \log\frac{\Delta\Gamma}{h^{3N}} = \log\Delta\Gamma - 3N\log h.$$

Then the change in entropy

$$\delta\sigma = \delta\log\Delta\Gamma, \qquad ...(10)$$

is independent of the system of units. It is to be noted that $h$ = Planck's constant is a natural unit of action in phase space.

Obviously the entropy $\sigma$ defined by equation (9) has a definite value for an ensemble in statistical equilibrium, hence *the change in entropy* $(d\sigma)$ *is an exact differential.* Thus if the ensemble is specified in terms of the spread in phase space, the entropy is known. If $\Delta\Gamma$ is interpreted as a measure of the randomness or imprecision of a system, then the entropy is also interpreted as the randomness or imprecision.

It may readily be established that *entropy* $\sigma$ *is additive quantity.* Let there be a system composed of two parts, one having $N_1$ particles and the other having $N_2$ particles, so that $N = N_1 + N_2$.

The phase space of the combined system is equal to the product space of the phase space of individual parts *i.e.*

$$\Delta\Gamma = \Delta\Gamma_1 \, . \, \Delta\Gamma_2 \qquad \text{...(11)}$$

We have

$$\sigma = \log \Delta\Gamma = \log \Delta\Gamma_1 \, \Delta\Gamma_2 = \log \Delta\Gamma_1 + \log \Delta\Gamma_2$$

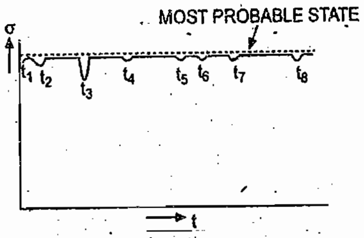
$$= \sigma_1 + \sigma_2.$$

Obviously the entropy $\sigma$ is additive quantity.

To discuss the law of increase of entropy we make the fundamental assumption that *the equilibrium state of a system is the most probable state.* According to this assumption the average values of physical quantities in equilibrium may be replaced by their values in the most probable state of the system. The assumption is satisfied adequately for all actual physical situations.

If the equlibrium state is the most probable state, then according to def. (9) the volume of phase space $\Delta\Gamma$ in equilibrium state will be maximum. Thus we see that *the entropy of a closed system is maximum when the system is in equilibrium state.*

Now the question is how to understand the general tendency for the entropy of a closed system to increase. If we have a system in a state of low entropy, then according to thermodynamics the system will evolve in such a way that the entropy increases towards the maximum value characterising the equilibrium condition. Let us consider the variation of entropy with time for a closed system as shown in fig. 7.3.



**(Fig. 7.3) Time variation of the entropy of a closed system**

The concept of statistical entropy may be extended to non-equilibrium system by considering a physical quantity $A$ as follows; We can find the volume of phase space $\Delta\Gamma(A)$ for which $A$ has a value in some arbitrary desired range. Obviously $\Delta\Gamma$ will be maximum at $\Delta\Gamma(\bar{A})$, but it can be computed for other values of $A$. Then the entropy of a system in non-equilibrium state can be defined as

$$\sigma = \log \Delta\Gamma(A). \qquad \text{...(12)}$$

This definition is an extension of definition (9) for statistical equilibrium.

For $A = \bar{A}$, the value of entropy given by def. (12) agrees with def. (9). The tendency of the entropy to increase does not mean that we shall never get a lower value of entropy but a large number of observations *on the average* will not give a lower value of entropy. Thus if in fig. 7.3 we observe the value of entropy at an arbitary time $t_2$ then it is possible that an observation at a later time $t_3$ may show a lower entropy; but the average of many observations $t_4, t_5, t_6, \ldots$ will not exceed $\sigma(t_2)$ and will be higher than $\sigma(t_3)$. Thus we see that the tendency of the entropy to increase must be interpreted in a statistical sense : if we observe a system with non-equilibrium properties, the probability is that an observation at a later time will show an increase in entropy. In terms of ensemble this means that if we consider a system in the region of phase space associated with unusual macroscopic properties, the probability is that any other system chosen at random from the ensemble will have the properties closer to the average for the ensemble as a whole.

In quantum mechanics statistical entropy $\sigma$ is defined as

$$\sigma = \log \hat{N}, \qquad \text{...(13)}$$

where $\hat{N}$ is the number of quantum states accessible to the system.

## SOLVED EXAMPLE

**Ex. 1.** *Keeping the energy constant, the volume of a perfect gas of N atoms is doubled. Calculate the change in entropy.*

**Solution.** We have

$$\frac{\Delta\Gamma_2}{\Delta\Gamma_1} = \frac{V_2^N}{V_1^N} = 2^N,$$

so

$$\Delta\sigma = \log V_2^N - \log V_1^N = \log\left(\frac{V_2}{V_1}\right)^N = N \log 2.$$

## 7.3 Condition for Equilibrium

We have seen that condition of statistical equilibrium is given by the most probable condition for a closed system. Therefore, we may state that *the entropy $\sigma$ has the maximum value when a closed system is in equilibrium state.*

In general the entropy $\sigma$ of a system in equilibrium will depend upon.

(i) The energy $U\,(= \bar{E})$ of the system,

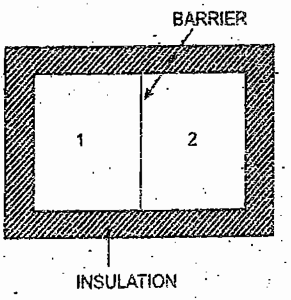
(ii) the number $n_i$ of each molecular species $i$ in the system, and

(iii) the external variables $x_j$ like volume, strain, magnetization etc.

*i.e.,*

$$\sigma = \sigma(U, n_i, x_j), \qquad \text{...(1)}$$

Now we shall find the condition for equilibrium in a system of two inter-connected sub-systems as shown in Fig. 7.4. Consider that initially the sub-systems are separated from each other by a rigid, insulating and non-permeable barrier.



**(Fig. 7.4) Two sub-systems 1 and 2 separated by a barrier**

**1. Thermal equilibrium :** Let us suppose that the barrier allows the transmission of energy. If the condition of two sub-systems 1 and 2 does not change, then they are said to be in *thermal equilibrium.* In thermal equilibrium the entropy $\sigma$ of the total system must have a maximum value with respect to small transfer of energy from one sub-system to the other.

If $\sigma_1$ and $\sigma_2$ are the entropies of the sub-systems 1 and 2, then according to the additive property of the entropy

$$\sigma = \sigma_1 + \sigma_2 \qquad \text{...(2)}$$

We also have

$$\sigma = \sigma(U_1, U_2) \qquad \text{...(3)}$$

and

$$U = U_1 + U_2 \, . \qquad \text{...(4)}$$

For transfer of energy from one system to the other, we have

$$\delta\sigma = \delta\sigma_1 + \delta\sigma_2$$

$$= \left(\frac{\partial\sigma_1}{\partial U_1}\right)\delta U_1 + \left(\frac{\partial\sigma_2}{\partial U_2}\right)\delta U_2 \qquad \text{...(5)}$$

and

$$\delta U = \delta U_1 + \delta U_2 \, . \qquad \text{...(6)}$$

For thermal equilibrium, we have

$$\delta U = \delta U_1 + \delta U_2 = 0 \quad \text{or} \quad \delta U_2 = -\delta U_1 \, , \qquad \text{...(7)}$$

and $$\delta\sigma = \left(\frac{\partial \sigma_1}{\partial U_1}\right)\delta U_1 + \left(\frac{\partial \sigma_2}{\partial U_2}\right)\delta U_2 = 0. \qquad \text{...(8)}$$

Using equations (7), (8) becomes

$$\delta\sigma = \left[\frac{\partial \sigma_1}{\partial U_1} - \frac{\partial \sigma_2}{\partial U_2}\right]\delta U_1 = 0.$$

Since $\partial U_1$ is arbitrary variation, *i.e.* $\partial U_1 \neq 0$, therefore,

$$\frac{\partial \sigma_1}{\partial U_1} = \frac{\partial \sigma_2}{\partial U_2}. \qquad \text{...(9)}$$

Let us now define quantity $\tau$ by

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right), \qquad \text{...(10)}$$

where $\tau$ is called the *statistical temperature.*

Using equation (10), equation (9) gives for thermal equilibrium. ...(11)

*Hence the condition for thermal equilibrium is that the temperature of the two sub-systems should be equal.*

The statistical temperature $\tau$ will be shown later related to the absolute temperature $T$ by the relation

$$\tau = kT, \qquad \text{...(12)}$$

where $k$ is Boltzmann's constant, its value being $1{\cdot}38 \times 10^{-23}$ joule/K.

**2. Mechanical equilibrium :** Let us now suppose that the barrier separating the sub-systems is such that it moves itself and allows to pass energy; but not the particles. The volumes $V_1$ and $V_2$ af the two sub-systems readjust in such a way that the entropy is maximum. In this case

$$\sigma = \sigma(V_1, V_2, U_1, U_2) = \sigma_1(V_1, U_1) + \sigma_2(V_2, U_2). \qquad \text{...(13)}$$

In mechanical equilibrium $\delta\sigma = 0$

*i.e.* $$\delta\sigma = \left(\frac{\partial \sigma_1}{\partial V_1}\right)\delta V_1 + \left(\frac{\partial \sigma_1}{\partial U_1}\right)\delta U_1 + \left(\frac{\partial \sigma_2}{\partial V_2}\right)\delta V_2 + \left(\frac{\partial \sigma_2}{\partial U_2}\right)\delta U_2 = 0. \qquad \text{...(14)}$$

When the thermal equilibrium has been established, we have from equation (8)

$$\left(\frac{\partial \sigma_1}{\partial U_1}\right)\delta U_1 + \left(\frac{\partial \sigma_2}{\partial U_2}\right)\delta U_2 = 0$$

So in mechanical equilibrium, equation (14) yields

$$\left(\frac{\partial \sigma_1}{\partial V_1}\right)\delta V_1 + \left(\frac{\partial \sigma_2}{\partial V_2}\right)\delta V_2 = 0. \qquad \text{...(15)}$$

Since the total volume $V = V_1 + V_2$ is constant, so that we have

$$\delta V = \delta V_1 + \delta V_2 = 0 \;\; i.e. \;\; \delta V_2 = -\delta V_1. \qquad \text{...(16)}$$

Substituting this value in equation (15), we get

$$\left[\left(\frac{\partial \sigma_1}{\partial V_1}\right) - \left(\frac{\partial \sigma_2}{\partial V_2}\right)\right]\delta V_1 = 0. \qquad \text{...(17)}$$

As $\delta V_1$ is an arbitrary variation *i.e.*, $\delta V_1 \neq 0$, we must have for mechanical equilibrium

$$\frac{\partial \sigma_1}{\partial V_1} = \frac{\partial \sigma_2}{\partial V_2}. \qquad \text{...(18)}$$

Let us now define a quantity $\Pi$ by

$$\frac{\Pi}{\tau} = \left(\frac{\partial \sigma}{\partial V}\right)_{U,N} \qquad \text{...(19)}$$

Thus from equation (18) we see that *for a system in thermal equilibrium, the condition for mechanical equilibrium is*

$$\Pi_1 = \Pi_2, \qquad \text{...(20)}$$

we shall now see that $\Pi$ has the essential characteristics of the usual pressure $p$.

Consider two sub-systems in thermal equilibrium are not initially in mechanical equilibrium, but that $\Pi_1 > \Pi_2$. Then the system will evolve so that $\delta\sigma > 0$.

*i.e.*, from equation (17), we have

$$\delta\sigma = \frac{1}{\tau}[\Pi_1 - \Pi_1]\,\delta V_1 > 0. \qquad \text{...(21)}$$

According to this equation under given condition $\delta V_1$ is the positive *i.e.*, the sub-system expands in volume as it does ordinarily at higher pressure. Thus $\Pi$ has the characteristics of the pressure.

It is easy to show that $\Pi$ for a perfect gas is actually the ordinary pressure. The energy of a perfect gas is independent of the volume, so that the entropy expression the term involving the volume may be written as

$$\log V^N = N \log V \;\; \text{for } N \text{ atoms.}$$

Thus, we have

$$\left(\frac{\partial \sigma}{\partial T}\right)_{U,N} = \frac{N}{V} = \frac{\Pi}{\tau}. \qquad \text{...(22)}$$

*i.e.* $$\Pi V = N\tau. \qquad \text{...(23)}$$

But for a perfect gas, the equation is

$$pV = NkT. \qquad \text{...(24)}$$

Comparing equations (23) and (24), we get

$$\Pi = p, \qquad \text{...(25)}$$

and $$\tau = kT. \qquad \text{...(26)}$$

Equation (25) is the desired relation and equation (26) is the same as equation (12).

**3. Particle equilibrium :** Let us now suppose that the barrier allows through it the diffusion of the molecules of the *i*th chemical species.

In this case, we have

$$\sigma = \sigma(n_{i1}, n_{i2}, V_1, V_2 ; U_1, U_2) = \sigma_1(n_{i1}, V_1, U_1) + \sigma_2(n_{i2}, V_2, U_2).$$

We have in equilibrium $\delta\sigma = 0$,

*i.e.,* $$\delta\sigma = \left(\frac{\partial \sigma_1}{\partial n_{i1}}\right)\delta n_{i1} + \left(\frac{\partial \sigma_1}{\partial V_1}\right)\delta V_1 + \left(\frac{\partial \sigma_1}{\partial U_1}\right)\delta U_1 + \left(\frac{\partial \sigma_2}{\partial n_{i2}}\right)\delta n_{i2} + \left(\frac{\partial \sigma_2}{\partial V_2}\right)\delta V_2 + \left(\frac{\partial \sigma_2}{\partial U_2}\right)\delta U_2 = 0. \qquad \text{...(27)}$$

After the system has attained the *thermal* and *mechanical equilibrium*, we have from equations (28) and (15)

$$\left(\frac{\partial \sigma_1}{\partial U_1}\right)\delta U_1 + \left(\frac{\partial \sigma_2}{\partial U_2}\right)\delta U_2 = 0.$$

and
$$\left(\frac{\partial\sigma_1}{\partial V_1}\right)\delta V_1+\left(\frac{\partial\sigma_2}{\partial V_2}\right)\delta V_2=0.$$

Using above conditions equation (27) yields for *particle equilibrium*.

$$\left(\frac{\partial\sigma_1}{\partial n_{i1}}\right)\delta n_{i1}+\left(\frac{\partial\sigma_2}{\partial n_{i2}}\right)\delta n_{i2}=0, \qquad \text{...(28)}$$

Since total number of *i*th chemical species is constant, we must have

$$\delta n_{i1}+\delta n_{i2}=0 \text{ i.e., } \delta n_{i2}=-\delta n_{i1}.$$

Using this, equation (28) becomes

$$\left[\left(\frac{\partial\sigma_1}{\partial n_{i1}}\right)-\left(\frac{\partial\sigma_2}{\partial n_{i2}}\right)\right]\delta n_{i1}=0. \qquad \text{...(29)}$$

As $\delta n_{i1}$ is an arbitrary variation, *i.e.*, $\delta n_{i1}\neq 0$, we must have

$$\frac{\partial\sigma_1}{\partial n_{i1}}=\frac{\partial\sigma_2}{\partial n_{i2}}. \qquad \text{...(30)}$$

Let us now define a quantity $\mu_i$ by the relation

$$-\frac{\mu_i}{\tau}=\left(\frac{\partial\sigma}{\partial n_i}\right)_{U,V}. \qquad \text{...(31)}$$

where $\mu_i$ is called the *chemical potential* of the *i*th species.

From equation (30) we see that *for a system in thermal and mechanical equilibrium, the condition for particle equilibrium is*

$$\mu_1=\mu_2 \qquad \text{...(32)}$$

## 7.4 Connection between Statistical and Thermodynamic Quantities

The statistical and the corresponding thermodynamic quantities are closely related to one another. For a system in equilibrium, we have

$$\sigma=\sigma(U, n_i, x_j), \qquad \text{...(1)}$$

where $U$ is the energy, $n_i$ are the numbers of molecules of the several chemical species present and $x_j$ is the set of external parameters describing the system.

If the conditions of the system are changed slightly, but reversibly in such a way that the resulting system is in equilibrium, we have

$$d\sigma=\left(\frac{\partial\sigma}{\partial U}\right)dU+\sum_i\left(\frac{\partial\sigma}{\partial n_i}\right)dn_i+\sum_j\frac{\partial\sigma}{\partial x_j}dx_j. \qquad \text{...(2)}$$

We have from § 7.3.

$$\frac{\partial\sigma}{\partial U}=\frac{1}{\tau} \text{ and } \frac{\partial\sigma}{\partial n_i}=-\frac{\mu_i}{\tau}$$

Therefore, equation (2) may be written as

$$d\sigma=\frac{dU}{\tau}-\sum_i\frac{\mu}{\tau}dn_i+\frac{1}{\tau}\sum_i X_j\,dx_j. \qquad \text{...(3)}$$

where $X_j$ is the *generalised force* related to the co-ordinates $x_j$, defined as

$$\frac{X_j}{\tau}=\frac{\partial\sigma}{\partial x_j}. \qquad \text{...(4)}$$

Eqn. (3) gives

$$dU=\tau d\sigma+\sum_i\mu_i\,dn_i-\sum_j X_j\,dx_j. \qquad \text{...(5)}$$

Now let us first consider a simple example where system consists of fixed number of particles and the volume only as the external parameter; *i.e.*

$$dn_i=0,\ x_j=V,\ X_j=\Pi$$

Substituting these values in eqn. (5), we get

$$dU=\tau\,d\sigma-\Pi\,dV. \qquad \text{...(6)}$$

It is clear from above equation that the change in internal energy $dU$ consists of two parts :

(i) The first part $\tau\,d\sigma$ represents the change in internal energy when the external parameters are held constant. This is just the quantity of heat added to the system in a reversible process, *i.e.*

$$\Delta Q=\tau\,d\sigma \text{ i.e. } d\sigma=\frac{\Delta Q}{\tau} \qquad \text{...(7)}$$

The symbol $\Delta$ is used in place of $d$, because $\Delta Q$ is not a perfect differential, *i.e.*, $Q$ is not a *state function*.

(ii) The second part $(-\Pi\,dV)$ represents the change in internal energy caused by the change in external parameters. This is simply the mechanical work done on the system, *i.e.*

$$\Delta W=-\Pi\,dV \qquad \text{...(8)}$$

By elementary mechanics the work done on the system must be given by

$$\Delta W=-p\,dV. \qquad \text{...(9)}$$

Comparing (8) and (9).

$$\Pi=p. \qquad \text{...(10)}$$

Thus we see that eqn. (6) is equivalent to the equation

$$dU=\Delta Q+\delta W. \qquad \text{...(11)}$$

which is the mathematical form of the *first law of the thermodynamics*.

From second law of thermodynamics, we have

$$dS=\frac{\Delta Q}{T} \qquad \text{...(12)}$$

Comparing eqns. (7) and (12), we have

$$T\,dS=\tau\,d\sigma. \qquad \text{...(13)}$$

As $dS$ and $d\sigma$ are perfect differentials as $S$ and $\sigma$ are state functions) we note from eqns. (7) and (12) that both $1/T$ and $1/\tau$ are integrating factors for $\Delta Q$ and we know that all integrating factors for $\Delta Q$ differ only by a constant of proportionality. Thus $T$ and $\tau$ are proportional to each other.

But
$$\tau=kT. \qquad \text{...(14)}$$

where $k$ is Boltzmann's constant. This relation may be taken as an experimental face. It may be established for any problem in which $\frac{\partial\sigma}{\partial U}$ may be calculated. We have already established it for a perfect gas in § 7.3 (refer eqn. 26).

Keeping relation (14) in mind, it is evident from eqn. (13) that $dS$ and $d\sigma$ are proportional to each other and further $S$ and $\sigma$ are related by the equation,

$$S=k\sigma. \qquad \text{...(15)}$$

This is an important relation between thermodynamic entropy $S$ and statistical entropy $\sigma$.

As
$$U=U(\sigma, V)\text{ ; therefore}$$

$$dU=\left(\frac{\partial U}{\partial\sigma}\right)_V d\sigma+\left(\frac{\partial U}{\partial V}\right)_\sigma dV. \qquad \text{...(16)}$$

Comparing eqn. (6), (10) and (16), we get

$$\tau = \left(\frac{\partial U}{\partial \sigma}\right)_V \qquad \text{...(17)}$$

$$-p = \left(\frac{\partial U}{\partial V}\right)_\sigma \qquad \text{...(18)}$$

Now σ, V are often quite inconvenient independent variables. For example it is often more convenient to work with τ, p or τ, V. For this we introduce auxiliary functions : Helmholtz free energy $F$, the enthalpy $H$ and Gibbs free energy $G$, known as the *thermodynamic potentials*.

**(i) Helmholtz Free Energy F :** Helmholtz free energy $F(V, \tau)$ is defined as

$$F = U - TS = U - \tau\sigma \qquad \text{...(19)}$$

On differentiation, we get

$$\begin{aligned} dF &= dU - \tau\, d\sigma - \sigma\, d\tau \\ &= -\Pi\, dV - \sigma\, d\tau \text{ using (6).} \\ &= -p dV - \sigma\, d\tau. \end{aligned} \qquad \text{...(20) using (10)}$$

Again as $F = F(V, \tau)$.

We have $$dF = \left(\frac{\partial F}{\partial V}\right)_\tau dV + \left(\frac{\partial F}{\partial \tau}\right)_V d\tau. \qquad \text{...(21)}$$

Comparing equation (20) and (21), we get

$$\left.\begin{aligned} p &= \left(\frac{\partial F}{\partial V}\right)_\tau \\ -\sigma &= \left(\frac{\partial F}{\partial \tau}\right)_V \end{aligned}\right\} \qquad \text{...(22)}$$

Therefore, if $V, \tau$ are independent variables, the Helmholtz free energy $F$ is introduced to evaluate readily $p$ and σ.

**(ii) Enthalpy H :** The enthalpy $H(\sigma, p)$ is defined as...

$$H = U + pV. \qquad \text{....(23)}$$

On differentiation, we get,

$$dH = dU + p\, dV + V\, dp = dU + \Pi\, dV + V\, dp \text{ since } p = \Pi \quad \text{[Using equation (6)]} \qquad \text{...(24)}$$

Again as $H = H(\sigma, p)$, therefore

$$dH = \left(\frac{\partial U}{\partial \sigma}\right)_p d\sigma + \left(\frac{\partial H}{\partial p}\right)_\sigma dp. \qquad \text{...(25)}$$

Comparing equations (24) and (25), we get

$$\left.\begin{aligned} \tau &= \left(\frac{\partial H}{\partial \sigma}\right)_p \\ V &= \left(\frac{\partial H}{\partial p}\right)_\sigma \end{aligned}\right\} \qquad \text{...(26)}$$

Therefore, if σ, p are independent variables, the enthalpy $H$ is introduced to evaluate readily τ and V.

**(iii) Gibb's free energy G :** The Gibb's free energy $G(\tau, p)$ is defined as,

$$G = U - TS + pV = U - \tau\sigma + pV \qquad \text{...(27)}$$

On differentiation, we have

$$\begin{aligned} dG &= dU - \tau\, d\sigma - \sigma\, d\tau + p\, dV + V\, dp \\ &= -\sigma\, d\tau + V\, dp. \end{aligned} \qquad \text{...(28)}$$

[using eqn. (6) with $p = \Pi$]

Since $G = G(\tau, p)$, we have

$$dG = \left(\frac{\partial G}{\partial \tau}\right)_p d\tau + \left(\frac{\partial G}{\partial p}\right)_\tau dp. \qquad \text{...(29)}$$

Comparing eqns. (28) and (29), we get

$$\left.\begin{aligned} -\sigma &= \left(\frac{\partial G}{\partial \tau}\right)_p \\ V &= \left(\frac{\partial G}{\partial p}\right)_\tau \end{aligned}\right\} \qquad \text{...(30)}$$

Therefore, if τ, p are independent variables, the Gibb's free energy $G$ is introduced to evaluate readily σ and U.

## SOLVED EXAMPLE

**Ex. 2.** *Show that the work done on the body in a reversible process at constant temperature is the change of its Helmholtz free energy.*

**Solution.** In a reversible process work done on the body

$$\begin{aligned} \Delta W &= dU - \Delta Q \\ &= dU - \tau\, d\sigma \qquad \text{(since } \Delta Q = T\, dS = \tau\, d\sigma) \\ &= d(U - \tau\sigma)_\tau \\ &= d(U - TS)_\tau = dF_\tau, \end{aligned}$$

Thus the work done on the body in a reversible process at constant temperature is the change in its Helmholtz free energy.

**Note :** $-dF$ is the maximum work which can be done by a system in a change at constant temperature.

### 7.5 Perfect gas in Microcanonical Ensemble

Let us consider a microcanonical ensemble of a perfect gas. Let there be $n$ point particles of a perfect gas each of mass $m$ confined in a volume $V$ with total energy $U$ within the energy range $\delta U$. The corresponding volume in the phase space is

$$\Delta\Gamma = \int dq_1 \ldots\ldots dq_{3n} \int dp_1 \ldots\ldots dp_{3n} \qquad \text{...(1)}$$

where $q$'s and $p$'s refer respectively to the position and momentum coordinates.

As the particles of a perfect gas are non-interacting, the energy of a perfect gas is independent of the position of the particles, so we have

$$\int dq_1 \ldots\ldots dq_{3n} = V^n. \quad \text{(since } V \text{ is volume of a single particle)}$$

Therefore $$\Delta\Gamma = V^n \int dp_1 \ldots\ldots dp_{3n}. \qquad \text{...(2)}$$

The momentum space integral is to be evaluated subject to the constraint of the ensemble.

$$U - \delta U \le U_r \le U.$$

$$U_r = \sum_{i=1}^{n} \frac{p_i^2}{2m}.$$

So the constraing condition may be written as

$$U - \delta U \leq \frac{1}{2m} \sum_{i=1}^{n} p_i^2 \leq U. \qquad \text{...(3)}$$

The integral in eqn. (2) is the volume contained betwen $3n$ dimensional hyper-sphere of radius $(2mU)^{1/2}$ and $3n$ dimensional hyper-sphere of radius $[2m\,(U - \delta U)]^{1/2}$. That is the accessible volume in momentum space is the volume of a spherical hyper-shell of radius $(2mU)^{1/2}$ and thickness $\left(\frac{m}{2U}\right)^{1/2} \delta U$.

The volume of three dimensional sphere of radius $R$ is

$$V_3\,(R) = \tfrac{4}{3}\,\pi R^3 = \frac{\pi^{3/2}}{\Gamma\left(\frac{3+2}{2}\right)} R^3 = C_3 R^3$$

In analogy the volume of $f$ dimensional hyper-sphere of radius $R$ is

$$V_f(R) = \frac{\pi^{f/2}}{\Gamma\left(\frac{f}{2}+1\right)} R^f = \frac{\pi^{f/2}}{(f/2)\,!} R^f$$

$$= C_f R^f \qquad \text{...(4a)}$$

where

$$C_f = \frac{\pi^{f/2}}{(f/2)\,!} \qquad \text{...(4b)}$$

Therefore for $3n$ dimensional hyper-sphere of radius $(2mU)^{1/2}$, the volume is

$$V_{3n}\,(R) = \frac{\pi^{3n/2}}{(3n/2)\,!} (2mU)^{3n/2}. \qquad \text{...(5)}$$

Therefore the volume occupied between hyper-spheres of radii $(2mU)^{1/2}$ and $[2m\,(U - \delta U)]^{1/2}$ is

$$\int dp_1 \ldots\ldots dp_{3n} = \frac{\pi^{3n/2}}{(3n/2)\,!} [(2mU)^{3n/2} - \{2m\,(U - \delta U)\}^{3n/2}]$$

$$= \frac{\pi^{3n/2}}{(3n/2)\,!} (2mU)^{3n/2} \left[1 - \left(1 - \frac{\delta U}{U}\right)^{3n/2}\right]$$

$$= \frac{\pi^{3n/2}}{(3n/2)\,!} (2mU)^{3n/2} \left[1 - \exp\left(-\frac{3n}{2} \cdot \frac{\delta U}{U}\right)\right]$$

(by the definition of exponential function)

For a macroscopic system $3n \approx 10^{23}$, therefore $\frac{3n}{2}\,\delta U >> U$.

Hence we can drop the exponential term in above expression as compared to 1,

Thus
$$\int dp_1 \ldots\ldots dp_{3n} = \frac{\pi^{3n/2}}{(3n/2)\,!} (2mU)^{3n/2} \qquad \text{...(6)}$$

Substituting this in eqn. (2), the volume in phase space is given by

$$\Delta\Gamma = V^n \frac{\pi^{3n/2}}{(3n/2)\,!} (2mU)^{3n/2}. \qquad \text{...(7)}$$

According to classical statistical mechanics, the entropy $\sigma$ in statistical equilibrium is given by

$$\sigma = \log_e \Delta\Gamma = \log_e \left[ V^n \frac{\pi^{3n/2}}{(3n/2)\,!} (2mU)^{3n/2} \right]$$

$$= n \log_e [V\,\pi^{3/2}\,(2mU)^{3/2}] - \log\left(\frac{3n}{2}\right)!$$

Now using *Stirling approximation* $\log n\,! = n \log n - n$, we get

$$\sigma = n \log_e [V\,\pi^{3/2}\,(2mU)^{3/2}] - \frac{3n}{2} \log \frac{3n}{2} + \frac{3n}{2}$$

$$= n \log_e \left[ \frac{V\pi^{3/2}\,(2mU)^{3/2}}{(3n/2)^{3/2}} \right] + \frac{3n}{2}$$

$$= n \log_e \left[ V \left(\frac{4\pi m}{3}\right)^{3/2} \left(\frac{U}{n}\right)^{3/2} \right] + \frac{3n}{2} \qquad \text{...(8a)}$$

We know that the entropy should not depend upon the unit of hypervolume $\Delta\Gamma$. To make it dimensionless we divide it by $h^{3n}$, where $h$ is Planck's constant. So the entropy $\sigma$ is now given by

$$\sigma = \log_e \frac{\Delta\Gamma}{h^{3n}}$$

$$= n \log_e \left[ \frac{V\,(4\pi m/3)^{3/2}\,(U/n)^{3/2}}{h^3} \right] + \frac{3n}{2}. \qquad \text{...(8b)}$$

If we examine this expression for entropy, it does not satisfy the additive property of entropy $\sigma$, because in this expression the volume $V$ appears in the argument of the logarithms. Therefore it is not possible to divide the system into two parts and to write the total entropy as the sum $\sigma = \sigma_1 + \sigma_2$. The mistake is because for $n$ identical particles we must not count as different conditions of the total system which differ only by the interchange of identical particles in the phase space. This mistake leads to over-estimate the volume of the phase space by a factor $n\,!$ under classical conditions. If we take this factor into account, the entropy satisfying additive property will be given by

$$\sigma = \log \frac{\Delta\Gamma}{h^{3n}\,n\,!} \qquad \text{...(9)}$$

$$= n \log_e \left[ \frac{(V/n)\,(4\pi m/3)^{3/2}\,(U/n)^{3/2}\,e}{h^3} \right] + \frac{3n}{2} \qquad \text{...(10a)}$$

where $e$ is the base of natural logarithm.

Eqn. (10a) may be written as

$$\sigma = n \log_e \left[ \frac{(V/n)\,(4\pi m/3)^{3/2}\,(U/n)^{3n/2}}{h^3} \right] + \frac{5n}{2} \qquad \text{...(10b)}$$

This expression for entropy satisfies the additive property because now the argument of logarithm does not contain the total volume $V$ and total energy $U$; but instead $\frac{V}{n}$ *i.e.* the *volume per particle* and $\frac{U}{n}$ *i.e., energy per particle.*

We shall now establish the connection of statistical quantities with corresponding thermodynamic quantities.

**1. Internal Energy :** By the definition of statistical temperature $\tau$,

$$\frac{1}{\tau}=\left(\frac{\partial\sigma}{\partial U}\right)_{T,n}$$

$$=\frac{\partial}{\partial U}\left[n\log_e\left\{\frac{(V/n)\,(4\pi m/3)^{3/2}\,(U/n)^{3/2}}{h^3}\right\}+\frac{5n}{2}\right]_{V,n}$$

$$=\frac{\partial}{\partial U}\left[n\log V-n\log n+n\log\left(\frac{4\pi m}{3}\right)^{3/2}+\frac{3n}{2}\log U-\frac{3n}{2}\log n-n\log h^3\right]+\frac{\partial}{\partial U}\left(\frac{5n}{2}\right)$$

$$=\frac{\partial}{\partial U}\left(\frac{3n}{2}\log U\right)$$ because $V$ and $h$ are constant, therefore rest terms are zero.

$$=\frac{3n}{2}\cdot\frac{1}{U}$$

so that

$$U=\frac{3}{2}n\tau \qquad \text{...11(a)}$$

$$=\frac{3}{2}nkT, \qquad \text{(because } \tau=kT\text{), ...11(b)}$$

which is the well-known *result for the internal energy of a perfect monoatomic gas.*

**2. Relation between τ and T :** From equation (11) we see that

$$\tau=kT, \qquad \text{...(12)}$$

which is same are equation (26) of section 7.3.

**3. Relation between τ and p :** From equation (19) of section 7.3, we have

$$\frac{p}{\tau}=\left(\frac{\partial\sigma}{\partial V}\right)_{n,U} \quad (\text{since } p=\Pi)$$

$$=\frac{\partial}{\partial V}\left[n\log_e\left\{\frac{(V/n)\,(4\pi m/3)^{3/2}\,(U/n)^{3/2}}{h^3}\right\}+\frac{5n}{2}\right]_{n,U}$$

$$=\frac{\partial}{\partial V}(n\log_e V)$$ since the differentiation of other terms is zero for constants $n$ and $U$

$$=\frac{n}{V}$$

so $$pV=n\tau \qquad \text{...13 (a)}$$

$\Rightarrow$ $$pV=nkT. \qquad \text{...13 (b)}$$

**4. Thermodynamic entropy S of perfect gas :** The relation between thermodynamic entropy $S$ and statistical entropy $\sigma$ is

$$S=k\sigma$$

$$=kn\log_e\left[\frac{(V/n)\,(4\pi m/3)^{3/2}\,(U/n)^{3/2}}{h^3}\right]+k\cdot\frac{5}{2}n.$$

Substituting, $U=\frac{3}{2}nkT$, we get

$$S=nk\log_e\left[\left(\frac{V}{n}\right)\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]+\frac{5}{2}nk. \qquad \text{...(14 (a)}$$

$$=nk\log_e\left[\frac{V}{nh^3}(2\pi mkT)^{3/2}e^{5/2}\right] \qquad \text{...14 (b)}$$

This is is the famous *Sackur-Tetrode formula* for the entropy of a perfect gas. This formula is valid for a monoatomic gas of atoms with zero total angular momentum.

The *thermal de-Broglie wavelength associated with a molecule* may be defined as

$$\lambda=\frac{h}{\text{average thermal momentum of a molecule}}$$

$$=\frac{h}{(2\pi mkT)^{1/2}} \qquad \text{...(15)}$$

because the quantity $(2\pi mkT)^{1/2}$ has the character of an average thermal momentum of a molecule.

Using (15), equation (10) and (14) may be written as

$$\sigma=n\log_e\left[\left(\frac{V}{n}\right)\cdot\frac{1}{\lambda^3}\right]+\frac{5}{2}n, \qquad \text{...(16)}$$

and $$S=nk\log_e\left[\left(\frac{V}{n}\right)\cdot\frac{1}{\lambda^3}\right]+\frac{5}{2}nk. \qquad \text{...(17)}$$

Above equations show that the entropy of a perfect gas is determined essentially by the ratio of the volume per particle to the volume $\lambda^3$ associated with the de-Broglie wavelength.

**5. Chemical potential of a perfect gas :** From equation 31 of section 7.3, the chemical potential of a perfect gas is given by

$$-\frac{\mu}{\tau}=\left(\frac{\partial\sigma}{\partial n}\right)_{U,V}$$

$$=\frac{\partial}{\partial n}\left[n\log_e\left\{\left(\frac{V}{n}\right)\left(\frac{1}{\lambda^3}\right)\right\}+\frac{5}{2}n\right]_{U,V}$$

$$=\frac{\partial}{\partial n}[n\log V-n\log n-n\log\lambda^3]_{U,V}+\frac{\partial}{\partial n}\left(\frac{5}{2}n\right)$$

$$=\log V-1-\log n-\log\lambda^3+\frac{5}{2}$$

$$=\log\left(\frac{V}{n\lambda^3}\right)+\frac{3}{2} \quad \text{or} \quad \frac{\mu}{\tau}=\log\left(\frac{n\lambda^3}{V}\right)-\frac{3}{2}$$

From eqn. (13a) substituting $\frac{p}{\tau}$ for $\frac{n}{V}$, we get

$$\frac{\mu}{\tau}=\log\left(\frac{p\lambda^3}{\tau}\right)-\frac{3}{2}$$

$$\mu=\tau\log p+\tau\log\left(\frac{\lambda^3}{\tau}\right)-\frac{3\tau}{2}$$

or $$\mu=\tau\log p+f(\tau), \qquad \text{...(18)}$$

where $f(\tau)$ is the function of the temperature alone.

## 7.6 Partition Functions

For developing the concept of partition function let us consider an assembly of ideal gas molecules obeying classical statistics. Let the distribution of gas molecules be such that $n_i$ molecules occupy the $i$th state with energy between $\varepsilon_i$ and $\varepsilon_i + d\varepsilon_i$ and degeneracy (*i.e.*, the number of energy levels) $g_i$. Then from Maxwell-Boltzman distribution law,

$$n_i = g_i e^{-\alpha} e^{-\varepsilon_i/kT}. \qquad ...(1)$$

[refer eqn. (7) of section 6.15]

Le us substitute $e^{-\alpha} = A$. Then

$$n_i = g_i A e^{-\varepsilon_i/kT}.$$

If the total number of gas molecules in the assemble in $N$, then

$$N = \sum_i n_i = \sum_i g_i A e^{-\varepsilon_i/kT}$$

$$= A \sum_i g_i e^{-\varepsilon_i/kT}. \qquad ...(2)$$

The term $A\ (= e^{-\alpha})$ has been taken out of the summation sign because $\alpha$ is a constant, the Lagrangian undetermined multiplier,

From equation (2), we get

$$\frac{N}{A} = \sum_i g_i e^{-\varepsilon_i/kT} = Z \text{ (say)} \qquad ...(3)$$

The quantity $Z$ is called the Boltzmann partition function or simply the *partition function.* In equation (3) the expression for $Z$ represents the sum of all the $g_i e^{-\varepsilon_i/kT}$ terms for every energy state of the given molecule. Therefore, *the quantity Z indicates how the gas molecules of an assembly are distributed or partitioned among the various energy levels.*

If the energy of the $i$th level is $\varepsilon_i$, then keeping in mind that the weight of an individual level is unity, eqn. (3) can be written as

$$Z = \sum_i e^{-\varepsilon_i/kT}. \qquad ...(4)$$

In above equation the term $Z$ is the sum over all the levels of a system in the assembly. That is why it is customary to call $Z$ as the partition function for a system in the assembly. The energy term in the expression for partition function does not mean only the translational component, as is the case for structureless molecules, but in general, it may contain the components corresponding to other degrees of freedom too *e.g.* rotational, vibrational and electronic.

The partition function can be used for calculating the various thermodynamical properties of ensembles having independent systems obeying classical statistical laws. It does not matter whether the ensembles have distinguishable or indistinguishable independent systems.

Classically a gas molecule is assumed to be a structureless identity and the total energy of the gas molecule is practically equal to the sum of the kinetic energies of individual molecules. In classical treatments the distribution of energy states is considered continuous. The number of energy levels in the momentum range $p$ and $p + dp$ is given by

$$g(p)\,dp = \frac{V \cdot 4\pi p^2\, dp}{h^3}$$

[refer eqn. (13) of section 6.15]

Therefore, the number of energy levels between energy $\varepsilon$ and $\varepsilon + d\varepsilon$ is now written by substituting $p^2 = 2m\varepsilon$ and $dp = \frac{m\,d\varepsilon}{\sqrt{2m\varepsilon}}$ in above equation, *i.e.*,

$$g(\varepsilon)\,d\varepsilon = \frac{V \cdot 4\pi\, 2m\varepsilon}{h^3} \cdot \frac{m\,d\varepsilon}{\sqrt{(2m\varepsilon)}}$$

or

$$g(\varepsilon)\,d\varepsilon = \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{1/2}\,d\varepsilon \qquad ...(5)$$

Since here the distribution of energy states is continuous, eqn. (3) may be written as

$$Z = \sum_i g_i e^{-\varepsilon_i/kT}$$

$$= \int_0^\infty g(\varepsilon)\,d\varepsilon \cdot e^{-\varepsilon/kT}$$

$$= \int_0^\infty \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{1/2}\,d\varepsilon \cdot e^{-\varepsilon/kT}. \qquad \text{[Using eqn. (5)]}$$

$$= \frac{2\pi \cdot V(2m)^{3/2}}{h^3}\int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/kT}\,d\varepsilon$$

The definite integral can be shown to have the value

$$\int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/kT}\,d\varepsilon = \frac{\sqrt{\pi}}{2}\cdot(kT)^{3/2}.$$

$$Z = \frac{2\pi \cdot V(2m)^{3/2}}{h^3}\cdot\frac{\sqrt{\pi}}{2}(kT)^{3/2}. \qquad ...(6)$$

This equation gives the translational *partition function* for a gas molecule.

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

Partition function of distribution of perfect gas)

## 7.7. Partition Function and Thermodynamical Quantities

Entropy (S)

Now we shall establish relations between the partition functions and the thermodynamical quantities. The entropy of an assembly and the weight of the most probable configuration are related by the equation.

$$S = k \log \Omega_{\max}. \qquad ...(1)$$

the weight of the configuration for a classical system is given by

$$\Omega = N!\prod_i \frac{g_i^{n_i}}{n_i!}$$

[refer eqn. (7) of section 6.10]

Therefore

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

Now using Stirling approximation $\log n! = n \log n - n$, we get

$$\log \Omega = N \log N - N + \sum_i (n_i \log g_i - n_i \log n_i + n_i) \qquad ...(2)$$

According to Maxwell-Boltzmann distribution law, for a most probable configuration

$$n_i = g_i e^{-\alpha} e^{-\beta\varepsilon_i} \qquad ...(3)$$

[refer eqn. (7) of section 6.15]

As the total number of molecules is constant, we have

$$N = \sum_i n_i. \qquad \text{...(6)}$$

Substituting these values in eqn. (2), we get

$$\log \Omega_{\max} = N \log N - N + \Sigma\,[n_i \log g_i - n_i \log (g_i e^{-\alpha} e^{-\beta\varepsilon_i}) + n_i]$$

$$= N \log N - N + \sum_i n_i \log g_i - \sum_i n_i \log g_i + \sum_i n_i\,\alpha + \sum_i n_i\,\beta\varepsilon_i + \sum_i n_i$$

As

$$N = \sum_i n_i$$

$$\therefore \quad \log \Omega_{\max} = N \log N + \alpha N + \beta \sum_i n_i\,\varepsilon_i. \qquad \text{...(5)}$$

If the total energy of the gas molecules of the assembly is $E$, then

$$E = \sum_i n_i\,\varepsilon_i \qquad \text{...(6)}$$

So equation (5) may be written as

$$\log \Omega_{\max} = N \log N + \alpha N + \beta E \qquad \text{...(7)}$$

Let us substitute $A = e^{-\alpha}$, *i.e.*, $\alpha = +\log A$.

So eqn. (7) may be written as

$$\log \Omega_{\max} = N \log N - N \log A + \beta E$$

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

$$= N \log Z + \beta E. \qquad \text{...(8)}$$

(since partition function, $Z = N/A$)

But $\beta = \dfrac{1}{kT}$, so

$$\log \Omega_{\max} = N \log Z + \frac{E}{kT} \qquad \text{...(9)}$$

Therefore, the entropy of the ensemble (or assembly), is given by

$$S = k \log \Omega_{\max}$$

$$= Nk \log Z + \frac{E}{T} \qquad \text{...(10)}$$

For an ideal gas, we have

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

Therefore eqn. (10) yields

$$S = Nk \log Z + \frac{3}{2} Nk. \qquad \text{...(11)}$$

The equation gives the expression for the *entropy of the assembly of ideal gas molecules*. The other thermodynamical functions can now be evaluated easily as follows :

**Helmholtz Free Energy F :** The Helmholtz free energy $F$ is given by

Using eqn. (10), we get $F = E - TS$.

$$F = E - T\,(Nk \log Z + E/T).$$

$$= NkT \log_e Z. \qquad \text{...(12)}$$

This is the required expression for Helmholtz free energy $F$ in terms of partition function.

**Total Energy E :** If $\bar{\varepsilon}$ is the average energy of a system of an assembly of $N$ such independent systems, then

$$\bar{\varepsilon} = \frac{E}{N} = \frac{\sum_i n_i \varepsilon_i}{\sum_i n_i}$$

Using Maxwell-Boltzmann distribution law, we get

$$\bar{\varepsilon} = \frac{\sum_i g_i e^{-\alpha} e^{-\beta\varepsilon_i} \varepsilon_i}{\sum_i e^{-\alpha} e^{-\beta\varepsilon_i}}$$

$$= \frac{\sum_i g_i \varepsilon_i e^{-\beta\varepsilon_i}}{\sum_i g_i e^{-\beta\varepsilon_i}} = \frac{\sum_i g_i \varepsilon_i e^{-\varepsilon_i/kT}}{\sum_i g_i e^{-\varepsilon_i/kT}} \qquad \left(\text{Since } \beta = \frac{1}{kT}\right)$$

$$= \frac{\sum_i g_i \varepsilon_i e^{-\varepsilon_i/kT}}{Z}. \qquad \text{...(13)}$$

Since partition function

$$Z = \sum_i g_i e^{-\beta\varepsilon_i} = \sum_i g_i e^{-\varepsilon_i/kT} \qquad \text{...(14)}$$

We have

$$\left\{\frac{\partial Z}{\partial T}\right\}_V = \sum_i g_i \frac{\varepsilon_i}{kT^2} e^{-\varepsilon_i/kT},$$

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

for isothermal-isochoric transformation $\sum_i g_i \varepsilon_i e^{-\varepsilon_i\,kT} = kT^2 \left(\dfrac{\partial Z}{\partial T}\right)_V$

Therefore for *isothermal isochoric transformation*, we have

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

or

$$\bar{\varepsilon} = kT^2 \left[\frac{\partial\,(\log Z)}{\partial T}\right]_V$$

Therefore

$$E = N\bar{\varepsilon} = NkT^2 \left[\frac{\partial\,(\log)\,Z}{\partial T}\right]_V \qquad \text{...(15)}$$

This is the expression for total energy of an ensemble in terms of partition function.

**Enthalpy H.** The enthalpy $H$ is given by

$$H = E + pV.$$

For 1 mole of an ideal gas, we have $pV = RT.$

Therefore $H = E + RT.$

Using eqn. (15), we get

$$H = NkT^2 \left[\frac{\partial\,(\log Z)}{\partial T}\right]_V + RT. \qquad \text{...(16)}$$

This is expression for enthalpy in terms of partition function

**Gibb's potential G :** The Gibb's potential $G$ is given by

$$G = H - TS.$$

Using eqn. (11) and (16), we get

$$G = NkT^2\left[\frac{\partial(\log Z)}{\partial T}\right]_V + RT - T\left(Nk\log Z + \tfrac{3}{2}Nk\right).$$

$$= NkT^2\left[\frac{\partial(\log Z)}{\partial T}\right]_V + RT - NkT\log Z - \tfrac{3}{2}NkT \qquad \text{...(17)}$$

**Pressure of a gas p :** The pressure of a gas $p$ is given by

$$p = -\left\{\frac{\partial F}{\partial V}\right\}_T \qquad \text{[refer eqn. (6) of section 2.12].}$$

$$= NkT\left[\frac{\partial(\log Z)}{\partial V}\right]_T \qquad \text{...(18) using (12)}$$

**Specific heat at constant volume $C_V$ :** For an isothermal isochoric transformation the internal energy $U$ of the assembly is equal to its total energy $E$. Therefore

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

Using eqn. (15), we get

$$C_V = \frac{\partial}{\partial T}\left\{NkT^2\left(\frac{\partial \log Z}{\partial T}\right)_V\right\},$$

$$= Nk\left[2T\frac{\partial(\log Z)}{\partial T} + T^2\frac{\partial^2(\log Z)}{\partial T^2}\right]_V \qquad \text{...(19)}$$

## Solved Examples

**Ex. 3.** *Show that if the partition function is given by Z, the mean energy $\bar{\varepsilon}$ is given by*

$$\bar{\varepsilon} = -\frac{\partial \log Z}{\partial \beta} \quad \textit{where } \beta = \frac{1}{kT}.$$

*(Rohilkhand 2005, 1993; Agra 1992; Kanpur 2006)*

**Solution.** If $\bar{\varepsilon}$ is the mean energy of a system of an ensemble consisting $N$ such independent systems, then

$$\bar{\varepsilon} = \frac{E}{N}, \text{ where } E \text{ is the total energy of the ensemble.}$$

$$= \frac{\sum_i \varepsilon_i n_i}{\sum n_i}.$$

According to Maxwell-Boltzmann distribution law, we have

$$n_i = g_i e^{-\alpha} \varepsilon^{-\beta\varepsilon_i} \quad \text{where } \beta = \frac{1}{kT}.$$

Therefore

$$\bar{\varepsilon} = \frac{\sum_i \varepsilon_i g_i e^{-\alpha} e^{-\beta\varepsilon_i}}{\sum_i g_i e^{-\alpha} e^{-\beta\varepsilon_i}}.$$

Since $\alpha$ is a constant, being Lagrangian undetermined multiplier, we have

$$\bar{\varepsilon} = \frac{\sum_i g_i \varepsilon_i e^{-\beta\varepsilon_i}}{\sum_i g_i e_i^{-\beta\varepsilon_i}}$$

$$= \frac{\sum_i g_i \varepsilon_i e^{-\beta\varepsilon_i}}{Z} \qquad \text{...(1)}$$

$(Z = \sum_i g_i e_i^{-\beta\varepsilon_i})$ = partition function)

Since partition function

$$Z = \Sigma g_i e^{-\beta\varepsilon_i} \qquad \text{...(2)}$$

From eqn. (2), we have

$$\frac{\partial Z}{\partial \beta} = -\sum_i g_i \varepsilon_i e_i^{-\beta\varepsilon_i} \qquad \text{...(3)}$$

Using eqn. (3), eqn. (1) may be written as

$$\bar{\varepsilon} = -\frac{(\partial Z/\partial\beta)}{Z},$$

or

$$\text{mean energy } \bar{\varepsilon} = -\frac{\partial(\log Z)}{\partial \beta}. \qquad \text{...(4)}$$

where

$$\beta = \frac{1}{kT}.$$

This is the required expression.

### 7.8 Entropy of a Perfect gas : Gibb's Paradox

The partition function of a perfect gas is

$$Z = \frac{V}{h^3}(2\pi m kT)^{3/2}. \qquad \text{...(1)}$$

[Refer eqn. (6) of section (7.6)]

The entropy of a perfect gas is

$$S = Nk\log Z + \tfrac{3}{2}Nk. \qquad \text{...(2)}$$

[Refer eqn. (11) of section 7.6]

Substituting value of $Z$ from eqn. (1), the expression for the entropy of a perfect gas becomes

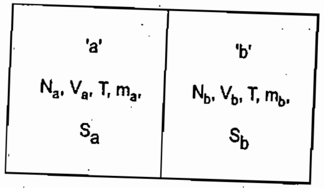
$$S = Nk\log\left[\frac{V}{h^3}(2\pi m kT)^{3/2}\right] + \frac{3}{2}Nk. \qquad \text{...(3a)}$$

This may also be written as

$$S = Nk\left[\log V + \tfrac{3}{2}\log m + \tfrac{3}{2}\log T + C\right]. \qquad \text{...(3b)}$$

where $C$ is a constant term including constant factors $h$, $k$.

The entropy given by above equation does not satisfy the additive property, thus giving paradoxial results. To explain this consider two systems denoted by indices $a$ and $b$ held at the same temperature $T_a = T_b = T$ (say) and partitioned by a barrier as shown in Fig. 7.5.



**(Fig. 7.5)**

If the particles of the two systems are *different*, then using eqn. (3b), the entropies of the systems *'a'* and *'b'* are given by

$$S_a = N_a k\,[\log U_a + \tfrac{3}{2}\log m_a + \tfrac{3}{2}\log T + C], \qquad \text{...(4a)}$$

$$S_b = N_b k\,[\log V_b + \tfrac{3}{2}\log m_b + \tfrac{3}{2}\log T + C], \qquad \text{...(4b)}$$

where $N_a$, $m_a$ and $V_a$ refer respectively to the number of particles, mass of each particle and the volume of system '*a*' and $N_b$, $m_b$ and $V_b$ refer to the corresponding quantities for system '*b*'.

As the entropy is an extensive quantity, it must satisfy the additive property. It the entropy given by eqn. (3) had satisfied the additive property, then by removing the partition and allowing the gas molecules to mix freely, the entropy of the joint system would have been given by

$$S_{ab} = S_a + S_b = N_a k\,[\log V_a + \frac{3}{2}\log m_a + \frac{3}{2}\log T + C]$$
$$+ N_b k\,[\log V_b + \tfrac{3}{2}\log m_b + \frac{3}{2}\log T + C]. \qquad \text{...(5)}$$

However, if the particles of the two systems are the *same* and if for convenience we take $V_a = V_b = V$ and $N_a = N_b = N$, the entropy of each of the individual system would be

$$S = S_a = S_a = Nk\,[\log V + \tfrac{3}{2}\log m + \tfrac{3}{2}\log T + C]. \qquad \text{...(6)}$$

Then the entropy of the combined system would have been

$$S_{ab} = S_a + S_b = 2Nk\,[\log V + \tfrac{3}{2}\log m + \frac{3}{2}\log T + C], \qquad \text{...(7)}$$

Now we shall find the *actual entropy* of the combined system using eqn. (3) for entropy. Let the partition be removed to allow the molecules of the gas to mix freely. Now we have to consider the mixed system having $2N$ particles in a volume $2V$. Therefore using eqn. (3b) for entropy, the entropy of the joint system may be obtained by replacing $N$ and $V$ in eqn. (4b) by $2N$ and $2V$. Thus the entropy of the joint system '*ab*', using eqn. (3) is

$$S_{ab} = 2\,Nk\,[\log 2V + \tfrac{3}{2}\log m + \tfrac{3}{2}\log T + C]$$
$$= 2Nk\,[\log V + \tfrac{3}{2}\log m + \tfrac{3}{2}\log T + C] + 2Nk\log 2$$
$$= S_a + S_b + 2Nk\log_e 2, \qquad \text{...(8)}$$

[Refer eqn. (6)]

which is not eqn. (7); but contains an extra factor $2Nk\log_e 2$. this indicates that by mixing two different gases, each containing same number of molecules $N$, by removing a partition between them the entropy of the joint system increases by an unaccountable amount $2Nk\log_e 2$. This additional entropy is called the *entropy of mixing*. Thus if we use equation (3) for entropy, we get paradoxial results; because entropy being an extensive thermodynamic function the total entropy of the joint system would have been given by eqn. (7). This peculiar behaviour of the entropy is called *Gibb's paradox*.

Gibb's paradox can be resolved in the following manner :

Gibbs solved this puzzling paradox by considering the two systems as the *same*, hence the *gas molecules completely identical and indistinguishable*. In this case one cannot observe or label the individual particle. So we must apply here the idea of *indistinguishability*. Hence if two systems containing same number $N$ of identical particles are mixed by removing a partition between them the diffusion takes place unnoticeably. In this situation $N$ molecules of each system cannot be distinguished in $N!$ ways. Hence to arrive at the correct result we must divide the weight of the configuration by $N!$. therefore the weight of the configuration in this case will be

$$\Omega = \prod_i \frac{g_i^{n_i}}{n_i!} \quad \text{in place of } N!\prod \frac{g_i^{n_i}}{n_i!}$$

This leads to the following expression for the entropy of a perfect gas

$$S = Nk\log_e\left[\frac{V}{h^3}\frac{(2\pi m\,kT)^{3/2}}{N!}\right] + \frac{3}{2}Nk$$
$$= Nk\log_e\left[\left\{\frac{V}{N}\right\}\left\{\frac{2\pi m\,kT}{h^2}\right\}^{3/2}\right] + \frac{5}{2}Nk. \qquad \text{...(9)}$$

The entropy given by this equation satisfies the additive property since here in the argument of logarithm we have $V/N$ *i.e.* volume per particle in place of total volume $V$. In eqn. (9) replacing $N$ by $2N$ and $V$ by $2V$, the entropy of the combined system would be given by

$$S_{ab} = 2Nk\log_e\left[\left\{\frac{2V}{2N}\right\}\left\{\frac{2\pi m\,kT}{h^2}\right\}^{3/2}\right] + \frac{5}{2}2Nk$$
$$= 2\left[Nk\log_e\left\{\left(\frac{V}{N}\right)\left(\frac{2\pi m\,kT}{h^2}\right)^{3/2}\right\} + \frac{5}{2}Nk\right]$$
$$= 2S = S_a + S_b. \qquad \text{...(10)}$$

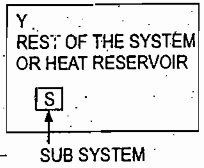
Obviously the entropy given by eqn. (9) satisfies the additive property. Thus Gibb's paradox is resolved.

To resolve the Gibb's paradox we have used the quantum property : because *in the quantum picture the particles are completely indistinguishable* and hence have introduced the factor $\frac{1}{N!}$ in the definition of entropy. Thus the resolution of Gibb's paradox is an example of the success of the quantum theory.

Now we conclude that if we employ the method of microcanonical ensemble to define the entropy of a perfect gas, we get unreasonable results (*e.g.* Gibb's paradox) if we do not include the factor $\frac{1}{N!}$.

## 7.9 Gibb's Canonical Ensemble :

The microcanonical ensemble is a general basis for the statistical method; but in practice it is very difficult to use it because of the difficulty arising in the calculation of evaluating the volume of the phase space or the number of accessible microscopic states that have a specific energy. Gibb's invented another ensemble called the *canonical ensemble* which avoids some of the difficulties. The microcanonical ensemble describes the systems which are perfectly insulated and have given energy. In thermodynamics we do not know the exact value of energy as we usually deal with systems kept in thermal contact with a heat reservoir at a given temperature. Thus we know only its temperature *i.e. its average energy*. The energy varies from instant to instant; but the time average is known. On the other hand *the canonical ensemble describes those systems which are not isolated; but are in thermal contact with a heat reservoir.* In this situation the system of interest together with a heat reservoir forms a large closed system and then the system of interest treated as a *sub-system (i.e.* a small macroscopic part of a much large system). If the energy of the large closed system is constant (*i.e.* the closed system is perfectly insulated), then it would represent a *microcanonical system* whereas the subsystem which can exchange energy with a heat reservoir would represent a *canonical system.* Thus *any part or subsystem of an isolated system in statistical equilibrium can be represented by a canonical ensemble.*



**(Fig. 7.6) Division of asystem into a subsystem and a heat reservoir.**

Now consider a microcanonical ensemble representing a very large isolated system. Let us imagine that each system of the ensemble is made up of a large number of subsystems which are in mutual thermal contact and can exchange energy, but not the particles with each other. Let us choose a subsystem denoted by $s$, the rest of the system will be denoted by $r$ and is sometimes called the *heat reservoir* (fig. 5.6). The total system is denoted by $t$. As the total system is a member of the microcanonical ensemble, it is isolated and hence its energy $E_t$ is constant. Let the energies of the subsystem and the rest of the system (*i.e.* heat reservoir) be denoted by $E_s$ and $E_r$ so

$$E_t = E_r + E_s. \qquad \text{...(1)}$$

As the subsystem $s$ can exchange energy; but not the particles, it is a member of the canonical ensemble. The subsystem is comparatively small; but usually macroscopic containing $10^{24}$ particles (say). In the case of a gas, if the interactions between molecules are very weak, thereby permitting us to specifiy accurately the energy of a molecule, the subsystem may be a single molecule.

We shall now proceed to find out the density-distribution function $\rho (E)$ of the representative points of the subsystem in its own phase space, under the condition that the total system is in statistical equilibrium and is isolated (*i.e.*, $E_t = E_s + E_r =$ constant).

Let $d\omega_t$ represent the probability that the total system $t$ is in an element of volume $d\Gamma_t$ of the appropriate space. Then for a microcanonical ensemble, we have

$$\left.\begin{aligned} d\omega_t (E) &= C\, d\Gamma_t \text{ for } E_t < E < E_t + \delta E_t \\ &= 0 \text{ outside this energy range} \end{aligned}\right\} \qquad \text{...(2)}$$

where C is a constant.

As the volume element $d\Gamma$ of phase space can be expressed in terms of position and momentum co-ordinates, *i.e.*,

$$d\Gamma = \int\int dq_1 \,......\, dq_f\, dp_1 \,........\, dp_f\,;$$

we can split $d\Gamma_t$, the volume element of total phase space into two factors :

(1) The factor $d\Gamma_s$ containing co-ordinates and momenta of the sub-system.

(2) The factor $d\Gamma_r$ containing co-ordinates and momenta of heat reservour.

Thus we write $d\Gamma_t = d\Gamma_s\, d\Gamma_r$.

Hence equation (2) may be written as

$$\left.\begin{aligned} dw_t (E) &= C\, d\Gamma_s\, d\Gamma_r \text{ for } E_t < E < E_t + \delta E_t \\ &= 0 \text{ outside this energy range} \end{aligned}\right\}$$

Now we wish to fine the probability $dw$, that the sub-system is in the volume $d\Gamma_s$, *without specifying the condition of the reservoir* provided the total energy remains between $E_t$ and $E_t + \delta E_t$

Then we write

$$dw_s = C\, d\Gamma_s\, \Delta\Gamma_r, \qquad \text{...(5)}$$

where $\Delta\Gamma_r$ is the volume of the phase space of the reservoir which corresponds to the energy of the total system at $E_t$ within the range $\delta E_t$. Now the problem reduces to finding $\Delta\Gamma_r$, *i.e.*, volume of the phase space accessible to the heat reservour when we know that the sub-system is in volume element $d\Gamma_s$.

Now the entropy of the reservoir is

$$\sigma_r = \log \Delta\Gamma_r. \qquad \text{...(6)}$$

This gives $\qquad \Delta\Gamma_r = e^{\sigma_r}.$

As from equation (1) $E_r = E_t - E_s$, therefore we can write

$$\begin{aligned} \sigma_r (E_r) &= \sigma_r (E_t - E_s) \\ &= \sigma_r (E_t) - \frac{\partial \sigma_r (E_t)}{\partial E_t} E_s + ..... \end{aligned}$$

As the sub-system is small in comparison with the total system, we have $E_s << E_t$. Then we may use the expansion

$$\sigma_r (E_r) = \sigma_r (E_t) - \frac{\partial \sigma_r (E_t)}{\partial E_t} E_s \qquad \text{...(8)}$$

Substituting $\sigma_t$ in eqn. (7), we get

$$\Delta\Gamma_r = \exp.\, [\sigma_r (E_t)] \exp.\left[ -\frac{\partial \sigma_r (E_t)}{\partial E_t} \cdot E_s \right] \qquad \text{...(9)}$$

As $E_s << E_t$, we may take $E_t \approx E_r$. So we can use eqn. (5) $\left( i.e., \frac{1}{\tau} = \frac{\partial \sigma}{\partial E} \right)$ to introduce the temperature in our ensemble which in this case takes the form

$$\frac{1}{\tau} = \frac{\partial \sigma_r (E_t)}{\partial E_t} \qquad \text{...(10)}$$

Here $\tau$ is the temperature characterising every part of the system, because system is in thermal contact.

Using equation (10), eqn. (9) becomes

$$\Delta\Gamma_r = \exp.\, [\sigma_r (E_t)] \,.\, \exp.\left( -\frac{E_s}{\tau} \right). \qquad \text{...(11)}$$

Substituting value of $\Delta\Gamma_r$ from above equation, in equation (5), we get

$$\begin{aligned} d\omega_s &= C\, d\Gamma_s \,.\, \exp.\, [\sigma_r (E_t)] \exp.\left( -\frac{E_s}{\tau} \right). \\ &= C e^{\sigma_r (E_t)} e^{-E_s/\tau} d\Gamma_s \\ &= A e^{-E_s/\tau} d\Gamma_s. \end{aligned} \qquad \text{...(12)}$$

where $\qquad A = C e^{-\sigma_r (E_t)}$ $\qquad$ ...(13)

The normalization factor $A$ is to be determined such that

$$\int d\omega_s = 1 = A \int e^{-E_s/\tau} d\Gamma_s. \qquad \text{...(14)}$$

According to equation (6) of section 6.4, the *normalization condition* is

$$1 = \int \rho\, d\Gamma, \qquad \text{...(15)}$$

where $\rho$ is the density of distribution of phase points in the phase space. This equation simply mean that *the sum of the probabilities of all possible states is unity.*

Comparing equations (14) and (15), the probability density for the sub-system is given by

$$\rho (E) = A e^{-E/\tau}, \qquad \text{...(16)}$$

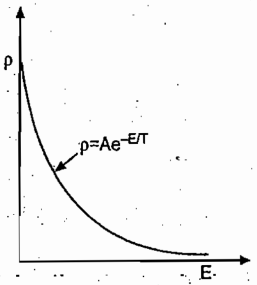
where we have dropped the subscript $s$ to emphasize that $E$ is the energy of the *entire sub-system.* An ensemble characterized by the probability density $\rho(E)$ given by eqn. (16) is called the *Gibb's canonical ensemble* (or *macrocanonical ensemble*).

Since the sub-systems are in thermal contact, they are continuously changing their energies therefore in a canonical ensemble we deal with systems of more than a single energy.

Consequently the distribution function in the canonical ensemble depends both on $E$ and $\tau$ *i.e.* the temperature $T$ [since $\tau = kT$, refer eqn. (16)].

As the sub-system is in the thermal equilibrium with the reservoir, fluctuations do not appear in temperature; but appear in energy. From the theoretical point of view it is much more easier to work with the canonical ensemble, because we do not have to arrange to keep the total energy constant or within bounds.

It is desirable to forget the method of derivation of the canonical ensembles equation (16) and treat it as alternative to the microcanonical ensembles equation (1) of the section 7.1. The distribution function $\rho$ as a function of energy $E$ for the canonical ensemble is plotted in fig. 7.7. The quantity $\tau\,(= kT)$ is called the *modulus* of the canonical ensemble.



(Fig. 7.7)

It is important to note that ***for two sub-systems in thermal contact with the reservoir*** $\log \rho$ ***is additive.***

From equation (16), we get

$$\log \rho = \log A - \frac{E}{\tau}.$$

Therefore, for sub-systems 1 and 2, we have

$$\log \rho_1 = \log A_1 - \frac{E_1}{\tau} \qquad ...(17)$$

$$\log \rho_2 = \log A - \frac{E_2}{\tau} \qquad ...(18)$$

Adding equations (17) and (18), we

$$\log \rho_1 + \log \rho_2 = \log A_1 + \log A_2 - \frac{(E_1 + E_2)}{\tau},$$

or

$$\log \rho_1 \rho_2 = \log A_1 A_2 - \frac{E_1 + E_2}{\tau} \qquad ...(19)$$

So that with $\rho = \rho_1 \rho_2$, $A = A_1 A_2$, $E = E_1 + E_2$, we have

$$\log \rho = \log A - \frac{E}{\tau}$$

for the combined system. Obviously,

$$\log \rho = \log (\rho_1, \rho_2) = \log \rho_1 + \log \rho_2 \text{ is additive}$$

*This additive property is central to the use of the canonical ensembles.*

According to equation (4) of section 6.13, the average value of any quantity $u\,(q, p)$ is given by

$$\bar{u} = \frac{\int u\,(q, p)\,\rho\,(q, p)\,d\Gamma}{\int \rho\,(q, p)\,d\Gamma}$$

where $\rho\,(q, p)$ is the probability distribution function.

For a canonical distribution, we have

$$\rho\,(q, p) = Ae^{-E\,(q, p)/\tau}. \qquad ...(20)$$

Therefore, the average value of any quantity $u\,(q, p)$ over a canonical distribution is

$$\bar{u} = \frac{\int u\,(q, p)\,Ae^{-E\,(q, p)/\tau}\,d\Gamma}{\int Ae^{-E\,(q, p)/\tau}\,d\Gamma}$$

$$= \frac{\int u\,(q, p)\,e^{-E\,(q, p)/\tau}\,d\Gamma}{\int e^{-E\,(q, p)/\tau}\,d\Gamma} \qquad ...(21)$$

Now, we *summarize* below the useful *features of the canonical ensemble :*

1. The canonical ensemble describes the systems which are in thermal contact with a heat reservoir.
2. Any part (or a sub-system) of a microcanonical ensemble in statistical equilibrium can be represented by a canonical ensemble.
3. The probability density of a canonical ensemble depends both on energy $E$ and temperature $T$.

   It is given by

   $$\rho\,(E, T) = Ae^{-E/\tau},$$

   where $\tau = kT$.
4. As $\log \rho$ is additive, we may couple two canonical ensembles with the same modulus ($\tau$), so that the resulting ensemble is again a canonical ensemble.
5. Canonical ensemble is applicable equally to microscopic and atomic sub-systems.
6. As the sub-system is in thermal contact with a reservoir, therefore, in thermal equilibrium with the reservoir, the fluctuations do not occur in temperature, but appear in energy.
7. The average value of any quantity $u\,(q, p)$ for a caonical ensemble is given by equation (21).

## 7.10 Thermodynamical Functions for the Canonical Ensemble and Partition Function :

In this section we shall calculate the thermodynamical function (*e.g.*, entropy, energy, Helmholtz free energy) and partition function of the canonical ensemble.

In thermodynamics the entropy is determined by the energy independently of whether the system is isolated or in contact with a heat reservoir. Now consider an isolated system with total energy $E_0$. Further, suppose that this system is a part of a very large hypothetical system (*i.e.* microcanonical ensemble). The microcanonical ensemble minus our system is the heat reservoir. Our system is in thermal equilibrium with the heat reservoir in such a way that the mean energy $\bar{E}$ of our system is equal to the total energy $E$ (*i.e.*, $\bar{E} = E_0$). Let our system in the microcanonical ensemble be defined in the energy range between $E_0$ and $E_0 + \delta E$. But in the microcanonical ensemble the precise value of energy width $\delta E$ is unimportant as far as the entropy given by $\sigma = \log \Delta\Gamma$ is concerned, where $\Delta\Gamma$ is the volume of phase space corresponding to energies between $E_0$ and $E_0 + \delta E$. Then we may choose $\delta E$ to be equal to the range of reasonably probable values of the energy in the *canonical ensemble*. Therefore, we may now define the entropy of the canonical ensemble with the mean energy $E$ to be equal to the entropy of a microcanonical ensemble with energy $\bar{E}$. Obviously this corresponds to the situation in thermodynamics where the entropy of the system determined by its energy is independent of the presence or absence of the heat reservoir.

Now consider the volume $\Delta\Gamma$ of the phase space corresponding to the energies between $E$ and $E + \delta E$. Let us now try to write $\Delta\Gamma$ in the terms of $\delta E$. If $\Gamma(E)$ denotes the volume of the phase space corresponding to the energies less than or equal to $E$, then its variation with $E$ can be expressed as $\frac{\partial \Gamma(E)}{\partial E}$. Therefore the phase space volume $\Delta\Gamma$ can be written as

$$\Delta\Gamma = \left[\frac{\partial \Gamma(E)}{\partial E}\right]_E \delta E, \qquad \text{...(1)}$$

where $\delta E$ is the range of reasonable probable values for the canonical ensemble.

To estimate the value of $\delta E$, let $\omega(E)\,dE$ represent the *canonical ensemble probability* for a system to have energy in the range $E$ and $E + dE$. Further, if $\rho(E)$ is the *probability density* or the *distribution function or occupancy probability* of unit volume of the phase space at energy $E$, then the probability fo volume $\Delta\Gamma$ of phase space corresponding to energies in the range $E$ and $E + dE$ will be $\rho(E)\,\Delta\Gamma(E)$. So that

$$\omega(E)\,dE = \rho(E)\,\Delta\Gamma(E) \qquad \text{...(2a)}$$

$$= \rho(E)\left(\frac{\partial \Gamma(E)}{\partial E}\right)_E dE. \qquad \text{...(2b)}$$

[using equation (1)]

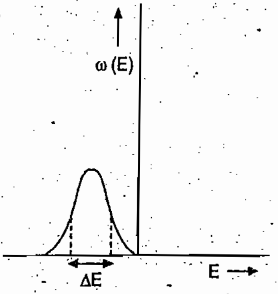
Fig. 7.8 represents the variation $\omega(E)$ as a function of $E$.

the normalization condition is

$$\int \omega(E)\,dE = 1. \qquad \text{...(3)}$$

This simply means that the area under the curve $\omega = \omega(E)$ is equal to unity.

Since the mean energy of the canonical ensemble is $\bar{E}$, the function $\omega(E)$ will have an extremely sharp maximum at $E = \bar{E}$ differing appreciably from zero only in the immediate neighbourhood of this point. So on normalizing the plot we can introduce the width $\delta E$ of the curve $\omega = \omega(E)$, defining it as the width of the rectangle whose height is equal to the value of the function $\omega(E)$ at its maximum and whose area is equal to unity. Thus, the width $\delta E$ of the curve of the normalized plot is determined by the normalization condition,



(Fig. 7.8)

$$\omega(\bar{E})\,\delta E = 1. \qquad \text{...(4)}$$

Therefore, comparing equations (2a) and (4) with $E = \bar{E}$, we get

$$\rho(\bar{E})\,\Delta\Gamma = 1,$$

or

$$\Delta\Gamma = \frac{1}{\rho(\bar{E})}$$

But from equation (16) of section 7.9, we have

$$\rho(\bar{E}) = Ae^{-\bar{E}/\tau}.$$

$$\therefore \quad \Delta\Gamma = A^{-1}e^{\bar{E}/\tau}. \qquad \text{...(5a)}$$

$$= A^{-1}e^{U/kT}, \qquad \text{...(5b)}$$

where $\bar{E} = U$ is the energy of the system and $\tau = kT$.

So that the *statistical entropy* $\sigma$ is given by

$$\sigma = \log \Delta\Gamma = \log(A^{-1}e^{U/kT})$$

$$= -\log A + \frac{U}{kT}. \qquad \text{...(6)}$$

This gives

$$\log A = \frac{U}{kT} - \sigma = \frac{U - k\sigma T}{kT} = \frac{U - ST}{kT} \qquad \text{...(7)}$$

where $S = k\sigma$ is the thermodynamic entropy.

As the Helmholtz's free energy is defined as

$$F = U - \tau\sigma = U - ST, \qquad \text{...(8)}$$

therefore, in terms of Helmholtz's free energy, expression (7) becomes

$$\log A = \frac{F}{kT},$$

giving

$$A = e^{F/kT}, \qquad \text{...(9)}$$

So that the *canonical distribution function* takes the form

$$\rho(E) = Ae^{-E/\tau} = e^{F/kT}e^{-E/kT} \qquad \text{(since } \tau = kT).$$

*i.e.*

$$\rho(E) = e^{(F-E)/kT}. \qquad \text{...(10)}$$

Now applying the normalization condition,

$$\int \rho(E)\,d\Gamma = 1.$$

we get

$$\int e^{(F-E)/kT}\,d\Gamma = 1,$$

or

$$e^{-F/kT} = \int e^{-E(p,q)/kT}\,d\Gamma. \qquad \text{...(11)}$$

Now the *partition function* is defined as

$$Z = \int e^{-E(p,q)/kT}\,d\Gamma \ \text{(classical)} \qquad \text{...(12a)}$$

$$Z = \sum_i e^{-E_i/kT} \ \text{(quantum)}. \qquad \text{...(12b)}$$

So eqn. (7) is written as

$$e^{-F/kT} = Z.$$

Taking log of both the sides, we get

$$-\frac{F}{kT} = \log Z.$$

*i.e.*

$$F = -kT\log Z = -\tau\log Z. \qquad \text{...(13)}$$

This equation represents the expression for the *Helmholtz free energy* in tesms of the partition function. In the problems containing $n$ independent identical spinless particles we must correct the classical partition function dimensionally and take into account the indistinguishability of the particles, so that the correct expression is

$$Z = \frac{1}{N!\,h^{3N}}\int e^{-E(p,q)/kT}\,d\Gamma \ \text{(classical)} \qquad \text{...(14)}$$

**Entropy of a system :** The *statistical entropy* of a system in a *canonical ensemble* is given by

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V,$$

$$= \frac{\partial}{\partial \tau}(\tau\log Z)$$

$$= \log Z + \tau\frac{\partial}{\partial \tau}(\log Z). \qquad \text{...(15)}$$

If $E_i$ is the $i^{th}$ energy eigen value of a system, we have

$$Z=\sum_i e^{-E_i/\tau}.$$

i.e. $$\log Z=\log\left(\sum_i e^{-E_i/\tau}\right).$$

i.e. $$\frac{\partial}{\partial\tau}(\log Z)=\frac{\partial}{\partial\tau}\left[\log\left(\sum_i e^{-E_i/\tau}\right)\right]$$

$$=\frac{1}{\tau^2}\frac{\sum_i E_i e^{-E_i/\tau}}{\sum_i e^{-E_i/\tau}}=\frac{1}{\tau^2}\bar{E}=\frac{U}{\tau^2} \qquad \text{...(16)}$$

(since $\bar{E}=U$ energy of the system).

Substituting this in eqn. (15), we have the expression for *statistical entropy* as

$$\sigma=\log Z+\frac{U}{\tau} \qquad \text{...(17)}$$

Therefore the *thermodynamical entropy* $S$ of a system in a canonical ensemble is given by

$$S=k\sigma=k\left[\log Z+\frac{U}{\tau}\right] \qquad \text{...(18a)}$$

$$=k\log Z+\frac{U}{T} \quad (\text{since } \tau=kT) \qquad \text{...(18b)}$$

## 7.11 STATISTICAL MECHANICAL FORMULATION OF THIRD LAW OF THERMODYNAMICS

If $E_i$ is the entropy corresponding to $i^{th}$ energy eigen state, then the *partition function (i.e. sum over states)* of the system is expressed as

$$Z=\sum_i e^{-E_i/\tau}$$

At absolute zero $T=0$, hence $\tau=kT=0$. In the limit as $\tau\to 0$, $e^{-E_i/\tau}\to 0$, therefore in the limit of absolute zero, the only appreciable contribution in the sum is only due to those states which have the lowest possible value of the energy $E_i$. But the lowest possible energy is the ground state energy $E_0$. If $g_0$ states correspond to the ground state energy $E_0$ *i.e.* if $g_0$ is the statistical weight of the ground state, then as $T\to 0$, the partition function

$$Z\to g_0\,e^{-E_0/\tau},$$

and the mean energy $\bar{E}=U\to E_0$.

Therefore according to eqn. (18b) the entropy $S_0$ at absolute zero is expressed as

$$S_0=k\log\left(g_0\,e^{-E_0/\tau}\right)+\frac{E_0}{T}$$

$$=k\log g_0-\frac{kE_0}{\tau}+\frac{E_0}{T}$$

$$=k\log g_0-\frac{E_0}{T}+\frac{E_0}{T} \quad (\text{since } \tau=kT)$$

$$=k\log g_0. \qquad \text{...(19)}$$

∴ As ground-state consists of only one state or relatively small number of states, eqn. (19) indicates that *the entropy becomes vanishingly small as the temperature of the system approaches absolute zero.* This statement refers to the *third law of thermodynamics* (or *Nernst heat theorem*). Hence eqn. (19) represents the *statistical mechanical formulation* of the third law of thermodynamics.

## SOLVED EXAMPLES

**Ex. 4.** *Show that the entropy of a system in canonical ensemble can be expressed as*

$$\sigma=-\sum_i \rho_i\log\rho_i.$$

*where* $\rho_i$ *is the probability of the system to be found in* $i^{th}$ *state.*

**Solution.** The probability of a system to be found in $i^{th}$ state in the canonical ensemble is given by

$$\rho_i=\frac{e^{-E_i/\tau}}{\sum_i e^{-E_i/\tau}}=\frac{e^{-E_i/\tau}}{Z}.$$

Hence

$$\sum_i \rho_i\log\rho_i=\sum_i\left(\frac{e^{-E_i/\tau}}{Z}\right)\log\left(\frac{e^{-E_i/\tau}}{Z}\right)$$

$$=\frac{1}{Z}\sum_i e^{-E_i/\tau}\cdot\left(-\frac{E_i}{\tau}-\log Z\right)$$

$$=-\frac{1}{\tau}\frac{\sum_i E_i e^{-E_i/\tau}}{Z}-\frac{\log Z}{Z}\sum e^{-E_i/\tau}$$

$$=-\frac{1}{\tau}\frac{\sum_i E_i e^{-E_i/\tau}}{\sum_i e^{-E_i/\tau}}-\log Z=\frac{1}{\tau}\bar{E}-\log Z$$

$$=-\left[\log Z+\frac{U}{\tau}\right] \quad (\text{since } \bar{E}=U=\text{energy of the system}).$$

Comparing above eqn. with eqn. (17) of section (7.10), we get

$$\sigma=-\sum_i \rho_i\log\rho_i. \qquad \text{...(19)}$$

### 7.12 Perfect Monatomic gas in Canonical Ensemble

Now we shall find the partition function and the thermodynamical functions for monatomic perfect gas using the canonical ensemble.

**Partition Function :** The *classical partition function* $Z$ for a canonical ensemble is given by

$$Z=\frac{1}{N!\,h^{3N}}\int e^{-E/\tau}\,d\Gamma. \qquad \text{...(1)}$$

[Refer eqn. (14) of section 7.10]

For a perfect gas, there are no mutual interactions between the molecules, so we have

$$E=\sum_i\frac{p_i^2}{2m}.$$

$$\Gamma = \prod_i d\Gamma_i = \prod_i dq_i\, dp_i$$

So that $$e^{-E/\tau} = \prod_i e^{-p_i^2/2m\tau}.$$

Then eqn. (1) for partition function takes the form

$$Z = \frac{1}{N!\,h^{3N}} \int \left[ \prod_{i=1}^{3N} e^{-p_i^2/2m\tau}\, dq_i\, dp_i \right] \qquad \ldots(2)$$

But $$\int \prod_{i=1}^{3N} dq_i = V^N$$

Therefore eqn. (2) may be written as

$$Z = \frac{1}{N!\,h^{3N}} \cdot V^N \left[ \int_{-\infty}^{+\infty} e^{-p_i^2/2m\tau}\, dp_i \right]^{3N} \qquad \ldots(3)$$

Now we have the standard definite integral

$$\int_{-\infty}^{+\infty} e^{-ay^2}\, dy = \sqrt{\left(\frac{\pi}{a}\right)}$$

therefore $$\int_{-\infty}^{+\infty} e^{-p_i^2/2m\tau}\, dp_i = (2\pi m\tau)^{1/2}.$$

Substituting this in eqn. (3), we get

$$Z = \frac{1}{N!\,h^{3N}} \cdot V^N (2\pi m\tau)^{3N/2}$$

$$= \frac{V^N}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} \qquad \ldots(4)$$

[since $\tau = kT$].

Now according to definition of *thermal de-Broglie wavelength*, refer equation (15) of section 7.5., we have

$$\lambda = \frac{h}{(2\pi mkT)^{1/2}} \qquad \ldots(5)$$

So equation (4) for partition function takes the form

$$Z = \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N \qquad \ldots(6)$$

It is to be pointed out that here $Z$ is purely translational since gas is monatomic.

We can further write equation (4) or (6) in the form

$$Z = \frac{f^N}{N!} \qquad \ldots(7)$$

where $$f = V \left( \frac{2\pi mkT}{h^2} \right)^{3/2} = \frac{V}{\lambda^3} \qquad \ldots(8)$$

is the *one particle partition function.*

**Helmholtz Free Energy F :** The Helmholtz free energy $F$ in terms of partition function is given by

$$F = -kT \log Z \qquad \text{[refer equation (13) of section 7.10]}$$

$$= -kT \log \left( \frac{f^N}{N!} \right) \qquad \text{[using equation (7)]}$$

Now using Stirling approximation,

$\log N! = N \log N - N$, we get

$$F = -kT [\log f^N - N \log N + N]$$

$$= -kT [N \log f - N \log N + N]$$

$$= -NkT \log \left( \frac{f}{N} \right) - NkT. \qquad \ldots(9)$$

**Entropy :** The entropy $S$ is given by

$$S = -\left( \frac{\partial F}{\partial T} \right)_V \qquad \text{[refer equation (6) of section 2.12]}$$

Now substituting the value of $F$ from equation (9), we get

$$S = -\frac{\partial}{\partial T} \left[ -NkT \log \left( \frac{f}{N} \right) - NkT \right]$$

$$= Nk \log \frac{f}{N} + NkT \frac{\partial}{\partial T} \left( \log \frac{f}{N} \right) + Nk \qquad \text{[using eqn. (8)]}$$

$$= Nk \log \left( \frac{f}{N} \right) + NkT \frac{\partial}{\partial T} \left[ \log \frac{V}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right]_V + Nk$$

$$= Nk \log \left( \frac{f}{N} \right) + NkT \cdot \frac{1}{\frac{V}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2}} \frac{V}{N} \times \left( \frac{2\pi mk}{h^2} \right)^{3/2} \cdot \frac{3}{2} T^{1/2} + Nk$$

$$= Nk \log \frac{f}{N} + \frac{3}{2} Nk + Nk$$

$$= Nk \log \frac{V}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} + \frac{5}{2} Nk$$

$$= Nk \log_e \left[ \frac{V}{Nh^3} (2\pi mkT)^{3/2} e^{5/2} \right] \qquad \ldots(10)$$

which is the *Sackur-Tetrode equation* in agreement with equation (14) of section 7.5. derived for perfect monatomic gas in microcanonical ensemble, thus verifying the statement that the entropy is determined by energy independently of whether the system is isolated or in thermal contact with a heat reservoir.

**Internal Energy :** The *mean energy* is defined as

$$\bar{E} = \frac{\sum_i E_i e^{-E_i/\tau}}{\sum_i e^{-E_i/\tau}} \qquad \ldots(11)$$

where $E_i$ is the energy of the system in $i$th state.

The partition function $Z = \sum_i e^{-E_i/\tau}$

$$\therefore \qquad \log Z = \log \left( \sum_i e^{-E_i/\tau} \right)$$

i.e.,
$$\frac{\partial}{\partial \tau}(\log Z)=\frac{1}{\tau^2}\frac{\sum_i E_i e^{-E_i/\tau}}{\sum_i e^{-E_i/\tau}}=\frac{\overline{E}}{\tau^2}$$

Thus,
$$\overline{E}=\tau^2\frac{\partial}{\partial \tau}(\log Z). \qquad ...(12)$$

From equation (13) of section 7.10, we have

$$F=-\tau \log Z \text{ i.e., } \log Z=-\frac{F}{\tau}.$$

Substituting this value of log Z in equation (12), we get

$$\overline{E}=-\tau^2\frac{\partial}{\partial \tau}\left(\frac{F}{\tau}\right) \qquad ...(13)$$

From equation (9), we have

$$F=-NkT\log\frac{\partial}{\partial \tau}\left(\frac{f}{N}\right)-NkT$$
$$=-N\tau\log\left(\frac{f}{V}\right)-N\tau \qquad \text{[since } \tau=kT\text{].}$$

Now substituting value of $F$ from above equation in eqn. (13), we get

$$\overline{E}=\tau^2\frac{\partial}{\partial \tau}\left[N\log\frac{f}{N}+N\right]$$
$$=N\tau^2\frac{\partial}{\partial \tau}\log\left(\frac{f}{N}\right)=N\tau^2\frac{\partial}{\partial \tau}\left[\log\left\{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\}\right]$$
$$=N\tau^2\frac{\partial}{\partial \tau}\left[\log\left\{\frac{V}{N}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\right\}\right]$$
$$=N\tau^2\cdot\frac{1}{\left\{\frac{V}{N}\cdot\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\right\}}\cdot\frac{V}{N}\left(\frac{2\pi m}{h^2}\right)^{3/2}\cdot\frac{3}{2}\tau^{1/2}$$
$$=\frac{3}{2}N\tau=\frac{3}{2}NkT.$$

Hence the internal energy of the system is given by

$$U=\overline{E}=\frac{3}{2}kNT, \qquad ...(14)$$

which agrees with that derived fro microcanonical ensemble.

## 7.13 Maxwellian Velocity Distribution from Canonical Distribution

The canonical ensemble is applicable equally to microscopic and to atomic sub-systems. Let us apply it to a single atom or particle of mass $m$ in a volume $V$. Then from eqn. (10) of section 7.10, the probability of finding the particle in a region of momentum space $d\Gamma_p=dp_x\,dp_y\,dp_z$ at $(p_x, p_y, p_z)$ is given by

$$\rho(E)\,d\Gamma=\rho(E)\,V\,d\Gamma_p=e^{(F-E)/kT}\,V\,d\Gamma_p$$

$$\therefore \qquad \rho(E)\,d\Gamma=e^{F/kT}\,.\,e^{-p^2/2mkT}\,.\,V\,.\,\frac{dp_x\,dp_y\,dp_z}{h^3} \qquad ...(1)$$

Therefore the probability of finding the particle in the velocity range $dv_x\,dv_y\,dv_z$ at $(v_x, v_y, v_z)$ is given by

$$\omega(v_x, v_y, v_z)\,dv_x\,dv_y\,dv_z=e^{F/kT}\,.\,e^{-m^2(v_x^2+v_y^2+v_z^2)/2mkT}\,.\,V\,.\,\frac{m^3\,dv_x\,dv_y\,dv_z}{h^3} \qquad ...(2)$$

But $F=-kT\log Z$, [refer eqn. (13) of section 7.10]/

Therefore
$$e^{F/kT}=1/Z. \qquad ...(3)$$

Referring eqn. (4) of section 7.11, we have

$$Z=\frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}$$

For a single particle $N=1$, therefore, we have

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

Substituting this value of Z in equation (3), we have

$$e^{F/kT}=\frac{1}{V}\left(\frac{2\pi mkT}{h^2}\right)^{-3/2} \qquad ...(4)$$

Using equation (2) and (4), the probability $\omega(v_x, v_y, v_z)\,dv_x\,dv_y\,dv_z$ of finding the particle in the velocity range $dv_x\,dv_y\,dv_z$ at $(v_x, v_y, v_z)$ is given by

$\omega(v_x, v_y, v_z)\,dv_x\,dv_y\,dv_z$

$$=\frac{1}{V}\left(\frac{2\pi mkT}{h^2}\right)^{-3/2}e^{-m(v_x^2+v_y^2+v_z^2)/2kT}\,.\,V\cdot\frac{m^3\,dv_x\,dv_y\,dv_z}{h^2}$$
$$=\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-m(v_x^2+v_y^2+v_z^2)/2kT}\,dv_x\,dv_y\,dv_z. \qquad ...(5)$$

Now we can find the probability of finding the particle having $x$-component of velocity in the range $v_x$ to $v_x+dv_x$ irrespective of $v_y$ and $v_z$ by integrating equation (5) for all values $v_y$ and $v_z$,

i.e.,
$$\omega(v_x)\,dv_x=\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-mv_x^2/2kT}\,dv_x\int_{-\infty}^{+\infty}e^{-mv_y^2/2kT}\,dv_y\int_{-\infty}^{+\infty}e^{-mv_z^2/2kT}\,dv_z$$
$$=\left(\frac{m}{2\pi kmT}\right)^{3/2}e^{-mv_x^2/2kT}\,dv_x\left(\frac{2\pi kT}{m}\right)^{1/2}\cdot\left(\frac{2\pi kT}{m}\right)^{1/2}. \qquad ...(6)$$

Here we have used the standard definite integral

$$\int_{-\infty}^{+\infty}e^{-av^2}\,dv=\sqrt{(\pi/a)}.$$

On simplification, equation (6) yields

$$\omega(v_x)\,dv_x=\left(\frac{m}{2\pi kT}\right)^{1/2}e^{-mv_x^2/kT}\,dv_x. \qquad ...(7)$$

The equation represents the *Maxwellian distribution law for velocities.*

The *probability function* for velocity $v_x$ is given by

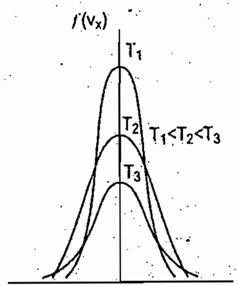
$$f(v_x) = \omega(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} \qquad ...(8)$$

This equation gives the probability of finding the particle with velocity $v_x$.

The probability distribution function $f(v_x)$ is plotted against $v_x$ for three different temperatures $T_1$, $T_2$ and $T_3$ such that $T_1 < T_2 < T_3$ in Fig. 7.9.

As $T$ increases the peak at $v_x = 0$ becomes lower and the distribution spreads out. The area under the curve is always unity since normalisation condition is

$$\int f(v_x)\, dv_x = 1.$$



(Fig. 7.9)

## 7.14 Equipartition Theorem :

Let us consider a system described by $f$ position coordinates $(q_1, q_2, ..... q_f)$ and corresponding $f$ momentum coordinates $(p_1, p_2, .... p_f)$. The total energy $E$ of the system can then be written as a function of these position and momentum coordinates *i.e.*

$$E = E(q_1, q_2, ..... q_f, p_1, p_2, ..... p_f). \qquad ...(1)$$

If $p_i$ is any particular momentum, then the total energy can be broken into a sum of two parts and written as

$$E = \varepsilon_i(p_i) + E'(q_1, q_2, .... q_f, p_1, p_2, .... p_f) \qquad ...(2)$$

where $\varepsilon_1(p_i)$ is a function of momentum $p_i$ alone and the second term $E'(q_1, q_2, .... q_f, p_1, p_2 .... p_f)$ is a function of all position and momentum coordinates excluding the momentum $p_i$.

Let us further assume that $\varepsilon_i$ is quadratic in $p_i$ and written as

$$\varepsilon_i(p_i) = Cp_i^2 \qquad ...(3)$$

where C is a constant.

If the system is in *thermal equilibrium* at a particular temperature $T$, it will be characterised by *canonical distribution* and the mean energy $\bar{\varepsilon}_i$ can then be expressed as

$$\bar{\varepsilon}_i = \frac{\sum\limits_i \varepsilon_i A e^{-E/kT}}{\sum\limits_i A e^{-E/kT}} \qquad ...(4)$$

where $A$ is a constant.

As in classical theory the energy levels are very close and hence the energy values or eigen states may be taken as continuous, so the summation, in eqn. (4) may be replaced by integration, *i.e.*,

$$\bar{\varepsilon}_i = \frac{\int \varepsilon_i e^{-E/kT} dq_1 ..... dq_f dp_1 ... dp_f}{\int e^{-E/kT} dq_1 ...dq_f dp_1 ... dp_f}$$

$$= \frac{\int \varepsilon_i e^{-(\varepsilon_i + E')/kT} dq_1 ..... dq_f dp_1 ....dp_f}{\int e^{-(\varepsilon_i + E')/kT} dq_1 ... dq_f dp_1 ... dp_f}$$

$$= \frac{\int \varepsilon_i e^{-\varepsilon_i/kT} dp_i}{\int e^{-\varepsilon_i/kT} dp_i} \cdot \frac{\int e^{-E'/kT} dq_1 ... dq_f dp_1 ...dp_f}{\int e^{-E'/kT} dq_1 ....dq_f dp_1 ....dp_f}$$

Here the integrals containing $e^{-E'/kT}$ extend over all $q$'s and $p$'s except $p_i$ such as a separation of integrals is possible because $E'$ is independent of $p_i$. It is obvious that the integrals containing $e^{-E'/kT}$ are equal and hence cancel out. Thus we have

$$\bar{\varepsilon}_i = \frac{\int_{-\infty}^{+\infty} \varepsilon_i e^{-\varepsilon_i/kT} dp_i}{\int_{-\infty}^{+\infty} e^{-\varepsilon_i/kT} dp_i}$$

$$= \frac{\int_{-\infty}^{+\infty} Cp_i^2 e^{-Cp_i^2/kT} dp_i}{\int_{-\infty}^{+\infty} e^{-Cp_i^2/kT} dp_i} \qquad \text{using eqn. (2)}$$

Using the standard definite integrals

$$\int_{-\infty}^{+\infty} x^2 e^{-ax^2} dx = \frac{1}{2}\sqrt{\left(\frac{\pi}{a^3}\right)}$$

and

$$\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\left(\frac{\pi}{a}\right)},$$

we get

$$\varepsilon_i = \frac{C'\frac{1}{2}\left[\frac{\pi}{(C/kT)^3}\right]^{1/2}}{\left[\frac{\pi}{C/kT}\right]^{1/2}} = \frac{1}{2} kT. \qquad ...(5)$$

This indicates that *the mean energy associated with each variable* (position or momentum) *like $p_i$ which contributes a quadratic term to the energy has the value $\frac{1}{2}kT$ in thermal equilibrium*. This result is called the *principle of equipartition of energy* of classical statistical mechanics.

For a free atom the Hamiltonian is expressed as a total of three quadratic terms :

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2).$$

Therefore the thermal energy of a free atom is

$$3 \cdot \frac{1}{2} kT = \frac{3}{2} kT.$$

Thus for $N$ atoms the thermal energy is

$$U = \frac{3}{2} NkT, \qquad ...(6)$$

and the heat capacity at constant volume is

$$C_V = \frac{dU}{dT} = \frac{3}{2} Nk. \qquad ...(7)$$

## SOLVED EXAMPLES

**Ex. 6.** *Derive Dulong-Petit's law on the basis of equipartition theorem.*

**Solution.** Consider a monatomic solid whose atoms are bound by linear elastic forces to fixed positions. The Hamiltonian of such an atom is given by

$$H=\frac{p^2}{2m}+\tfrac{1}{2}kq^2$$

$$=\frac{1}{2m}(p_x^2+p_y^2+p_z^2)+\tfrac{1}{2}K(q_x^2+q_y^2+q_z^2), \qquad ...(i)$$

where $K=m\omega^2$ is the force constant.

Obviously equation (1) consists of the sum of six quadratic terms. According to equipartition theorem of classical statistical mechanics, the energy of each quadratic term is $\frac{1}{2}kT$, therefore the energy of each monatomic atom of the solid in the classical (high temperature) limit is $6.\frac{1}{2}kT=3kT$.

If $N$ is the Avogadro number, the thermal energy of one mole of a monatomic solid is

$$U=3NkT \qquad ...(2)$$

Therefore the heat capacity in the classical limit at constant volume is

$$C_V=\frac{dU}{dT}=3Nk=3R, \qquad ...(3)$$

where $R$ is the gas constant.

Eqn. (3) states that *the heat capacity* (at high temperature) *of one mole of a monatomic solid is, 3 R* which is **Dulong-Petit's law.**

## 7.15 Grand Canonical Ensemble

In the microcanonical ensemble each system contains same fixed energy as well as the same number of particles. The microcanonical ensemble would not be applied to thermodynamics; because in thermodynamics we deal with systems which are kept in contact with a heat reservoir at a given temperature and we do not know the exact value of energy but the temperature *i.e.*, only the *time average of energy* is known. In canonical ensemble we relaxed the condition of constant energy and allowed the subsystem to exchange energy, but not particles, with the remainder of the system. This simplifies the calculation in thermodynamics where the exchange of energy is a common phenomenon and provides a useful model for simple systems, like the perfect gas, diatomic molecule and a simple crystal. The canonical ensemble model could not be applied to processes where the number of particles varies *e.g., chemical processes* and *quantum processes* where the particles (photons) are created and destroyed. Therefore, for wider application of the method of ensembles the next logical step is to relax the condition of constant total number of particles. Therefore we must seek for an ensemble which allows the subsystem to exchange energy as well as the particles with the remainder of the system (*i.e.*, reservoir). *Such an ensemble which allows the subsystem to exchange energy as well as the number of particles with the reservoir is called the* **grand canonical ensemble.**

In the canonical ensemble $T$, $V$ and $n$ are independent variables. In grand canonical ensemble the variable $n$ changes to $\mu$, the chemical potential per particle. Thus in grand canonical ensemble the independent variables are $T$, $V$ and $\mu$. Then instead of free energy function $F=U-TS$, we have *grand potential.*

$$\Omega=U-TS-\mu n \qquad ...(1)$$

which is minimal when $T$, $V$ and $\mu$ are held fixed.

Obviously in the grand canonical esemble the distribution function as well as the phase space will depend on the number of particles in the subsystem.

Now consider a microcanonical ensemble representing a very large isolated system. Let us imagine that each system of the microcanonical ensemble is made up of a large number of sub-systems which are in mutual thermal contact and can exchange energy as well as particles with each other. Let us choose a sub-system denoted by $S$, the rest of the system is called the heat reservoir and is denoted by $r$ (fig. 7.6). The total system is denoted by $t$. Obviously $t$ is represented by a microcanonical ensemble with constant energy $E_t$ and constant number of particles $n_t$. Let $E_s$ and $E_r$ represent the energies of the subsystem and the reservoir. Also let $n_s$ and $n_r$ represent the number of particles in the subsystem and the reservoir. Then the subsystem and the reservoir may exchange energy and particles subject to the conditions

$$E_s+E_r=E_t, \qquad ...(2)$$

and

$$n_s+n_r=n_t. \qquad ...(3)$$

Now we want to find the probability $d\omega_s(n_s)$ of finding the sub-systems in a state in which subsystem $S$ contains $n$ particles and is found in the element $d\Gamma(n_s)$ of its phase space. The notation $d\Gamma(n_s)$ indicates that the nature of the phase space of the subsystem changes with $n_s$.

By analogy with the case of the canonical ensemble, we can write

$$d\omega_s=C\,d\Gamma_s(n_s)\,\Delta\Gamma_r(n_t-n_s). \qquad ...(4)$$

As the entropy of the reservoir is

$$\sigma_r=\log\Delta\Gamma_r$$

*i.e.*

$$\Delta\Gamma_r=\exp[\sigma_r(E_t-E_s,n_i-n_s)].$$

Therefore eqn. (4) may be written as

$$d\omega_s=C\,d\Gamma_s(n_s)\exp.[\sigma_r(E_t-E_s,n_i-n_s)]. \qquad ...(5)$$

On expanding $\sigma_r$ in a power series, we get

$$\sigma_r(E_t-E_s,n_i-n_s)=\sigma_r(E_t,n_t)-\frac{\partial\sigma_r(E_t,n_i)}{\partial E_i}E_s-\frac{\partial\sigma_r(E_t,n_i)}{\partial n_i}n_s+....$$

Now, using the relations [10] and [31] section 7.3, *viz.,*

$$\frac{1}{\tau}=\left(\frac{\partial\sigma}{\partial E}\right)_{V,n} \quad\text{and}\quad \frac{\mu}{\tau}=\left(\frac{\partial\sigma}{\partial n}\right)_{E,V}$$

we get

$$\sigma_r(E_t-E_s,n_t-n_s)=\sigma_r(E_t,n_t)-\frac{E_s}{\tau}+\frac{n_s\mu_s}{\tau} \qquad ...(6)$$

Using equation (6) in eqn. (5) becomes

$$d\omega_s(n)=C\,d\Gamma_s(n_s)\exp\left[(\sigma_r(E_t\,n_i)+\frac{n_s\mu_s-E_s}{\tau}\right]$$

$$=C\exp.[(\sigma_r\,E_t,n_t)]\exp.[(n_s\mu_s-E_s)/\tau].d\Gamma_s(n_s)$$

$$=A\exp.[(n_s\mu_s-E_s)/\tau]\,d\Gamma_s(n_s), \qquad ...(7)$$

where

$$A=C\exp.[\sigma_r(E_t,n_t)] \qquad ...(8)$$

is the *normalisation constant.*

Now, dropping the suffix $s$ in above equation to emphasize that $n$ and $E$ represent respectively the number of particles and the energy of the entire sub-system, we have for *grand canonical ensemble*

$$d\omega(n)=A\exp.[(n\mu-E)/\tau]\,d\Gamma(n). \qquad ...(9)$$

Conventionally normalization constant $A$ is written as

$$A = \exp\left(\frac{\Omega}{\tau}\right) \qquad ...(10)$$

where Ω is called the *grand potential* or the *thermodynamic potential*.

Then equation (9) becomes

$$d\omega(n) = \exp[(\Omega + n\mu - E)/\tau]\, d\Gamma(n). \qquad ...(11)$$

The normalization condition is

$$\int d\omega(n) = 1 = \int [\exp(\Omega + n\mu - E)/\tau]\, d\Gamma(n). \qquad ...(12)$$

According to equation (6) of section 6.4, the normalization condition is

$$1 = \int \rho(n)\, d\Gamma(n), \qquad ...(13)$$

where ρ is the density of distribution of phase points in the phase space.

Comparing equations (12) and (13), we get

$$\rho(n) = \exp[(\Omega + n\mu - E/\tau)]. \qquad ...(14)$$

An ensemble characterized by the probability distribution $\rho(n)$ given by equation (14) is called the *grand canonical ensemble.* In the case when several molecular species are present, $n\mu$ is replaced by $\Sigma n_i \mu_i$.

## 7.16 Partition Function and Thermodynamic Function for Grand Canonical Ensemble :

In the grand canonical ensemble we allow the sub-system to exchange energy as well as particles with the heat reservoir (*i.e.* remainder of the system) with the conditions

$$\left.\begin{aligned} E_s + E_r &= E_t \\ n_s + n_r &= n_t \end{aligned}\right\} \qquad ...(1)$$

and

where $E_s, n_s$ refer to the energy and the number of particles of the sub-system; $E_r, n_r$ refer to the energy and the number of particles of the reservoir while $E_t$ and $n_t$ refer to the energy and the number of particles of the total system.

We have seen in last section that the grand canonical ensemble is characterised by the probability distribution $\rho(n)$ given by

$$\rho(n) = \exp[(\Omega + n\mu - E)/\tau], \qquad ...(2)$$

where Ω is the grand potential and μ is the *chemical potential per particle.*

The *grand partition function* (*i.e.,* the partition function for grand canonical ensemble) is defined as

$$\mathbf{Z} = \exp\left(-\frac{\Omega}{\tau}\right) = \Sigma e^{\mu n/\tau} \int e^{-E/\tau}\, d\Gamma(n) \text{ (classical)} \qquad ...(3a)$$

$$Z = \sum_n \sum_i \exp[\mu n - E_{n,i})/\tau] \text{ (quantum)}. \qquad ...(3b)$$

We may write above equations in the form

$$\mathbf{Z} = \sum_i e^{\mu n/\tau} Z_n \qquad ...(3c)$$

where

$$\mathbf{Z}_n = \int e^{-E/\tau}\, d\Gamma(n) \text{ (classical)}$$

$$= \sum_i e^{-E_{n,i}/\tau} \text{ (quantum)}$$

is the canonical partition function.

*i.e. the grand particle functions* **Z** *is the sum of the canonical partition functions $Z_i$ for ensemble with different n's with weighing factors $e^{-\mu n/\tau}$.*

From equation (3a) grand partition function is given by

$$\boxed{\Omega = -\tau \log \mathrm{Z}.} \qquad ...(4)$$

By the similar arguments used in the discussion of canonical ensemble, the entropy σ may be written as

$$\sigma = \log \Delta\Gamma = \left[\frac{1}{\rho(\bar{n}, \bar{E})}\right]$$

$$= -(\Omega + \bar{n}\mu - \bar{E})/\tau = -(\Omega - \bar{n}\mu - U)/\tau \qquad ...(5)$$

[since $\bar{\mathrm{E}} = U \doteq$ Energy of the system]

This gives $U - \tau\sigma = \Omega + \bar{n}\mu.$

Therefore Helmholtz's free energy, $F = U - \tau\sigma$ ...(6)

$= \Omega + \mu\bar{n}$, ...(7)

and Gibb's free energy $G = U - \tau\sigma + pV$, ...(8a)

$= F + pV.$ ...(8b)

On differentiation equation (8a) yields

$$dG = dU - \tau\, d\sigma - \sigma\, d\tau + p\, dV + V\, dp.$$

But from equation (5) of section 7.4, we have

$$dU = \tau\, d\sigma - p\, dV + \mu dn. \qquad ...(9)$$

$$\therefore \quad dG = -\sigma\, d\tau + V\, dp + \mu\, dn.$$

This gives

$$\left(\frac{\partial G}{\partial n}\right)_{p,\tau} = \mu. \qquad ...(10)$$

Hence $G = \mu n$ for fixed $p$ and τ.

In this case we have $\bar{n}$ in place of $n$, therefore

$$G = \mu\bar{n}. \qquad ...(11)$$

Using equations (8b) and (11), we get

$$F + pV = \mu\bar{n}. \qquad ...(12)$$

Substituting value of $F$ from equation (7), we get

$$\Omega + \mu\bar{n} + pV = \mu\bar{n}$$

*i.e.,*

$$\Omega = -pV. \qquad ...(13a)$$

Now using (8a) and (11), we get

$$U - \tau\sigma + pV = \mu\bar{n}$$

$$-pV = U - \tau\sigma - \mu\bar{n}.$$

*i.e.*, Therefore equation (13a) becomes

$$\Omega = U - \tau\sigma - \mu\bar{n}. \qquad ...(13b)$$

so that

$$d\Omega = dU - \tau\, d\sigma - \sigma\, d\tau - \mu\, d\bar{n} - \bar{n}\, d\mu$$

$$= \tau\, d\sigma - p\, dV + \mu\, d\bar{n} - \tau\, d\sigma - \sigma\, d\tau - \mu\, d\bar{n} - \bar{n}\, d\mu$$

[using equation (9)]

$$= -p\, dV - \sigma\, d\tau - \bar{n} d\mu. \qquad ...(14)$$

Then equation (14) yields

$$p = -\left(\frac{\partial\Omega}{dV}\right)_{\sigma, V} \qquad ...(15)$$

$$\sigma = -\left(\frac{\partial\Omega}{\partial\tau}\right)_{V,\mu} \qquad ...(16)$$

and

$$\bar{n} = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{V,\tau} \qquad ...(17)$$

From these relations we can evaluate the thermodynamic quantities for the *grand canonical ensembles.*

## 7.17 Perfect Gas in Grand Canonical Ensemble

The grand partition function is given by

$$Z = \sum_n e^{\mu n/\tau} Z_n, \qquad ...(1)$$

where $Z_n$ is the canonical partition function.

Taking into account the indistinguishability of the particles, the canonical partition function is written as

$$Z_n = \frac{1}{n!\,h^{3n}} \int e^{-E(n)/\tau}\, d\Gamma(n) = \frac{f^n}{n!} \qquad ...(2)$$

where

$$f = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} . V = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} . V. \qquad ...(3)$$

∴ The grand partition function

$$Z = \sum_n e^{\mu n/\tau} \frac{f^n}{n!} = \sum_n \frac{(e^{\mu/\tau} f)^n}{n!} \qquad ...(4)$$

Now using the series expansion

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$$

Equation (4) may be written as

$$Z = \exp\,[e^{\mu/\tau} . f] \qquad ...(5)$$

From equation (4) of section 7.15, we have

$$\Omega = -\tau \log Z.$$

Using equation (5), above equation becomes

$$\Omega = -\tau e^{\mu/\tau} . f$$

$$= -\tau e^{\mu/\tau} . \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} . V \qquad ...(6)$$

Now with the help of equations (15), (16) and (17) of section 7.15 we arrive at the following results of a perfect gas in grand canonical ensemble.

**Chemical potential per particle** μ.

From equation (17) of section 7.15, we have

$$\bar{n} = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{V,\tau}$$

$$= \frac{\partial}{\partial\mu}\left[\tau e^{\mu/\tau} \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} . V\right]_{V,\tau}$$

$$= \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} . V e^{\mu/\tau}$$

$$= -\frac{\Omega}{\tau} \qquad ...(6)$$

[using eqn. (6)]

This gives

$$\Omega = -\bar{n}\tau. \qquad ...(7)$$

Substituting this value in eqn. (6), we get

$$-\bar{n}\,\tau = -\tau e^{\mu/\tau} . \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} . V$$

This gives

$$e^{-\mu/\tau} = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} . \frac{V}{\bar{n}}$$

or

$$\mu = -\tau \log\left[\left(\frac{2\pi m\tau}{h^2}\right)^{3/2} . \frac{V}{\bar{n}}\right]$$

⇒

$$\mu = -\tau \log\left(\frac{f}{n}\right) \qquad ...(8)$$

[using (3)]

**Entropy.** This statistical entropy σ is given by

$$\sigma = -\left(\frac{\partial\Omega}{\partial\tau}\right)_{V,\mu} \qquad \text{[Refer eqn. (16) of section 7.15]}$$

$$= \frac{\partial}{\partial\tau}\left[\tau e^{\mu/\tau} \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\right]_{V,\mu}$$

$$= \left(\frac{2\pi m}{h^2}\right)^{3/2} . V \frac{\partial}{\partial\tau} [\tau^{5/2} e^{\mu/\tau}]_\mu$$

$$= \left(\frac{2\pi m}{h}\right)^{3/2} . V\left[-\frac{\mu}{\tau^2} e^{\mu/\tau} \tau^{5/2} + \frac{5}{2} \tau^{3/2} e^{\mu/\tau}\right]$$

$$= \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} . V . e^{\mu/\tau}\left[\frac{5}{2} - \frac{\mu}{\tau}\right] \qquad ...(9)$$

From eqn. (8), we have

$$\frac{\mu}{\tau} = -\log\left(\frac{f}{\bar{n}}\right) = \log\left(\frac{\bar{n}}{f}\right)$$

Substituting value of μ/τ from above eqn. in (9), we get

$$\sigma = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} . V e^{\log(\bar{n}/f)}\left[\frac{5}{2} + \log\frac{f}{\bar{n}}\right]$$

$$= \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} . V . \frac{\bar{n}}{f}\left[\frac{5}{2} + \log\left(\frac{f}{\bar{n}}\right)\right]$$

$$=\left(\frac{2\pi m\tau}{h^2}\right).V.\bar{n}\frac{1}{V}\cdot\left(\frac{2\pi m\tau}{h^2}\right)^{-3/2}\left[\frac{5}{2}+\log\left\{\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\frac{V}{\bar{n}}\right\}\right] \quad \text{using eqn. (3)}$$

$$=\bar{n}\left[\log\left\{\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\cdot\frac{V}{\bar{n}}\right\}+\frac{5}{2}\right] \qquad ...(10)$$

Therefore thermodynamical entropy $S$ is given by

$$S=k\sigma$$

$$=\bar{n}k\log\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\cdot\frac{V}{\bar{n}}\right]+\frac{5}{2}\bar{n}k. \qquad ...(11)$$

This is famous *Sakur-Tetrode equation* for the entropy of a perfect gas. This is in agreement with eqn. (14) of section 7.5. for microcanonical ensemble and eqn. (10) of section 7.11 for canonical ensemble.

**Internal Energy :** From eqn. (13b) of section 7.15 we have

$$U=\Omega+\tau\sigma+\mu\bar{n}$$

Now substituting value of $\Omega$ from (6) and $\sigma$ from (9) in above eqn., we get

$$U=-\tau\, e^{\mu/\tau}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}.V+\tau.\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}.V.e^{\mu/\tau}\left(\frac{5}{2}-\frac{\mu}{\tau}\right)+\mu\bar{n}$$

$$=\tau\, e^{\mu/\tau}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}.V\left\{\frac{3}{2}-\frac{\mu}{\tau}\right\}+\mu\bar{n}$$

From (7a), $\bar{n}=e^{\mu/\tau}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}V$, therefore

$$U=\bar{n}\tau\left\{\frac{3}{2}-\frac{\mu}{\tau}\right\}+\mu\bar{n}$$

$$=\frac{3}{2}\bar{n}\tau=\frac{3}{2}\bar{n}kT, \qquad ...(12)$$

which is well known relation for the *internal energy of a perfect gas.*

## SOLVED EXAMPLES

**Ex. 7.** *Show that for a perfect gas represented by a grand canonical ensemble, the probability of finding the subsystem with n atoms is given by Poisson distribution.*

$$\omega(n)=\frac{1}{n!}(\bar{n})^n\, exp.(-\bar{n})$$

*where $\bar{n}$ is the mean number of atoms present.* ***(Meerut 1989)***

**Solution.** The probability of finding the subsystem with $n$ atoms in the grand canonical ensemble is

$$\omega(n)=\int\rho(E,n)\,d\Gamma(n) \qquad \text{[Refer eqn. (11) of section 7.14]}$$

For a classical perfect gas

$$\rho(E,n)=\frac{1}{n!\,h^{3n}}.e^{(\Omega+n\mu-E)/\tau}$$

Therefore

$$\omega(n)=\frac{1}{n!\,h^{3n}}.e^{(\Omega+n\mu-E)/\tau}\,d\Gamma(n)$$

$$=e^{(\Omega+n\mu)/\tau}.\frac{1}{n!\,h^{3n}}\int e^{-E(n)/\tau}\,d\Gamma(n)$$

$$=e^{(\Omega+n\mu)/\tau}Z_n$$

where $Z_n=\frac{1}{n!\,h^{3n}}\int e^{-E(n)/\tau}\,d\Gamma(n)=\frac{f^n}{n!}$ is the canonical partition function

Thus

$$\omega(n)=e^{(\Omega+n\mu)/\tau}.\frac{f^n}{n}.$$

But

$$\frac{\Omega}{\tau}=-\bar{n} \qquad \text{[from eqn. (7) of section 7.16]}$$

and

$$\frac{\mu}{\tau}=-\log\left(\frac{f}{\bar{n}}\right) \qquad \text{[from eqn. (8) of section 7.16].}$$

Therefore

$$\omega(n)=\exp(-\bar{n}).\exp.\left\{-n\log\frac{f}{\bar{n}}\right\}\frac{f^n}{n!}$$

$$=\exp(-\bar{n})\exp\left\{\log\left(\frac{\bar{n}}{f}\right)^n\right\}\frac{f^n}{n!}$$

$$=\frac{1}{n!}\{\exp(-\bar{n})\}\left(\frac{\bar{n}}{f}\right)^n.f^n$$

$$=\frac{1}{n!}(\bar{n})^n\exp(-\bar{n}). \qquad ...(1)$$

## 7.18 Comparison of Various Ensembles

Now we know that all the three distributions : microcanonical, canonical and grand canonical, are applicable to the determination of the thermodynamic functions like entropy, internal energy, Helmholtz free energy etc. of a system. According to our convenience we may use any of the three methods for the determination of the thermodynamic poroperties of a system. However in practice the microcanonical ensemble is the most inconvenient and so is seldom used : while the grand canonical is the most convenient and so is commonly used. The three ensembles are already compared in brief in section 6.3. by figs. 7.1, 7.2 and 7.3. The summary of which is given by below :

In *microcanonical ensemble* the individual systems are separated by rigid, impermeable and well insulated walls so that neither the energy nor the number of particles can be exchanged between the systems; thus the energy as well as the number of particles in each of the systems is always constant.

In the *canonical ensemble* the individual systems are separated by rigid, impermeable and diathermal walls so that the energy and not the number of particles can be exchanged between the systems, thus the number of particles in each system is constant; but fluctuations in the energy of the individual system take place.

In the *grand canonical ensemble* the individual systems are separated by rigid, impermeable and diathermal walls so that the energy as well as the number of particles can be exchanged between the systems; thus the grand canonical ensemble allows the fluctuations in the energy as well as the number of particles.

A further comparison of three ensembles is shown in the table given below :

| S. No. | Property | Microcanonical Ensemble | Canonical Ensemble | Grand Canonical Ensemble |
|---|---|---|---|---|
| 1. | Contact with surroundings | None | Thermal | Thermal and material |
| 2. | Fluctuations in $n$ and $E$ | Flutuations do not take place in energy and number of particles of the individual systems, *i.e.*, the energy and number of particles of individual systems are constant. | Fluctuations take place in energy; but not in the number of particles of the individual systems, *i.e.*, the number of particles of individual systems is constant, but energy fluctuates. | Fluctuations take place in energy as well as the number of particles of the individual systems. Thus neither energy nor number of particle of individual systems is constant. |
| 3. | Probability distribution | $\rho(E) =$ constant in the range $E$ to $E + \delta E$ $= 0$ outside this energy range | $\rho(E) = Ae^{-E/kT}$ | $\rho(n) = \exp[\Omega + n\mu - E)/kT]$ |
| 4. | Partition function | $\Delta T$ or $\Omega(E, \delta E)$ | $Z = \int e^{-E/kT}\, dT$ | $Z = \Sigma\, e^{\mu n/kT} \int e^{-E/kT}\, d\Gamma(n)$ |
| 5. | Thermodynamic function | $-TS = -kT \log \Omega(E_0, \delta E)$ | $F = -kT \log Z$ | $\Omega = -pV - kT \log Z$ |
| 6. | Internal energy | $U = \frac{3}{2} nkT$ | $U = \frac{3}{2} nkT$ | $U = \frac{3}{2} \bar{n} kT$ |
| 7. | Entropy of perfect gas | $S = nk \log \left\{ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \times \left( \frac{V}{n} \right) \right\} + \frac{5}{2} nk$ | $S = nk \log \left\{ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \times \left( \frac{V}{n} \right) \right\} + \frac{5}{2} nk$ | $S = \bar{n}k \log \left\{ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \times \left( \frac{V}{n} \right) \right\} + \frac{5}{2} nk$ |

## 7.19 Separation of Partition Functions

For a dimensionless molecule the entire energy is due to its translational motion. However, if it has definite dimensions, then the total energy will have also the contributions from the rotational and vibrational motion of the molecule and the motion of its electrons along with the translational motion.

Therefore, it is desirable to separate the partition function for such a molecule into its components each depending on only one type of degree of freedom.

If $\varepsilon_t, \varepsilon_r, \varepsilon_v, \ldots$ represent the contributions to the energy corresponding to the translational, rotationa, vibrational motions etc., then the total energy of the molecule may be expressed as

$$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v + \ldots \qquad \ldots(1)$$

Further, the statistical weight $g$ of the molecule is equal to the product of the statistical weights for different forms of energy, *i.e.*,

$$g = g_t g_r g_v \ldots \qquad \ldots(2)$$

The subscripts $t, r$ and $v$ refer to the translational rotational and vibrational modes respectively.

According to section 7.6, the partition function for a molecules is

$$Z = \sum_i g_i e^{-\varepsilon_i/kT}. \qquad \ldots(3)$$

In this case this can be written as

$$Z = \sum_t \sum_r \sum_v \ldots g_t g_r g_v \exp[-(\varepsilon_t + \varepsilon_r + \varepsilon_v + \ldots)/kT] \qquad \ldots(4)$$

Now, assuming that the different types of energies are independent to each other, we may write equation (4) as

$$Z = \sum_i g_t e^{-\varepsilon_t/kT} \sum_r g_r e^{-\varepsilon_r/kT} \sum_v g_r e^{-\varepsilon_v}/kT \ldots$$

$$= Z_t Z_r Z_v \ldots,$$

where $Z_t, Z_r, Z_v, \ldots$ refer to the partition functions corresponding to translational and vibrational modes respectively.

Thus we see that *if the energy of a molecule is sum of independent contributions arising from translation, rotation, vibration etc., then the total partition function can be written as the product of separate partition functions :*

This method of separating the partition functions when two factors are independent of each other is most convenient and is generally used.

## 7.20 Partition Functions and Thermodynamic Properties of a Diatomic Molecule

In general a diatomic molecule is capable of performing the following types of motion :

1. The *translational motion* of the molecules as a whole which has three degrees of freedom.
2. The *rotational motion* of the moleculs as a whole. The molecule as a whole may rotate about an axis passing through the centre of mass. As only two such directions perpendicular to the line joining the atoms of the molecule are possible, the rotational motion has two degrees of freedom.
3. The *vibrational motion* of the atoms of the diatomic molecule along the line joining them. Thus, the vibrational motion has only one degree of freedom.
4. The *motion of the electrons* around the two nuclei of the diatomic molecule.
5. The *nuclear spin.*

The last two motions, *i.e.*, the electronic motion and the nuclear spin do not usually occur at ordinary temperatures. When the spacing $\Delta E$ between the energy levels around the mean energy $\bar{E}$ is small compared to the thermal energy $kT$, then the variation of energy may be considered as continuous and hence the classical treatment holds; but when $\Delta E >> kT$, then variation of energy is discrete and consequently classical treatment fails and quantum treatment is applicable. Here we shall use the classical description only.

Now, considering the translational, rotational and vibrational energies to be independent of each other, the *total partition function* $Z$ and *total energy* $\varepsilon$ of the diatomic molecule at ordinary temperature may be written as

$$Z = Z_t Z_r Z_v, \qquad \ldots(1)$$

and

$$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v, \qquad \ldots(2)$$

where the suffixes $t, r$ and $v$ refer to the translational, rotational and vibrational motion respectively.

**1. Translational motion.** In translational motion the number of degrees of freedom is only three whether the molecule is monoatomic or polyatomic. Hence the translational partition function for diatomic molecule is same as calculated for a monoatomic molecule. Considering **canonical ensemble, the translational partition function is**

$$Z_t = \frac{f_t^n}{n\,!}, \qquad \text{...(3)}$$

where

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

and $n$ is number of molecules in the gas.

**For a single diatomic molecule $n = 1$, therefore canonical partition function for a single molecule is**

$$Z_t = f_t = V \cdot \left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \frac{V}{\lambda^3}, \qquad \text{...(4)}$$

where $\lambda = \dfrac{h}{(2\pi mkT)^{1/2}}$ is the thermal de-Broglie wavelength associated with the molecule.

**The translational energy of a single diatomic molecule is**

$$\begin{aligned} E_t &= \tau^2 \frac{\partial}{\partial \tau} \log (z_t) \\ &= kT^2 \frac{\partial}{\partial T} \log \left[ V \cdot \left(\frac{2\pi mkT}{h^2}\right)\right]^{3/2} \\ &= \tfrac{3}{2} kT. \end{aligned}$$

**The total translational energy of $n$ diatomic molecules is**

$$\begin{aligned} E_t &= \tau^2 \frac{\partial}{\partial \tau} (\log Z_t) = kT^2 \frac{\partial}{\partial T} (\log Z_t) \\ &= kT^2 \frac{\partial}{\partial T}\left[ \log \left\{ \frac{V^n}{n\,!} \left(\frac{2\pi mkT}{h^2}\right)^{3n/2} \dots \right\}\right]_V \end{aligned}$$

On simplifying and using stirling approximation

$$\log n\,! = n \log n - n,$$

we get

$$U_t = \bar{E}_t = \frac{3}{2} nkT. \qquad \text{...(5)}$$

The specific heat due to translational motion at constant volume can be estimated as

$$(C_V)_t = \left(\frac{\partial E_t}{\partial T}\right)_V = \frac{3}{2} nk. \qquad \text{...(6)}$$

Similarly, the entropy contribution due to translational motion is

$$S_t = k \log Z_t + \frac{E_t}{T} \qquad \text{[refer equation (17) of section 7.10]}$$

$$= k \log \frac{f_t^{\,n}}{n\,!} + \frac{3}{2} nk.$$

Using again Stirling approximation, we get

$$\begin{aligned} S_t &= k\,[\log f_t^n - n \log n + n] + \tfrac{3}{2} nk. \\ &= nk \log \frac{f_t}{n} + \frac{5}{2} nk. \qquad \text{...(7)} \end{aligned}$$

**2. Rotational Motion :** The classical partition function, taking into account the indistinguishability of particles in canonical distribution is given by

$$Z = \frac{1}{n\,!\,h^f} \int \dots \int e^{-\varepsilon (p,\, q)/kT}\, dq_1 \dots dq_f\, dp_1 \dots dp_f. \qquad \text{...(8)}$$

Since a diatomic molecule has only two degrees of freedom ($f = 2$) of rotation, therefore for a single diatomic molecule ($n = 1$); the rotational partition function is expressed as

$$z_r = f_r = \frac{1}{h^2} \iiiint e^{-\varepsilon_r (p,\, q)/kT}\, d\theta\, d\phi\, dp_\theta\, dp_\phi, \qquad \text{...(9)}$$

where $\theta$, $\phi$ are spherical co-ordinates representing the direction of axis of rotation.

The energy of the rotation in polar co ordinates can be expressed as

$$\varepsilon_r (p, q) = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta}\right), \qquad \text{...(10)}$$

where $I$ is the moment of inertia of the diatomic molecule about the axes of rotation.

As both the axes of the molecule are symmetrical therefore $I$ will be same in both the cases.

Substituting value of rotational energy from (10) and writing the limits of integration, the rotational partition function (9) can be expressed as

$$z_r = \frac{1}{h^2} \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_{-\infty}^{+\infty} e^{-p_\theta^2/2IkT}\, dp_\theta \int_{-\infty}^{+\infty} e^{-p_\phi^2/2IkT \sin^2 \theta}\, dp_\phi. \qquad \text{...(11)}$$

Now, using the standard definite integral

$$\int_{-\infty}^{+\infty} \varepsilon^{-ax^2}\, dx = \sqrt{\left(\frac{\pi}{a}\right)} \qquad \text{...(12)}$$

equation (11) may be written as

$$\begin{aligned} z_r &= \frac{1}{h^2} \int_0^\pi d\theta \int_0^{2\pi} d\phi \,.\, (2\pi IkT)^{1/2} \,.\, (2\pi IkT \sin \theta)^{1/2} \\ &= \frac{2\pi IkT}{h^2} \int_0^\pi \sin \theta\, d\theta \int_0^{2\pi} d\phi \\ &= \frac{2\pi IkT}{h^2} \cdot 4\pi = \frac{8\pi^2 IkT}{h^2} = \frac{2IkT}{\hbar^2}. \qquad \text{...(13)} \end{aligned}$$

**The rotational energy per diatomic molecule** can be expressed

or

$$\begin{aligned} \varepsilon_r &= kT^2 \left[\frac{\partial}{\partial T} (\log z_r)\right]_V \\ &= kT^2 \left\{\frac{\partial}{\partial T} \log_e \left(\frac{2IkT}{\hbar^2}\right)\right\}_V \\ &= kT^2 \left[\frac{\partial}{\partial T} \left\{ \log_e \left(\frac{2Ik}{\hbar^2}\right) + \log_e T \right\}\right] \qquad \text{...(14)} \\ &= kT. \end{aligned}$$

Therefore, *the rotational energy for an assembly of n diatomic molecule is*

$$\overline{E}_r = nkT. \qquad \text{...(15)}$$

The *specific heat constant volume* due to rotational motion

$$(C_V)_r = \left(\frac{\partial \overline{E}_r}{\partial T}\right)_V = nk. \qquad \text{...(16)}$$

For a perfect gas of $n$ diatomic molecules, *the total rotational partition function* is

$$Z_r = (z_r)^n = \left(\frac{2IkT}{\hbar^2}\right)^n. \qquad \text{...(17)}$$

The *entropy contribution* due to rotational motion is

$$\begin{aligned} S_r &= k \log Z_r + \frac{\overline{E}_r}{T} \\ &= k \log \left(\frac{2IkT}{\hbar^2}\right)^n + nk \\ &= nk \log \frac{2IkT}{\hbar^2} + nk. \end{aligned} \qquad \text{...(18)}$$

**3. Vibrational Motion :** We know that the vibrational energy levels have large separations and hence the variation of energy not be treated as continuous. As a result the classical description is not appropriate for vibrational motion. As the diatomic molecule can vibrate only along its axis, the vibrational motion possessess only one degree of freedom. Therefore, for the calculation of vibrational partition function under the classical limit, we may treat the diatomic molecule as one dimensional harmonic oscillator.

Classically the energy of one dimensional harmonic oscillator is given by

$$\varepsilon_v(p, q) = \frac{p^2}{2m} + \frac{1}{2} Kq^2. \qquad \text{...(19)}$$

where $K$ is force constant defined as the restoring force per unit displacement.

For one degree of freedom $f = 1$, therefore, vibrational partition function for a single diatomic molecule ($n = 1$) is given by

$$\begin{aligned} z_v = f_v &= \frac{1}{h} \int\int e^{-\varepsilon_v(p, q)/kT} \, dp \, dq \\ &= \frac{1}{h} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-[(p^2/2m) + \frac{1}{2} Kq^2]/kT} \, dp \, dq \\ &= \frac{1}{h} \int_{-\infty}^{+\infty} e^{-p^2/2mkT} \, dp \int_{-\infty}^{+\infty} e^{-Kq^2/2kT} \, dq \end{aligned} \qquad \text{...(20)}$$

Now again using standard definite integral in (13), we get

$$\begin{aligned} z_v &= \frac{1}{h} \cdot (2\pi mkT)^{1/2} \cdot \left(\frac{2\pi kT}{K}\right)^{1/2} \\ &= \frac{kT}{h} \cdot 2\pi \sqrt{\left(\frac{m}{K}\right)}. \end{aligned}$$

As natural frequency of vibration ν one dimensional harmonic oscillator is given by

$$\nu = \frac{1}{2\pi} \sqrt{\left(\frac{K}{m}\right)} \qquad \text{...(21)}$$

$$\therefore \quad Z_v = \frac{kT}{h\nu} \qquad \text{...(22)}$$

The vibration energy per diatomic molecule is given by

$$\begin{aligned} \varepsilon_v &= kT^2 \left[\frac{\partial}{\partial T} (\log_e z_v)\right]_V \\ &= kT^2 \left[\frac{\partial}{\partial T} \left\{\log_e \left(\frac{kT}{h\nu}\right)\right\}\right] \\ &= kT. \end{aligned} \qquad \text{...(23)}$$

Therefore, the mean vibrational energy for essembly of $n$ diatomic molecules is

$$\overline{E}_v = nkT. \qquad \text{...(24)}$$

The specific heat at constant volume due to vibrational motion is

$$(C_V)_v = \left(\frac{\partial \overline{E}_v}{\partial T}\right)_V = nk. \qquad \text{...(25)}$$

For a perfect gas of $n$ diatomic molecules, the total vibrational partition function is

$$Z_v = \left(\frac{kT}{h\nu}\right)^n \qquad \text{...(26)}$$

The entropy contribution due to vibrational motion nis

$$\begin{aligned} S_v &= k \log Z_v + \frac{\overline{E}_v}{T} \\ &= k \log \left(\frac{kT}{h\nu}\right)^n + nk. \\ &= nk \log \left(\frac{kT}{h\nu}\right) + nk. \end{aligned} \qquad \text{...(27)}$$

Therefore, *the total partition function* $Z$ of a gas of $n$ diatomic molecules at ordinary temperature will be

$$\begin{aligned} Z &= Z_t \cdot Z_r \, Z_v \\ &= \frac{f_t^n}{n!} \cdot \left\{\frac{2IkT}{\hbar^2}\right\}^n \left\{\frac{kT}{h\nu}\right\}^n \end{aligned} \qquad \text{...(28)}$$

The *total energy* of an assembly of $n$ diatomic molecules will be given by

$$\begin{aligned} \overline{E} &= \overline{E}_t + \overline{E}_r + E_v \\ &= \frac{3}{2} nkT + nkT + nkT \\ &= \frac{7}{2} nkT. \end{aligned} \qquad \text{...(29)}$$

For a *single diatomic molecule* the mean energy is

$$\overline{\varepsilon} = \frac{7}{2} nkT \qquad \text{(since here } n = 1\text{). ...(30)}$$

The *total specific heat of an assembly of n* diatomic molecules at constant volume is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{7}{2} nk \qquad \text{...(31)}$$

**Note :** Here we have not considered the electronic and nuclear spin motion of the diatomic molecules which becomes appreciable at very high temperatures. We shall further treat this problem quantum mechanically in next chapter.

## 7.21 Theory of Imperfect Gases; Virial Coefficients

The equation of state of an ideal gas can often be applied to actual gases with sufficient accuracy. This approximation may, however, be inadequate and it is then necessary to take into account the deviations of the behaviour of an actual gas from that of a perfect gas. The basic difference in the behaviour of the perfect gas and actual gases is due to the fact that in contrast to the perfect gas particles, the actual gas particles experience the forces of mutual interaction. These forces of mutual interaction result in the potential energy of the gas and therefore, unlike to perfect gas where the petential energy is taken to be zero owing to the absence of any interaction between the gas particles, the total energy of imperfect (or actual) gas will include *kinetic energy* of the particles.

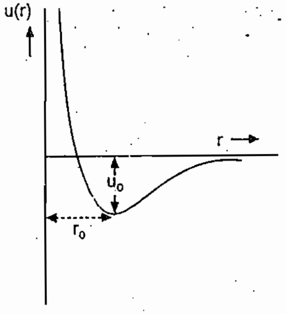
To simplify the calculations, let us consider a mono-atomic actual gas consisting $N$ particles each of mass $m$, contained in a vessel to volume $V$ at a temperature $T$. The motion of the particles of the gas may be treated classically, so that the total energy of this assembly can be expressed as

$$E(p,q) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(q), \qquad \text{...(1)}$$

where the first term is the kinetic energy of the gas particles and $U$ is the potential energy of their mutual interaction. In a monoatomic gas $U$ is a function only of the distance between the atoms. Let the potential ~~energy $U(q)$ be written as a sum~~ of terms each depending only on the distance apart $(r_i)$ of the two molecules $i$ and $j$. This assumes that the potential energy of three molecules, all close together, is the same as that of their independent pairs which can be formed of the group of three. In the assembly of $N$ molecules there are $\frac{1}{2}N(N-1)$ different pairs which can be formed. So this assumption is that $U(q)$ is the sum of $\frac{1}{2}N(N-1)$ terms namely,

$$U(q) = \sum_{i=j}^{N} \sum_{j=1}^{(N-1)} u(r_{ij}), \qquad \text{...(2)}$$

where $u(r_{ij})$ is the potential energy of the pair of molecules $i$ and $j$ as a function of their distance apart $r_{ij}$.



(Fig. 7.10)

The function $u(r)$ has the same general characteristic form for all neutral, chemically saturated molecules. It is zero for large values of argument $r$, decreasing to a minimum negative value at a distance, $r$ of a few Angstrom units and then decreasing rapidly as $r$ decreases to very high positive values for smaller distances of approach. Thus, if the potential energy $u(r)$ of interaction between a pair of molecules is plotted against $r$, we obtain a curve shown in fig. 7.10. For the present it is desirable to assume only that $u(r)$ decreases for large values of $r$ more rapidly than the inverse fifth power of the distance *i.e.*, for large values of $r$ we assume the power law $\sim r^{-p}$ such that $p > 5$.

The classical partition function of this assembly of $n$ molecules is written as

$$Z = \frac{1}{N!\,h^{3N}} \int \dots \int e^{-E(p,q)/kT}\, dq_1 \dots dq_{3N}\, dp_1 \dots dp_{3N} \qquad \text{...(3)}$$

Here the factor $N!$ is included to account for indistinguishability of the particles.

Using equation (1), we get

$$Z = \frac{1}{N!\,h^{3N}} \int \dots \int e^{-\left[\left\{\Sigma \frac{p_i^2}{2m} + U(q)\right\} / kT\right]} dq_1 \dots dq_{3N}\, dp_1 \dots dp_{3N}$$

$$= \frac{1}{N!\,h^{3N}} \int \dots \int e^{-\sum_i p_i^2/2mkT}\, dp_1 \dots dp_{3N} \int \dots \int e^{-U(q)/kT}\, dq_1 \dots dq_{3N}$$

$$= \frac{1}{N!\,h^{3N}} \left\{ \int_{-\infty}^{+\infty} e^{-p_i^2/2mkT}\, dp_i \right\}^{3N} \int \dots \int e^{-U(q)/kT}\, dq_1 \dots dq_{3N}$$

$$= \frac{1}{N!\,h^{3N}} \{(2\pi mkT)^{1/2}\}^{3N} \int \dots \int e^{-U(q)/kT}\, dq_1 \dots dq_{3N} \dots \qquad \text{...(4)}$$

Since the standard definite integral is

$$\int_{-\infty}^{+\infty} e^{-ax^2}\, dx = \sqrt{\left(\frac{\pi}{a}\right)}$$

Equation (4) may be written as

$$Z = \frac{1}{N!\,h^{3N}} (2\pi mkT)^{3N/2}\, Z_q, \qquad \text{...(5)}$$

where

$$Z_q = \int \dots \int e^{-U(q)/kT}\, dq_1 \dots dq_{3N}$$

$$= \int \dots \int e^{-U(q)/kT}\, d\tau_1 \dots d\tau_N, \qquad \text{...(6)}$$

where $d\tau_i = dx_i\, dy_i\, dz_i$.

The integral (6) depends upon the configuration of the molecules and hence is called the *configuration integral*.

Equation (5) represents the general expression for the partition function of an assembly of actual gas molecules. The form of the partition function $Z$ depends upon the configuration integral $Z_q$.

Substituting value of $U(q)$ from equation (2) in (6), we get

$$Z_q = \iint \exp\left( + \left\{ \sum_{i=j}^{N} \sum_{j=1}^{N} u(r_{ij}) \right\} \Big/ kT \right) d\tau_1 \dots d\tau_N. \qquad \text{...(7)}$$

Obviously the exponent of the integrand in above equation is sum of terms and then the integrand it self is a product. However the co-ordinates of two molecules occur in each term of the product and the co-ordinates of each molecule occur in $(N-1)$ different terms of the product. The complete integral is not be written as a product of integral like momenta integrals. We may write

$$e^{-U(q)/kT} = \prod_{N > i > j \geq 1} e^{-u(r_{ij})/kT} \qquad \text{...(8)}$$

Each term $e^{-u(r_{ij})/kT}$ approaches unity for large values of argument $r_{ij}$ for which $u(r_{ij})$ approaches zero.

Thus we may write

$$e^{-u(r_{ij})/kT} = (! + f_{ij}), \qquad \text{...(9)}$$

where the function $f(r_{ij}) = f_{ij}$ approaches zero for large values of $r_{ij}$,

Now equation (8) may be written as

$$e^{-U(q)/kT} = \prod_{N \ge i > j \ge 1} (1 + f_{ij}). \qquad \text{...(10)}$$

This product may be expanded into a sum of terms

$$e^{-U(q)/kT} = 1 + \sum_{N \ge i > j \ge 1} f_{ij} + \Sigma\Sigma f_{ij} f_{i'j'}, \qquad \text{...(11)}$$

In this expansion each term becomes zero if the argument $r_{ij}$ is large for any pair $ij$ occurring as a function of $f_{ij}$ in the term.

Now, for simplicity we consider the interaction of two molecules at a time neglecting the interaction of the other molecules (it does not matter which two as they are all identical. This unjustifiable assumption means that we need to consider the contribution to the integral of the unity and the $\frac{1}{2}N(N-1)$ terms containing only one $f_{ij}$ neglecting all the other terms. Using eqn. (11) in (6) with this assumption, we get

$$Z_q = \int . \int \{1 + \sum_{N \ge i > i \ge} f_{ij}\} \, d\tau_1 \dots d\tau_N$$

$$= \int \int d\tau_1 \dots d\tau_N + \int \dots \int \sum_{N \ge i > i \ge 1} f_{ij} \, d\tau_1 \dots d\tau_N. \qquad \text{...(12)}$$

As the configuration space allowed to each molecule is the volume of the system, therefore first integration for all the $N$ molecules is $V^N$. For an assembly of $N$ molecules the total number of interaction terms of the type $f(r_{ij})$ is equal to $\frac{1}{2}N(N-1)$ and the integration over each of these terms give the same value.

Therefore equation (12) may be written as

$$Z_q = V^N + \frac{1}{2} N(N-1) \int \dots \int f_{ij} \, d\tau_1 \dots d\tau_N. \qquad \text{...(13)}$$

**Note.** If $u(r)$ were identically zero for all values of $r$, then the function $f_{ij}$'s would be zero and the value of integration in above equation would be zero. Thus configuration integral $Z_q$ would be equal to $V^N$. This is the case of a perfect gas. Therefore the partition function for the perfect gas is.

$$Z = V^N$$

As $f_{ij}$ depends only on the co-ordinates $x_i, y_i, z_i$ and $x_j, y_j, z_j$ of $i$th and $j$th molecules, the remaining $(N-2)$ terms inside the integral when integrated over the configuration space would give $V^{N-2}$, since for each term, containing one $f_{ij}$, integration over the configuration space of a molecule other than $i$ or $j$ leads to $V$ as a factor.

Therefore equation (13) now takes the form

$$Z_q = V^N + \frac{1}{2} N(N-1) V^{N-2} \int f_{ij} \, d\tau_i \, d\tau_j. \qquad \text{...(15)}$$

In order to evaluate the integral we shall use spherical coordinates in place of cartesian co-ordinates. Let the origin of spherical co ordinates be at the molecule $j$ and let us assume that the function $f_{ij}$ drops rapidly to zero as intermolecular distance $r_{ij}$ become large.

Now, the volume element

$$d\tau_i = dx_i \, dy_i \, dz_i = dr \, r \, d\theta \, . \, r \sin\theta \, d\theta = r^2 \, dr \sin\theta \, d\theta \, d\phi,$$

therefore, we may write

$$\int f_{ij} \, d\tau_i = \int\int\int f(r) \, r^2 \, dr \sin\theta \, d\theta \, d\phi$$

$$= \int_0^\infty f(r) \, r^2 \, dr \int_0^\pi \sin\theta \, d\theta \int_0^\pi d\phi$$

$$= \int_0^\infty f(r) \, r^2 \, dr \, . \, (2) \, . \, (2\pi)$$

$$= \int_0^\infty f(r) \, 4\pi r^2 \, dr = \beta \text{ (say)}. \qquad \text{...(16)}$$

The integral $\beta$ has the dimensions of volume and is independent of the position of molecule $j$, at least to within a few angstroms of the wall of the gas containing vessel, so that

$$\int\int f_{ij} \, d\tau_i \, d\tau_j = \int \beta \, d\tau_j = \beta V. \qquad \text{...(17)}$$

Now equation (15) may be written as

$$Z_q = V^N + \tfrac{1}{2} N(N-1) \, V^{N-2} . \beta V$$

$$= V^N \left\{ 1 + \frac{1}{2} N(N-1) \cdot \frac{\beta}{V} \right\}. \qquad \text{...(18)}$$

As $N$ is very large we may write $N(N-1) \approx N^2$ ; then equation (18) becomes

$$Z_q = V^N \left\{ 1 + \frac{1}{2} N^2 . \frac{\beta}{V} \right\} \qquad \text{...(19)}$$

Taking log of both sides, we get

$$\log Z_q = N \log V + \log \left( 1 + \frac{1}{2} N^2 \cdot \frac{\beta}{V} \right). \qquad \text{...(20)}$$

Now we make the unjustifiable assumption that $\frac{1}{2}N^2 . \beta/V$ is very small as compared to unity, so that

$$\log \left( 1 + \frac{1}{2} N^2 \frac{\beta}{V} \right) \approx \frac{1}{2} N^2 \frac{\beta}{V}$$

Then equation (20) takes the from

$$\log Z_q = N \log V + \frac{1}{2} N^2 \cdot \frac{\beta}{V}. \qquad \text{...(21)}$$

The mean pressure $P$ of the gas in terms of the partition function is expressed as

$$P = kT \left\{ \frac{\partial \log Z}{\partial V} \right\}_T \qquad \text{...(22)}$$

Substituting value of $Z$ from equation (5), we get

$$P = kT \frac{\partial}{\partial V} \log \left[ \left\{ \frac{1}{N! \, h^{3N}} \cdot (2\pi m \, kT)^{3N/2} \, Z_q \right\} \right]$$

$$= kT \left[ \frac{\partial}{\partial V} \left\{ \log \frac{1}{N! \, h^{3N}} \cdot (2\pi m \, kT)^{3N/2} \right\} \right]_T + kT \left[ \frac{\partial}{\partial V} (\log Z_q) \right]_T$$

As only volume dependent factor is the configuration integral $Z_q$ above equation takes the form

$$P = kT\left\{\frac{\partial}{\partial V}(\log Z_q)\right\}_T$$

Substituting the value of $\log Z_q$ from equation (21), we get

$$P = kT\left[\frac{\partial}{\partial V}\left\{N\log V + \frac{1}{2}N^2 \cdot \frac{\beta}{V}\right\}\right]_T \qquad \text{...(23)}$$

$$= kT\left\{\frac{N}{V} - \frac{1}{2}\frac{N^2\beta}{V^2}\right\} \qquad \text{...(24a)}$$

$$= \frac{NkT}{V}\left\{1 - \frac{1}{2}\frac{N\beta}{V}\right\} \qquad \text{...(24b)}$$

i.e.,

$$PV = NkT\left\{1 - \frac{1}{2}\frac{N\beta}{V}\right\} \qquad \text{...(24c)}$$

This equation is anologus to *Vander Walls's gas equation*. Keeping in mind the assumptions made in its derivation, it is applicable only to those cases where the force of interaction between the gas molecules is very small and decreases to zero rapidly with the increase in the interatomic distance.

Equation (24a) may be written in the form

$$\frac{P}{kT} = \frac{N}{V} - \frac{1}{2}\frac{N^2}{V^2}\cdot\beta$$

$$= n - \frac{1}{2}\beta \,.\, n^2. \qquad \text{...(25)}$$

where $n = (N/V)$ is the number of particles per unit volume.

Equation (25) is of the general form

$$\frac{P}{kT} = An + Bn^2 + Cn^3 + \ldots. \qquad \text{...(26)}$$

The expansion is called *Virial expansion* and the coefficient $A$, $B$, $C$, .... are called *Virial coefficients*.

Comparing equations (25) and (26), we get

$$A = 1 \text{ and } B = -\frac{\beta}{2} \qquad \text{...(27)}$$

Thus in this case the quantities 1 and $-\beta/2$ are the *first* and *second Virial coefficients* respectively.

**The interpretation of a and b in Vander Wall's equation.**

$$\left\{P + \frac{N^2a}{V^2}\right\}[V - Nb] = NkT. \qquad \text{...(28)}$$

Here $N$ is the number of molecules and $V$ the volume of the container. The term $\frac{N^2a}{V^2}$ accounts for the force of attraction between the gas molecules and the term $Nb$ accounts for the finite size of the gas molecules.

Expanding eqn. (28), we get

$$PV - NbP + \frac{N^2}{V}a - \frac{N^2ab}{V^2} = NkT$$

Neglecting the smaller term containing $ab$, we get

$$PV = NkT - \frac{N^2a}{V} + NbP.$$

Now substituting $P = \frac{NkT}{V}$ as a zeroth order approximation for the pressure, we obtain

$$PV = NkT - \frac{N^2a}{V} + Nb\cdot\frac{NkT}{V}$$

$$= NkT\left[1 + \frac{N}{V}\left\{b - \frac{a}{kT}\right\}\right] \qquad \text{...(29a)}$$

i.e.

$$\frac{P}{kT} = \frac{N}{V}\left[1 + \frac{N}{V}\left\{b - \frac{a}{kT}\right\}\right]$$

$$= n + \left\{b - \frac{a}{kT}\right\}n^2 \qquad \text{...(29b)}$$

Comparing above eqn. with (26), the first and second virial coefficients are

$$A = 1 \text{ and } B = \left\{b - \frac{a}{kT}\right\} \qquad \text{...(30)}$$

Equating second virial coefficient from (27) and (30) we get

$$-\frac{\beta}{2} = \left\{b - \frac{a}{kT}\right\}$$

i.e.

$$\frac{\beta}{2} = \frac{a}{kT} - b. \qquad \text{...(31)}$$

where from eqn. (16),

$$\beta = 4\pi\int_0^\infty f(r)\, r^2\, dr$$

$$= 4\pi\int_0^\infty (e^{-u(r)/kT} - 1)\, r^2\, dr. \qquad \text{...(31b)}$$

Eqn. (31) represents the functional relationship of $\beta$ on temperature $T$. The relationship depends on the particular form of potential $u(r)$. Now we shall find the form of $u(r)$ that satisfies equation (30):

The necessary and sufficient condition for the validity of eqn. (31) is that $u(r)$ should be positive and extremely large compared to $kT$ for some range of variable $r$ and that for all other values of $r$ in absolute magnitude should be much smaller than $kT$.

Case (i). When $u(r)$ is positive and much greater than $kT$, then $e^{-u/(r)\,kT} \to 0$, so according to equation (31), $\beta$ becomes independent of $T$. Then eqn. (31) yields

$$\frac{\beta}{2} = -b, \text{ i.e. } b = -\frac{\beta}{2} \qquad \text{...(32)}$$

Case (ii). When $|\, u(r)\,| << kT$, then

$$\varepsilon^{-u(r)/kT} \approx 1 - \frac{u(r)}{kT} \qquad \text{...(33)}$$

So

$$\beta = 4\pi\int_0^\infty\left\{-\frac{u(r)}{kT}r^2\right\}dr = -\frac{4\pi}{kT}\int_0^\infty u(r)\, r^2\, dr. \qquad \text{...(34)}$$

Thus $\beta$ is inversely proportional to the temperature $T$.

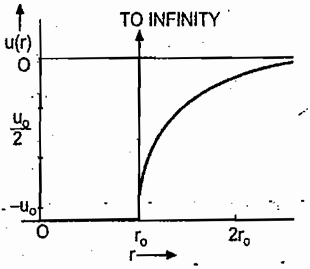
The simplest equation which satisfies the conditions of cases (i) and (ii) is rather a close approximation to the potential curve for real molecules and is written as

$$\left.\begin{aligned} u(r) &= \infty, 0 \le r \le r_0 \\ &= -u_0\left(\frac{r_0}{r}\right)^m, r_0 < r \le \infty \end{aligned}\right] \qquad \text{...(35)}$$

The form of the potential energy curve corresponding to above equation for $m = 6$ is shown in fig. 7.11.

The molecules obeying this potential law behave like hard spheres of radius $\frac{r_0}{2}$ and volume $V_0 = \frac{4}{3}\pi\left(\frac{r_0}{2}\right)^3 = \frac{\pi r_0^3}{6}$

When the centres of these two molecules are at a distance less than $r_0$ apart they repel each other infinitely. For distances greater than $r_0$ they attract each other and at $r = r_0$, they have a minimum negative potential energy $-u_0$. The value of $m$ which most closely approximates the true potential curve for most molecuels is about 6.



(Fig. 7.11) Plot of $u(r)$ against $r$ for $m = 6$.

For values of $r$ between 0 and $r_0$, $u(r) \to \infty$, so $e^{-u(r)/kT} \to 0$

Then
$$b = -\frac{\beta}{2} = -\frac{1}{2}\int_0^{r_0}(e^{-u(r)/kT} - 1)\, 4\pi r^2\, dr$$
$$= 2\pi\int_0^{r_0} r^2\, dr \qquad \text{...(36)}$$
$$= \frac{2}{3}\pi r_0^3 = 4V_0.$$

For values of $r$ between $r_0$ and infinity

$$e^{-u(r)/kT} - 1 \approx \frac{u(r)}{kT}$$

$$e^{-u(r)/kT} - 1 = \frac{u(r)}{kT} = \frac{1}{kT}\frac{u_0 r_0^m}{r^m} \qquad \text{using (35)}$$

Hence using (31) the constant $a$ may be defined as

$$a = \tfrac{1}{2}kT\beta = \tfrac{1}{2}\int_{r_0}^{\infty} 4\pi r^2 \,.\, u_0 r_0^m r^{-m}\, dr$$
$$= 2\pi r_0^m u_0 \int_{r_0}^{\infty} r^{-(m-2)}\, dr$$
$$= \frac{2\pi}{m-3}\cdot u_0 r_0^3 = \frac{12}{m-3}u_0 V_0. \qquad \text{...(37)}$$

Now from (36) and (37) it is obvious that Vander Waal's constant $b$ is four times the value $V_0$ of the molecules and constant $a$ is proportional to the volume of the molecules and also to the minimum potential $u_0$ with the proportionality constant $\left(\frac{12}{m-3}\right)$ dependent on the space of attractive potential determined by $m$. For actual gases both the constants $a$ and $b$ are found actually to be some what temperature dependent.

Many experimental investigations have been made to study the dependence of second virial coefficient $-\frac{1}{2}\beta$ in eqn. (25) on temperature for different gases. From these observations it becomes easy to choose a value for the potential $u(r)$ between the pair of molecules which when substituted in (23) gives the experimental value of $\beta$. Such determinations were made by Lennard-Jones who found the potential $u(r)$ in the form

$$u(r) = \frac{A}{r^n} - \frac{B}{r^m}, m < n.$$

Here $m$ is about 6 and $n$ takes the values from about 11 to 13. This is the best source of our experimental knowledge of the forces of interaction between chemically saturated molecules.

## 7.22 Determination of Virial Coefficients :

The general expansion of pressure $P$ terms of $n$, number of particles per unit volume, is written as

$$P = kT(An + Bn^2 + Cn^3 + \ldots), \qquad \text{...(1)}$$

where $A, B, C, \ldots$ are called first, second, third, ..... virial coefficients respectively.

Eqn. (25) of section (7.20) consists of first two terms of eqn. (1) with

$$A = 1 \text{ and } B = -\beta/2$$

The first term in the expansion (1) with $A = 1$ corresponds to an ideal gas *i.e.*, no interaction between molecules. The second term was obtained by taking into account the interaction between pairs of molecules. The subsequent terms must involve the interactions between groups of three, four etc., molecules. To determine the virial coefficients $J$, it is convenient to begin by calculating the thermodynamic potential $\Omega$. For an assembly of $N$ particles of monatomic gas the general expression for grand partition function is

$$\mathbf{Z} = e^{-\Omega/\tau} = \sum_{N=0}^{T} \frac{1}{N!\,h^3} e^{-\mu N/\tau}\; \overline{e^{-E_N(p,q)/\tau}\, d\Gamma(N)}. \qquad \text{...(2)}$$

The factor $N!$ is included to account for indistinguishability of the particles and the integration extends over whole phase space of the system of $N$ particles.

In the successive terms of the sum over $N$, the energy $E_N(p, q)$ has the following form :

For $N = 0$, $\qquad E_0(p, q) = 0$

For $N = 1$, the energy $E_1$ is simply the kinetic energy of atoms, *i.e.*,

$$E_1(p, q) = \frac{p^2}{2m}$$

For $N = 2$, the energy $E_2$ consists of the kinetic energy of atoms and the potential energy of their interaction *i.e.*,

$$E_2(p, q) = \sum_{i=1}^{n}\frac{p_i^2}{2m} + U_{12}$$

where $p_i$ is the momentum associated with $i^{th}$ degree of freedom and $U_{12}$ is the interaction energy of the two molecules.

Similarly for $N = 3$, we have

$$E_3(p, q) = \sum_{i=1}^{n}\frac{p_i^2}{2m} + U_{123}$$

Here $U_{123}$ is the interaction energy of three atoms and so on.

Now substituting these expressions in (2) and using the notation

$$\xi = \frac{e^{\mu/T}}{h^3}\int e^{-p^2/2m\tau}\, d^3p = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} e^{\mu/\tau}. \qquad \text{...(3)}$$

we get

$$\Omega = \tau \log \left\{ 1 + \xi V + \frac{\xi^2}{2!} \iint e^{-U_{12}/\tau} dV_1 \, dV_2 + \frac{\xi^2}{3!} \iiint e^{-U_{123}/\tau} dV_1 \, dV_2 \, dV_3 \ldots\ldots \right\}$$

Here each of the interaction energy terms $U_{12}$ ; $U_{123}$ .... is a function only of the distances between the atoms; hence by using the relative coordinates of atoms (relative to first atom, say), we reduce the multiplicity of integrals by entering a further factor $V$ ; thus

$$\Omega = -PV = -\tau \log \left[ 1 + \xi V + \frac{\xi^2 V}{2!} \right] e^{-U_{12}/\tau} dV_2 + \frac{\xi^3 V}{3!} \iint e^{-U_{123}/\tau} dV_2 \, dV_3 + \ldots \qquad \ldots(4)$$

Finally expanding this expression in powers of $\xi$, the resulting series can be written as

$$P = \tau \sum_{n=1}^{n} \frac{J_n}{n!} \xi^n, \qquad \ldots(5)$$

where
$$\left. \begin{aligned} J_1 &= 1, J_2 = \int (e^{-U_{12}/\tau} + 1) \, dV_2 \\ J_3 &= \iint (e^{-U_{123}/\tau} - e^{-U_{12}/\tau} - e^{-U_{13}/\tau} - e^{-U_{23}/\tau} + 2) \, dV_2 \, dV_3 \end{aligned} \right\} \qquad \ldots(6)$$

and so on.

The integrand in $J_n$ is appreciably different from zero only if $n$ atoms are close together *i.e.*, in a collision of $n$ atoms.

The thermodynamic potential $\Omega$ and the number of particles in a gas $(N)$ are related by

$$\begin{aligned} N &= -\left( \frac{\partial \Omega}{\partial \mu} \right)_{\tau, V} \\ &= V \left( \frac{\partial P}{\partial \mu} \right)_{\tau, V} \quad (\text{since } \Omega = -PV). \end{aligned} \qquad \ldots(7)$$

From equation (3), we have

$$\frac{\partial \xi}{\partial \mu} = \frac{\xi}{\tau} \qquad \ldots(8)$$

Now keeping in mind that $\xi$ is related to $P$, equation (7) may be written as

$$\begin{aligned} N &= V \cdot \left( \frac{\delta P \, \delta \xi}{\partial \xi \, \partial \mu} \right)_{\tau, V} = V \cdot \left( \frac{\partial P}{\partial \xi} \right)_{\tau, V} \cdot \frac{\xi}{\tau} \\ &= V\tau \sum_{n=1}^{\infty} \frac{J_n \, n \, \xi^{n-1}}{n!} \frac{\xi}{\tau} \\ &= V \sum_{n=1}^{\infty} \frac{J_n}{(n-1)!} \xi^n. \end{aligned} \qquad \ldots(9)$$

Equation (5) and (8) give in parametric form with parameter $\xi$ the relation between $P$, $V$ and $T$ *i.e.*, the equation of state of the gas. Eliminating $\xi$ we can obtain the equation of state in the form of series (1). Then by comparing the resulting series with (1) we can determine the virial coefficients. For example, in the first approximation eqns. (5) and (8) give $P = \tau\xi$ and $N = V\xi$.

Eliminating $\xi$, we get

$$P = N\frac{\tau}{V} = kT \cdot \frac{N}{V} = kTn = P, \qquad \ldots(10)$$

the pressure of the ideal gas.

Comparing this equation with (1), we get

**First virial coefficient** $A = 1$.

In the second approximation

$$P = \tau\xi \, (1 + \tfrac{1}{2} J_3 \, \xi) \text{ and } N = N\xi(1 + J_2 \, \xi).$$

Eliminating $\xi$ from these equations, we get

$$\begin{aligned} P &= \frac{N\tau}{V} - \frac{N^2 \tau}{2V^2} J_2 \\ &= \tau \left[ \frac{N}{V} - \frac{1}{2} J_2 \frac{N^2}{V^2} \right] = kT \, (n - \tfrac{1}{2} J_2 \, n^2) \end{aligned} \qquad \ldots(11)$$

Comparing this equation with (1), we get

**First virial coefficient,** $A = 1$.

**Second virial coefficient**

$$B = -\tfrac{1}{2} J_2 = -\tfrac{1}{2} \int [(e^{-U_{12}/\tau} - 1) \, dV_2] \qquad \ldots(12)$$

The virial coefficients are in agreement with those derived in second 7.20.

In the similar manner we may obtain the equation of state in the form of a series containing any desired number of terms and hence any desired virial coefficients.

## EXERCISES

### SHORT ANSWER QUESTIONS

1. What is meant by an ensemble. Give classification of ensembles. ***(Purvanchal 2006)***
2. What do you mean by microcanonical ensemble ?
3. What do you mean by Gibb's canonical ensemble ?
4. What do you mean by grand canonical ensemble ?
5. Compare microcanonical, canonical and grand canonical ensembles ?
6. State the conditions of equilibrium of subsystems.
7. State expression for entropy, internal energy anjd chemical potentials of a perfect gas using microcanonical ensemble.
8. What do you mean by partition function ? Write expression for translational partition function of a gas molecule.
9. Write expression for entropy, Helmholtz free energy, enthalpy and Gibb's potential in terms of partition function using canonical ensemble.
10. What is Gibb's paradox ? Explain it qualitatively.
11. Show that mean energy in terms of partition function is given by
$$\bar{\epsilon} = -\frac{\partial}{\partial \beta} \log Z \text{ where } \beta = \frac{1}{kT}$$
12. Write expressions for probability density for microcanonical, canonical and grand canonical ensembles.
13. Write partition functions in microcanonical, canonical and grand canonical ensembles.

14. Show that Helmholtz free energy

$$U = NkT^2 \frac{\partial (\log Z)}{\partial T}.$$

(Meerut 2005, 01)

15. State Boltzman's theorem connecting entropy and probability. Write Sucker Tetrode relation for the absolute value of entropy of an ideal monoatomic gas.

16. Show that the partition function $Z_{ij}$ of two independent systems '*i*' and '*j*' is given by
$Z_{ij} = Z_i \times Z_j$
where $Z_i$ and $Z_j$ are partition functions of systems *i* and *j* respectively. **(Mumbai 2002)**

## LONG ANSWER QUESTIONS

1. What do you mean by microcanonical essemble ? What are its implications ? Discuss analytical nature of a microcanonical ensemble representing a system of two independent free particles each of mass *m* and moving in one dimension on a line segment of length *l*. The energy of the system is *E*.
2. Discuss how statistical mechanics gives a physical picture of entropy. **(Meerut 2001)**
3. What do you mean by partition function ? Express Helmholtz's free energy and entropy in terms of the partition function. **(Kanpur 2002, Meerut 2004)**
4. Define partition function and show that
(a) $\bar{U} = -\frac{\partial \ln Z}{\partial \beta}$ (b) $S = \frac{\bar{U}}{T} + k \ln Z$ (c) $F = -kT \ln Z$
where $\bar{U}$ is average energy of a system in thermal equilibrium with heat bath, *S* is the entropy of system in heat bath, *F* is Helmholtz free energy. **(Mumbai 2003)**
5. Define partition function and calculate its value for an ideal monoatomic gas. Obtain expressions for pressure and entropy in terms of partition function. **(Rohilkhand 2004)**
6. (a) What do you mean by (i) thermal equilibrium, (ii) mechanical equilibrium and (iii) Particle equilibrium. Derive the condition for each of them. **(Meerut 2002)**
(b) Show that the particles tend to move from a region of higher chemical potential to lower chemical potential as the system approaches equilibrium. **(Meerut 1982)**
7. (a) What do you understand by statistical and thermal equilibria ? Give a brief account how statistical quantities are related to thermodynamical quantities ?
(b) Prove that the internal energy *U* of a system is given by

$$U = NkT^2 \frac{\partial \log Z}{\partial T},$$

where *Z* is the partition function of the system. **(Rohilkhand 1999)**
8. Describe how an expression for entropy is set up in statistical mechanics. Show how it has the same properties as the thermodynamical entropy. **(Meerut 2000)**
9. (a) Show that Helmholtz's free energy tends to a minimum in system at constant temperature and volume.
(b) Show that Gibb's free energy tends to a minimum in system at constant temperature and pressure.
10. Derive expressions for entropy, internal energy and chemical potential of a perfect gas in microcanonical ensemble.
11. What is Gibb's paradox ? How it has been resolved ?

12. Explain the drawbacks of simple time averages of thermodynamic parameters. How these are overcomed with ensemble averages ? **(Meerut 2006)**
13. How the statistical parameters are used to explain the thermodynamic parameters : entropy, enthalpy and Gibb's free energy. **(Meerut 2006)**
14. Define partition function and derive it for a system represented by a grand canonical ensemble. **(Meerut 2005)**
15. Derive an expression for the partition function for a system of free particles. Deduce Suckur-Tetrode relation using partition function. **(Kanpur 2006, 2002)**
16. (a) Define canonical ensemble and partition function. **(Meerut 1998)**
(b) Express the thermodynamical quantities–entropy, total energy. Gibb's free energy, Helmholtz's free energy, enthalpy, specific heat at constant volume in terms of the partition function.
(c) Calculate the entropy of a perfect monatomic gas. **(Meerut 1997)**
17. Give an account of Gibb's canonical ensemble. **(Meerut 1990)**
18. Consider a system that has only two accessible states, a ground state of energy zero and an excited state of energy *E*. If this system were in equilibrium with a heat both at temperature *E*, calculate the free energy, entropy and specific heat at constant volume. **(Meerut 1993)**
19. (a) State the prove Boltzmann's theorem connecting entropy and probability.
(b) Show that for an ideal monoatomic gas the absolute value of entropy is given by

$$S = Nk \log_e \left[ \frac{V}{Nh^3} (2\pi mT)^{3/2} e^{5/2} \right]$$

**(Agra 1996)**
20. Prove Boltzmann's theorem connecting entropy and probability. Calculate the entropy of a perfect gas using microcanonical ensemble. **(Agra 2002, Meerut 2006, 1997, 2004)**
21. Define the microcanonical ensemble. Use it to calculate the entropy a perfect gas. Show how the internal energy and equation of state for a perfect gas can be obtained from it ? **(Meerut 2005, 03, 01)**
22. (a) How does canonical ensemble differ from a microcanonical ensemble. **(Meerut 2002)**
(b) Derive an expression for the partition function of a canonical ensemble made up of ideal gas molecules. Use it to calculate the thermodynamical parameters like entropy free energy, pressure and chemical potential of the ensemble.
23. Establish the connection between statistical and thermodynamical quantities. Derive expressions for entropy, enthalpy, Helmholtz's free energy and Gibb's free energy in terms of statistical parameters. **(Meerut 2004, 1997)**
24. Show that in Boltzmann's statistics the Helmholtz's free energy plays the same role as the Gibb's free energy plays in classical statistics. **(Meerut 1994)**
25. Suppose we have an infinite column of classical gas consisting of *n* independent identical atoms of mass *m*, placed in a uniform gravitational field and at thermal equilibrium. Find – (i) the classical partition function. (ii) the mean energy per atom, (iii) the heat capacity per atom.
26. Using canonical distribution derive– (i) Maxwellian velocity distribution (ii) equipartition theorem.

27. (a) Show that for a perfect gas represented by a grand canonical ensemble, the probability of finding the sub-system of atoms given by Poisson distribution

$$\omega(n) = \frac{1}{n!}(\bar{n})^n \exp(-\bar{n})$$

where $\bar{n}$ is the mean number of atoms present. **(Meerut 2003, 2000)**

(b) Derive the grand canonical distribution for the case when there are several different kinds of molecules present.

28. Explain grand canonical ensemble. Write the partition function for the grand canonical ensemble. Use it to calculate the thermodynamical quantities–entropy, internal energy, and chemical potential per particle of a monoatomic perfect gas. **(Meerut 1986)**

29. Explain the concept of an ensemble. Distinguish clearly between canonical, micro-canonical and grand canonical ensembles. Apply it to the case of one dimensional oscillator. **(Rohilkhand 2004, 1997)**

30. Mention the drawbacks with the definition of thermodynamic entropy. How are these overcomed in the concept of statistical entropy ?

Derive the Sacker-tetrode equation for the entropy of a perfect gas. **(Meerut 2005)**

31. Deduce the relation between entropy and probability. Explain how it can be used to calculate the entropy of a monoatomic gas. **(Meerut 2005)**

32. Suppose the energy of a molecule is the sum of independent contribution arising from translation, rotation, vibration etc. Show that the total partition function can be written as the product of separate partition functions

$$Z = Z_{trans} Z_{rot} . Z_{vib} \ldots.$$ **(Rohilkhand 1999)**

33. Derive the expression for the classical partition function for an assembly of $n$ ideal diatomic molecules neglecting electronic and spin motion of the molecules. Hence derive the expression for entropy, internal energy and specific heat at constant volume of this assembly.

34. (a) Find the vibrational partition function for a diatomic molecule.

(b) Deduce an expression for partition function for a monoatomic molecule of a classical gas and show that entropy $S$ such as is

$$S = R \log Z + 3/2\, R.$$ **(Meerut 1990)**

35. Distinguish between three ensembles. Show that the density of distribution in a grand-canonical ensemble is

$$\rho = e^{-(\Omega + \mu N - E/\tau)}$$

where symbols wave using meanings. **(Meerut 1990)**

36. Discuss the important factors with which the classical theory of perfect gas failed for a real gas.

Derive the Virial equation for the theory of imperfect gas. **(Meerut 2005)**

37. (a) Give the theory of imperfect gases. Hence give interpretations of Vander Waals constants $a$ and $b$.

(b) How will you determine various Virial coefficients ? **(Meerut 1986, 85, 83)**

38. Write short on :

(i) Partition Function. **(Purvanchal 2005, Kanpur 2004; Meerut 1987)**

(ii) Ensemble and phase space.

(iii) Micro-canonical and canonical ensembles. **(Kanpur 2004)**

(iv) Grand canonical ensemble. **(Rohilkhand 2003)**

(v) Virial equation of imperfect gas **(Meerut 2006, 1996)**

(vi) Gibb's paradox. **(Kanpur 2005, 1986)**

## MULTIPLE CHOICE QUESTIONS : SELECT THE RIGHT CHOICE

1. A microcanonical ensemble is characterised by [$\rho(E) =$ density of distribution of phase points]

(a) $\rho(E) =$ constant throughout

(b) $\rho(E) =$ constant for $0 < E < E_1$ and 0 elsewhere

(c) $\rho(E) =$ constant for $E_1 < E < E_1 + \delta E_1$

(d) $\rho(E) = A\, e^{-E/kT}$

2. The relation between statistical entropy $\sigma$ and volume of phase space $\delta T$ accessible to system is

(a) $\sigma = C\delta T$  (b) $\sigma = \log_e \delta T$  (c) $\sigma = C(\delta T)^2$  (d) $\sigma = \dfrac{C}{\log_e \delta T}$

3. Keeping energy constant, the volume of a perfect gas of $\mu$-atoms is mode 10 times, the change in entropy will be

(a) $N$  (b) $2{\cdot}3026\, N$  (c) $\dfrac{N}{2{\cdot}3026}$  (d) 10

4. The condition of thermal equilibrium of two subsystems is

(a) Equality of temperature  (b) Equality of pressures

(c) quality of chemical potentials  (d) Equality of number of particles.

5. the condition of mechanical equilibrium is

(a) Equality of temperatures  (b) Equality of pressures

(c) Equality of chemical potentials  (d) Equality of all above

6. The condition of particle equilibrium is

(a) Equality of temperatures  (b) Equality of pressures

(c) Equality of chemical potentials  (d) Equality of all above

7. The condition of statistical equilibrium is

(a) Equality of temperatures  (b) Equality of pressures

(c) Equality of chemical potentials  (d) Equality of all above

8. Sackur Tetrode formula for entropy of a perfect gas is

(a) $S = nk \log_e\left[\dfrac{V}{nh^3}(2\pi mkT)^{3/2}\right]$  (b) $S = nk \log_e\left[\dfrac{V}{nh^3}(2\pi mkT)^{3/2} e^{3/2}\right]$

(c) $S = nk \log_e\left[\dfrac{V}{nh^3}(2\pi mkT)^{3/2} e^{5/2}\right]$  (d) $S = nk \log_e\left[\dfrac{V}{nh^3}(2\pi mkT)^{3/2}\right] + \dfrac{5}{2} nk.$

9. The partition function is defined as $Z =$

(a) $\sum_i g_i e^{-E_i/kT}$  (b) $\sum_i g_i e^{+E_i/kT}$  (c) $\sum_i \dfrac{g_i}{n_i!} e^{-E_i/kT}$  (d) $\sum_i \dfrac{g_i}{n_i!} e^{E_i/kT}$

**10.** The translational partition function for a gas molecule is

(a) $\frac{V}{h^3}\left(\frac{2\pi kT}{m}\right)^{3/2}$ (b) $\frac{V}{h^3}(2\pi mkT)^{3/2}$

(c) $\frac{V}{h^3}\left(\frac{2\pi kT}{m}\right)^{1/2}$ (d) $\frac{V}{h^3}(2\pi mkT)^{1/2}$

**11.** The entropy of assembly of $N$ molecules of an ideal gas is

(a) $S = Nk \log Z$ (b) $S = Nk \log Z + \frac{1}{2} Nk$

(c) $S = Nk \log Z + \frac{3}{2} Nk$ (d) $S = Nk \log Z + \frac{5}{2} Nk$

**12.** The mean energy $\bar{\varepsilon}$ in terms of partition function $Z$ is given by $(\bar{\varepsilon} = )$ where $\left(\beta = \frac{1}{kT}\right)$

(a) $k\frac{\partial}{\partial T}(\log Z)$ (b) $\frac{1}{k}\frac{\partial}{\partial T}(\log Z)$ (c) $\frac{\partial}{\partial \beta}\log Z$ (d) $-\frac{\partial}{\partial \beta}(\log Z)$

**13.** Gibb's paradox is that if systems are completely identical but distinguishable then for combined systems

(a) entropy is not additive (b) entropy is multiplicative

(c) entropy is additive (d) entropy becomes zero.

**14.** Gibb's parodox may be explained by taking weight of configuration

(a) $\Omega = \sum_i \frac{g_i^{ni}}{n_i!}$ (b) $\sum_i N!\frac{g_i^{n}}{n_i!}$ (c) $\Omega = \prod_i \frac{g_i^{ni}}{n_i!}$ (d) $\prod_i N!\frac{g_i^{ni}}{n_i!}$

**15.** Gibb's canonical ensemble is characterised by $\rho\,(E)$

(a) $\rho\,(E) = 0$ in the range $0 < E < E_1$ (b) $\rho\,(E) = A\,e^{-E/kT}$

(c) $\rho\,(E) = A\,e^{E/kT}$ (d) $\rho\,(E) = A\,\log_e \frac{E}{kT}$

**16.** For two subsystems in thermal contact with a heat reservoir, then for canonical ensemble. ($\rho$ = probability density)

(a) $\rho = \rho_1 + \rho_2$ (b) $\log \rho = \log \rho_1 + \log \rho_2$

(c) $\rho = \rho_1 - \rho_2$ (d) $\log \rho = \log \rho_1 - \log \rho_2$

**17.** The ensemble which allows the subsystems to allow exchange of energy as well as number of particles with a reservoir is called

(a) canonical ensemble (b) microcanonical ensemble

(c) grand canonical ensemble (d) fluctuating ensemble

**18.** The probability of finding subsystem with $n$ atoms of a perfect gas in grand canonical ensemble is ($\bar{n}$ is mean number of atoms present)

(a) $\omega\,(n) = \frac{1}{n!}(\bar{n})^n \rho^{-\bar{n}}$ (b) $\frac{1}{n!}\rho^{-\bar{n}}$ (c) $(\bar{n})^{n-1} e^{-\bar{n}}$ (d) $n!\,(\bar{n})^n e^{-\bar{n}}$

**19.** If $Z_1, Z_2, Z_3$ are independent partition functions a system, the total partition function of the combined system is

(a) $Z = Z_1 + Z_2 + Z_3$ (b) $Z = Z_1 \cdot Z_2 \cdot Z_3$ (c) $\frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3}$ (d) None of these

**20.** The general expression for pressure $P$ of real gas may be expressed as ($n$ = number density of particles)

(a) $P = n\,kT$ (b) $P = n\,kT + \frac{(n\,kT)^2}{2!}$

(c) $P = kT\,[An + Bn^2 + Cn^3 + \ldots]$ (d) $P = \left[\frac{A}{n} + \frac{B}{n^2} + \frac{C}{n^3} + \ldots\right]kT$

## ANSWERS

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** (c) | **2.** (b) | **3.** (b) | **4.** (a) | **5.** (b) | **6.** (c) | **7.** (d) | **8.** (c) |
| **9.** (a) | **10.** (b) | **11.** (c) | **12.** (d) | **13.** (a) | **14.** (c) | **15.** (b) | **16.** (b) |
| **17.** (c) | **18.** (a) | **19.** (b) | **20.** (c). | | | | |

# 8

# QUANTUM STATISTICS

## 8.1 Introduction

As pointed in preceding chapters, the study of statistical mechanics can be divided into two main classes :

1. Classical statistics or Maxwell-Boltzmann statistics.
2. Quantum statistics.

The classical statistics has already been discussed in preceding two chapters and is so called because it utilises the classical results of Maxwell-Boltzmann velocity distribution of particles of an assembly in equilibrium in interpreting the statistical system of interest. Classical statistics interpreted successfully many ordinarily observed phenomena such as temperature, pressure, energy, etc. But is failed to account adequately for several other experimentally observed phenomena such as black body radiation, photoelectric effect, specific heat at low temperature etc. This failure of classical statistics forced the issue in favour of the new quantum idea of discrete exchange of energy between systems and alongwith it a new quantum statistics was invisaged.

The quantum statistics was first formulated in 1924 by Bose in the deduction of Planck's radiation law by purely statistical reasoning on the basis of certain fundamental assumptions radically different from those of classical statistics. Einstein in the same year utilisd practically the same principles in evolving the kinetic theory of gases, as a substitute for the classical Boltzmann statitics.

Thus a new *quantum statistics* known as **Bose-Einstein statistics** came to be accepted. Two years later, in 1923, Fermi and Dirac quite independently modified Bose-Einstein statistics in certain gases on the basis of an additional principle, suggested first by Pauli in connection with electronic structure in atom and known as **Pauli's exclusion principle** according to which in *any given orbit in an atom, there can be one and only one electron, it being impossible for two electrons to coexist in the same quantum state.* In statistical mechanics this exclusion principle takes the form that *two or more phase points cannot possible occupy the same phase cell.* This led to the recognision for a second kind of quantum statistics, caled the **Fermi-Dirac-Statistics.** Thus quantum statistics can again be put into two sub classes :

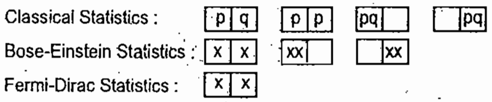
**(a) Bose Einstein statistics :** This is applicable to the identical, indistinguishable particles of zero or integral spin. These particles are called *Bosons.* The examples of Bosons are helium atoms at low temperature and the photons. The examples of Bosons are helium atoms at low temperature and the photons.

**(b) Fermi-Dirac statistics :** This is applicable to the identical indistinguishable particles of integral half spin. These particles obey Pauli's exclusion principle and are called *Fermions or Fermi particles.* The examples of Fermions are electrons, protons, neutrons etc.

The essential difference between the three statistics may be illustrated in the following simple manner :

Let there be only two particles of a collection and only two cells to be occupied.

In *classical statistics* each particle has a recogniziable individuality, hence the particles are distinguishable and each particle is as likely to be in one cell as in the other. This means that in classical statistics, each or both of the particles can occupy any one of the two cells. Thus in this case we have *four possible arrangements,* each of which is counted in assigning a probability to the distribution (refer Fig. 8.1).



**(Fig. 8.1) Illustration of essential difference between the three statistics.**

In *Bose-Einstein statistics* the particles lose their individuallity, hence they are indistinguishable. So, we must concentrate our attention on the cell rather than the individual particles. Each cell may have any number of particles, so that in this case we have only three possible arrangements.

In the *Fermi-Dirac statistics* the particles are indistinguisable and again we have to concentrate our attention on the cells rather than on individual particles. But in this case the particles obey Pauli's exclusion principle according to which it *is not possible to have more than one representative point in any one cell.* Hence, obvioully each cell will contain one particle, therefore in this cas only one arrangement is possible as shown in Fig. 8.1.

When there are a large number of cells and comparatively few particles to be arranged in them, there is no great difference between the three statistics, because the probability of any cell containing more than one particle is very small, But in a case when the number of particles is comparable with the number of cells, the three statistics ~~lead to divergent results.~~

Before developing the subject of quantum statistics, we shall first consider the basic concepts of quantum mechanics.

## 8.2 Basic Concepts of Quantum Mechanics

It is an experimental fact that *light has dual* (particle and wave) *nature.* In some phenomena such as interference, diffraction and polarization, light exhibits wave nature; while in some other phenomena such as photoelectric effect, Compton effect, emission and absorption of radiation, it exhibits particle nature.

In analogy with dual nature of light, de-Broglie thought that matter (material particles) has also dual nature. The particle nature of matter is well known and is verified by experiments in which $e/m$ of material particles is measured. In 1923, Louis de-Broglie proposed that the *moving particle, whatever its nature, has wave properties associated with it.* The wavelength λ associated with a moving particle is given by,

$$\lambda = \frac{h}{p} = \frac{h}{mv}, \qquad \ldots(1)$$

where $m$ is the mass and $v$ is the velocity of the particle.

This preposition of de-Broglie has been verified theoretically and experimentally and many physicists over a variety of material particles. Thus in some cases it behaves like a particle, while in the other cases like a wave. Now the question arises how do these contradictory aspects resort to friendship? The first attempt to explain this dual nature was made by Schroedinger by treating each of the moving particle and particularly electrons as a *wave packet.*

A wave packet comprises a group a waves, each with slightly different velocity and wavelength with phases and amplitudes so chosen that they interfere constructively over only a small region of space where the particle can be located outside of which they produce destructive intereference so that the amplitude reduces to zero rapidly. Such a packet moves with its own velocity $G$ called the group velocity which is equal to the velocity of the material particle $v$. Thus a material particle in motion is equivalent to a group of waves or a wave-packet. But a serious difficulty at once arises against the concent of a wave packet, since a wave-packet is, in general, very soon dissipated. For example, if we produce a wave crest at any point on the smooth surface of water, it spreads out and it dissipates in a very short time. Thus if a material particle is considered to be a wave-packet, it is necessary to postulate the existence of a *guiding wave* it is described by Schrödinger equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\,\psi = 0. \qquad \ldots(2)$$

Here $E$ is the total energy and $V$ is the potential energy of the material particle. The quantity $\psi$ is called the *wave function*

If $\psi^*$ is the complex conjugate of $\psi$, when according to Max-Born $\psi\psi^* = |\psi|^2$ represents the probability of finding the particle in unit volume *i.e.*, the probability density of the particle in the state $\psi$. The function $\psi$ is sometimes called the *probability amplitude* for the position of the particle. The postulate suggested by Born show that the quantum mechanical laws and the results of their measurements can be interpreted on the basis of probability consideration.

Thus the physical significance of the Schrödinger equation is that it relates the amplitude of the guiding wave to the probability of finding a material particle at a point. If the amplitue of the guiding wave is zero at a certain point in space, the probability of finding the material particle at this point is infinitesimal. As the value of the amplitude is small at all points except in the wave packet, hence the probability of finding the material particle within the region of the packet is maximum. Thus it is possible to find an equivalent particle in the region of the packet which travels with the group velocity $v$. Conclusively we can say that *the wave-packet plus guiding wave possess the properties of a particle moving with velocity $v$* and also exhibit the phenomenon of interference and diffraction. Thus the particle and wave properties of the matter are strictly complementary. The linkage betweent the two concepts is given by equation (1). A material particle can not behave as a particle and a wave at the same instant of time.

Classically a moving particle has a definite momentum and occupies a definite position in space and it is impossible to determine both its position and momentum simultaneously with accuracy. In recent years it has become apparent that the classical point of view represents an approximation which is adequate for the objects of appreciable size; but does not describe satisfactorily the behaviour of the particles of atomic dimensions. In quantum mechanics a particle is described by a wave-packet which represents and symbolises all about the particle and moves with group velocity. According to Born's probability interpretation the particle may be found anywhere within the wave-packet. This implies that the position of the particle is uncertain within the limits of the wave-packet. Moreover, the wave-packet has a velocity spread and hence there is uncertainty about the velocity or momentum of the particle. This means it is impossible to know where within the wave-packet the particle is and what is its exact momentum. For a large wave-packet with many crests, the velocity spead is very small and so that particle's velocity or momentum can be fairly accurately determined; but the position of the particle is very uncertain. On the other hand, for a small wave packet, the position of the particle can be more or less fixed; but the velocity spread of such a packet is very large and so the velocity or momentum of the particle becomes uncertain. Hence we conclude that quantum mechanically *it is possible to determine simultaneously both the position and momentum of the particle with accuracy.* Heisenberg state

a universal principle of uncertainty according to which, "*The product of the uncertainties in determining the position and momentum of the particle is approximately equal to the Planck's constant h,* i.e.

$$\Delta q\, \Delta p \approx h. \qquad \ldots(3a)$$

where $\Delta q$ is the uncertainty in determining the position and $\Delta p$ is the uncertainty in determining the momentum of the particle. Acording to above relation smaller is the value of $\Delta q$ *i.e.* more exactly we can determine the position, the larger is the value of $\Delta p$ *i.e.* less exactly we can determine the momentum and viceversa. This relation is known as *Heisenberg's uncertainty principle* and shows that it is impossible to determine simultaneously both position and momentum of the particle accurately.

Heisenberg's uncertainty relation is a direct consequence of wave-particle duality and Born's statistical interpretation. This holds for all the canonically conjugate physical quantities like position and momentum, energy and time, angular momentum and angle etc. *i.e.*

$$\left.\begin{aligned} \Delta q\, \Delta p &\approx h \\ \Delta E\, \Delta t &\approx h \\ \Delta J\, \Delta\theta &\approx h \end{aligned}\right\} \qquad \ldots(3b)$$

## 8.3 Postulates of Quantum Mechanics

**Postulate I :** In classical mechanics the state of a system is specified by specifying its generalised coordinates $q$'s and generalised momenta $p$'s at any instant $t$. In quantum mechanics the exact knowledge of $q$'s and $p$'s at a given time $t$ is impossible due to the uncertainly principle. Therefore in quantum mechanics the state of the system is completely determined by the state function or wave function $\psi\,(q, t)$. The wave function $\psi$ has the following properties :

(i) It is, in general, complex.

(ii) It is a continuous single valued and finite function of $q$ and $t$.

(iii) If $\psi^*$ is the complex conjugate of $\psi$, then $\psi\psi^*\, d\tau = |\psi|^2\, d\tau$ denotes the probability that the system will be found within the volume $d\tau$ at time $t$.

(iv) For a material particle in finite region (*e.g.* a box), we have

$$\psi\psi^* \to 0 \text{ as } q \to \infty,$$

and $$\int \psi\psi^*\, d\tau = 1\,;$$

where integration extends over the entire region.

**Postuate II :** *An operator is defined as an entity which operating on a function converts in into some other function.* In an operator $P$ is applied to the state function $\psi\,(q, t)$

$$P\psi\,(q, t) = \phi\,(q, t)$$

where $\phi\,(q, t)$ is the transformed function.

The typical examples of operations are differentiation, integration whose operators are, $\dfrac{d}{dq}$ and $\int dq$ respectively.

The second postuate of quantum mechanics is that *with every observable there is associated an operator which can operate on a state function.*

The operator $P$ under consideration must have the following properties :

(i) It must be *linear i.e.* it must satisfy the following condition.

(a) If $u$ and $v$ are arbitrary operands, then

$$P\,(u + v) = Pu + pv.$$

(b) For an arbitrary constant $c$

$$Pc = Pc.$$

In quantum mechanics we are concerned almost with linear operators.

(ii) It must be *Hermitian i.e.* for arbitrary complex functions $u$ and $v$

$$\int u^* Pv \, d\tau = \int (Pu)^* v^* \, d\tau.$$

**Postulate III :** *The only possible values, which a measurement of the observable whose operator is P, can yield are the eigen values $\lambda_n$ of the equation*

$$P\psi_n = \lambda_n \psi_n,$$

provided $\psi_n$ satifies the conditions :

(a) $\psi_n$ is single valued.

(b) $\int \psi_n^* \psi_n \, d\tau$ is finite.

**Postulate IV :** When a given system is in a state $\psi$, the expectation value (*i.e.* expected mean of a sequence of a measurements) of the observable whose operator is $P$ is given by

$$<p> = \int \psi^* P\psi \, d\tau$$

**Postulate V :** The time variation of a quantum mechanical state function $\psi(q, t)$ is determined by the time dependent Schrödinger's equation

$$H\psi(q, t) = i\hbar \frac{\partial \psi(q, t)}{\partial t}$$

with $\qquad \psi(q, t) = \psi(q) \, e^{-iEt/\hbar}$

where $H$ is the *Hamiltonion operator and* $\hbar = \frac{h}{2\pi}$

## 8.4 Quantum Statistics of Identical Particles (Indistinguishability and Quantum Statistics)

By identical particles we mean the particles like electrons which cannot be distinguished by means of any inherent property, since otherwise they would not be identical in all respects. In classical mechanics identical particles do not lose their identity despite of their physical properties due to the existence of sharply definable trajectories for individual particles since each particle can be followed during the course of an experiment. As an example of the classical mechanical particles consider the molecules at N.T.P.

Molecular density $= 10^{25}$ mol/metre$^3$.

Volume available for each particle $= 10^{-25}$ metre$^3$.

Molecular radius $= 10^{-10}$ metre.

Therefore, the molecular volume $= \frac{4}{3}\pi r^3 \approx 10^{-30}$ metre (order of magnitude).

As the molecule is much smaller than the volume available for it, we can, in principle, identify every molecule of the gas. Hence the molecules (classical particles) are *distinguishable*.

In quantum mechanics, a particle is described by a wave packet of finite size and spead and the exact *specification* of the position and momentum of the particle simultaneously is restricted by Heisenberg's uncertaintly principle $\Delta q \, \Delta p \approx h$. Therefore, there is no way of keeping track of individual particles separately, specially, if they interact with each other to an appreciable extent. Hence in quantum mechanics the wave functions of the particles, overlap considerably. As a result, the quantum mechanical particles can not be distinguished. As an example of the quantum particles consider the conduction electrons in metals.

The density of the electrons $\approx 10^{28}$ per metre$^3$ (order of magnitude).

Therefore, the volume available for each electron $= 10^{-28}$ metre$^3$.

For a 1 eV electron, the momentum, $p = (2mE)^{1/2}$

$$= [2 \times (9{\cdot}1 \times 10^{-31} \text{ kg}) \, (1 \times 1{\cdot}6 \times 10^{-19} \text{ joule})]^{1/2}$$

Therefore, uncertaintly in position of this electron,

$$\Delta q \approx \frac{h}{\Delta p} = \frac{6{\cdot}6 \times 10^{-34} \text{ joule second}}{0{\cdot}5 \times 10^{-24} \text{ joule second/metre}} \approx 1{\cdot}3 \times 10^{-9} \text{ metre.}$$

Therefore, the volume of the conduction electron

$$= \frac{4}{3}\pi r^3 \approx \frac{4}{3} \times 3{\cdot}14 \times (1{\cdot}3 \times 10^{-9} \text{ metre})^3$$

$$\approx 10^{-27} \text{ metre}^3 \text{ (order of magnitude).}$$

Comparing the volume of conduction electron to the volume available to it, we conclude that the electron wave-function overlaps considerably *i.e.* conduction electron can not be identified separately and hence they are *indistinguishable.*

Thus there are two general categories of particles :

(i) *classical particles* which are identical but *distinguishable*

(ii) *quantum particles* which are identical and *indistinguishable.*

It is to be noted that when quantum particle density is sufficiently low so that their uncertainty is small in comparision to the volume available to them, they also obey classical statistics, otherwise we must use quantum statistics

In the case of quantum statistics we can only distinguish between *the state of the system,* not the states $\varepsilon_i$ of the single particle.

The total energy

$$E(n) = \Sigma \, n_i \, \varepsilon_i.$$

Here we have used the summation while in classical statistics we use the integration; because in classical statistics the energy values of various cells are considered to be continuous; on the other hand, in quantum statistics the energy values of the various states of the system are discrete.

It is now obvious that in the case of quantum statistics of identical particles it makes no sense to use the partition function for a single particle *i.e.*

$$Z_\mu = \Sigma \, e^{-\beta\varepsilon_i},$$

but it is necessary to use the *partition function for* the system as a whole, *i.e.*

$$Z_T = \sum_n{}' e^{-\beta E(n)}.$$

The prime on the summation indicates that we must not count those distributions separate which are obtained by an interchange of two particles between two different quantum states since due to indistinguishability of particles this does not lead to a new distribution.

## 8.5 Symmetric and Antisymmetric Wave Functions

The schrödinger equation for '$n$' identical particles is written as

$$H(1, 2, \ldots n) \, \psi(1, 2, \ldots n, s) = i\hbar \frac{\partial}{\partial t} \psi(1, 2, \ldots n, t), \qquad \ldots(1)$$

where each of the number represents all the co-ordinates (positions and spin) of one of the particles. The Hamiltonian $H$ is symmetrical in its arguments due to the identity of particles. The identity of particles means that they can be substituted for each other without changing $H$ or indeed any other observable.

There are two kinds of solutions of wave function $\psi$ of equation (1) that have symmetry properties of particular interest.

**(i) Symmetric wave function $\psi_S$.** *A wave function is symmetric, if the interchange of any pair of particles among its arguments leaves the wave function unchanged.*

**(ii) Anti-symmetric wave function $\psi_A$.** *A wave function is antisymmetric, if the interchange of any pair of particles among its arguments changes the sign of the wave function.*

It may now be pointed out that the symmetry character of a wave function does not change with time. If $\psi_S$ is symmetric at a particular time $t$, then $H\psi_S$ is also symmetric and according to eqn. (1), $\frac{\partial\psi_S}{\partial t}$ is symmetric at time $t$. Since $\psi_S$ and $\frac{\partial\psi_S}{\partial t}$ are symmetric at time $t$, $\psi_S$ at infinitesimally later time $t+dt$ given by $\psi_S+\frac{\partial\psi_S}{\partial t}dt$ is also symmetric, Such a step by step integration of the wave function can, in principle, be continued for arbitrary large time intervals and $\psi_S$ is seen to remain symmetric always.

Similarly, if $\psi_A$ is anti-symmetric wave function at any time $t$, then $H\psi_A$ and hence $\frac{\partial\psi_A}{\partial t}$ are anti-symmetric and the integration of the wave function $\psi_A$ shows that $\psi_A$ is always anti-symmetric.

If $P$ is an an exchange operator, then we must have

$$P\psi_S(1,2)=\psi_S(2,1)$$

and $$P\psi_A(1,2)=-\psi_A(2,1).$$

The symmetry property of the wave function has also close relationship with the spin of the particle. This relationship is listed here in the following two postulates :

1. The identical particles having an integral spin quantum number are described by symmetric wave functions.

*i.e.* $$P\,\psi_S(1,2,3,\ldots,r,s,\ldots,n)=+\psi_S(1,2,3,\ldots,s,r,\ldots,n).$$

This class of particles, *i.e.*, the particles described by symmetric wave functions are known as *Bose particles* or *Bosons and obey Bose-Einstein Statistics.* The examples of Bosons are photons (spin 1), neutral helium atoms in normal states ($s=0$) etc.

2. The identical particles having half odd integral spin quantum number are described by anti-symmetric wave functions,

*i.e.,* $$P\psi_A(1,2,\ldots,r,s,\ldots,n)=-\psi_A(1,2,\ldots,s,r,\ldots,n)$$

This claass of particles, *i.e.* the particles described by antisymmetic wave functions obey Fermi-Dirac statistics and the particles are known as *Fermi particles* or *Fermions.* The examples of Fermions are electrons, protons, neutrons, muons all have spin $\frac{1}{2}$).

## 8.6 Construction of Symmetric and Anti-Symmetric wave functions from Unsymmetrized function; Exchange Degeneracy :

We shall now show how $\psi_S$ or $\psi_A$ can be constructed from a general unsymmetrized solution $\psi$ of schrödinger equation

$$H(1,2,\ldots\ldots n)\,\psi(1,2,\ldots\ldots n,s)=i\hbar\frac{\partial}{\partial t}\psi(1,2,\ldots\ldots n,t) \qquad \ldots(1)$$

If the arguments of the wave function $\psi$ are permuted in any way, then the resulting wave function is also a solution of equation (1). This is because same permutation applied throughout equation (1) does not impair its validity as it corresponds simply to a relabling of the particles. Since $H$ is symmetric, permuted, $H$ will be same as original $H$ and the resulting equation is same as equation (1) for the permuted $\psi$. In this way, $n\,!$ solutions can be obtained from any one solution, each of which corresponds to one of the $n\,!$ permutations of the $n$ arguments of $\psi$.

Evidently any linear combination of these functions is also a solution of the wave equation (1), The sum of all these functions is symmetric (unnormalised) wave function $\psi_S$, since the interchange of any pair of particles changes any one of the component function into another of them and the latter into the former, leaving the entire wave function unchanged.

An anti-symmetric unnormalized wave function can be constructed by adding together all the permuted wave functions that arised from the original solutions by means of an even number of interchanges of pairs of particles and subtracting the sum of all permuted wave functions that arise by means of an odd number of interchanges of pairs of particles in the original solution.

In the case where the Hamiltonian does not depend upon, time, stationary state solutions

$$\psi(1,2,\ldots,n;t)=\phi(1,2,\ldots,n)\,e^{-iE_n t/\hbar} \qquad \ldots(2)$$

can be found and the time independent Schrödinger's equation can be written as

$$H(1,2,\ldots,n)\,\phi(1,2,\ldots,n)=E\phi(1,2,\ldots,n). \qquad \ldots(3)$$

There are $n\,!$ solutions of this equation (re-eigen functions derived from $\phi(1,2,\ldots,n)$ by means of permutations of its arguments belonging to the same energy value $E$. Any linear combination of these eigen functions is also an eigen function (*i.e.* solution of equation (3)] belonging to eigen value $E$. Hence the system is degenerate* and this type of degeneracy is called *exchange degeneracy.*

Let us now consider a two particle wave function $\psi(1S_1\,2S_2)$. For a two particle wave function, the Schrödinger's time independent equation is written as

$$H(1,2)\,\psi(1,2)=E\psi(1,2).$$

The $2\,!=2$ solutions of this equation are $\psi(1,2)$ and $\psi(2,1)$. The solutions correspond to a single energy state $E$.

The symmetric wave function can be written as

$$\psi_S=\psi(1,2)+\psi(2,1) \qquad \ldots(5)$$

and the anti symmetric wave function is written as

$$\psi_A=\psi(1,2)-\psi(2,1). \qquad \ldots(6)$$

Similarly, for a system of 3 particles, the Schrödinger's equation is

$$H(1,2,3)\,\psi(1,2,3)=E\,\psi(1,2,3). \qquad \ldots(7)$$

This equation has $3\,!=6$ solutions corresponding to the same eigen value $E$. The six possible functions obtained by exchanging the indices of the particles are

$$\psi(1,2,3)\;\psi(2,3,1)\;\psi(3,2,1),\;\psi(1,3,2),\;\psi(2,1,3),\;\psi(3,1,2).$$

Out of these six functions, those arising by an even numbr of interchanges of the pairs of particles in orignial wave functions $\psi(1,2,3)$ are

$$\psi(1,2,3),\;\psi(2,3,1),\;\psi(3,1,2),$$

---

*A system having a number of eigen functions corresponding to the same eigen value is said to be degenerate system.

and the functions arising by an odd number of interchanges of pairs of particles in original function (1, 2, 3) are

$$\psi(2,1,3)\ \psi(1,3,2)\ \psi(3,2,1).$$

So, the *symmetric wave function* $\psi$ can be written as

$$\psi_S = \psi(1,2,3) + \psi(2,3,1) + \psi(3,1,2) + \psi(2,1,3) + \psi(1,3,2) + \phi(3,2,1) \qquad \ldots(8)$$

and the *anti-symmetric wave function is*

$$\psi_A = \psi(1,2,3) + \psi(2,3,1) + \psi(3,1,2) - \{\psi(2,1,3) + \psi(1,3,2) + \phi(3,2,1)\}. \qquad \ldots(9)$$

Hence $\psi_S$ and $\psi_A$ are unnormalised wave functions.

## 8.7 Average Value and Quantum Statistics

The average value of any dynamical quantity $<p>$ in the state $\psi$ given by

$$<p> = \frac{\int \psi^* P\psi\, d\tau}{\int \psi^* \psi\, d\tau} \qquad \ldots(1)$$

where $P$ is the operator corresponding to the dynamical quantity $p$. For example the operator $P$ associated with energy $E$ is $i\hbar\frac{\partial}{\partial t}$ and the operator $P$ associated with momentum p is $\frac{\hbar}{i}\nabla$.

If $\psi$ is normalised function, then $\int \psi^* \psi\, d\tau = 1$, therefore

$$<p> = \int \psi^* P\psi\, d\tau. \qquad \ldots(2)$$

The symmetric and anti-symmetic normalised eigen functions lead ~~to the~~ following results

$$<p_S> = \int \psi_S^* P\psi_S\, d\tau; \qquad \ldots(3)$$

and $$<p_A> = \int \psi_A^* P\psi_A\, d\tau. \qquad \ldots(4)$$

A little consideration shows that for symmetric solution an exchange of co-ordinates of particles leave both $\psi_S$ and $\psi_S^*$ unaltered. Consequently $<p_S>$ remains unchanged. In the case of antisymmetric solution an exchange of coordinates changes the signs of both $\psi_A$ and $\psi_A^*$. Consequently $<p_A>$ again remains unchanged. Therefore, we conclude that any interchange of two particles leaves the overage or the observed property of the system unaffected. Therefore, from the quantum mechanical point of view the similar particles cannot be distinguished.

## 8.8 Statistical Weight or a Priori Probability

In some cases there is only one eigen function corresponding to each eigen value. In such cases the eigen state or the energy level is said to be *non-degenerate.* However, in some other cases there are a number of eigen functions corresponding to a single eigen value. In these cases the eigen state is said to be *degenerate.* In the degenerate cases *the number of eigen states for the particular energy state or level is called the* **degeneracy of that state.** Thus, if $g_i$ is the degeneracy for the eigen value $\varepsilon_i$; then $g_i$ is the number of eigen states for the $i$th eigen state having energy $\varepsilon_i$. Obviously for a non-degenerate case $g_i = 1$. An important postulate of quantum statistics concerning the probability of eigen states is that *every eigen state possesses an equal a priori probability.* According to this postulate the eigen state in quantum statistics is equivalent to the unit cell in the phase space of classical statistics. The degeneracy $g_i$ is therefore often referred to as *a priori probability* or *the statistics* of the given eigen state.

## 8.9 Density Matrix

A pure quantum state of a system is represented by a single eigen vector $\psi_\alpha$ or $|\alpha>$; but if the knowledge of the system is described by non-negative probabilities $p_\alpha, p_\beta$ for being in states $|\alpha>, |\beta> \ldots$ a statistical approach is necessary if the theory of pure states is inadequate. This can be developed in close analogy with the classical situation. A pure classical state is one that is represented by a single moving point in phase space; that have definite value of co-ordinates $q_1, q_2, \ldots, q_f$ and canonical momenta $p_1, p_2, \ldots, p_f$ at each instant of time.

On the other hand a statistical state can be described by a non-negative density function

$$f(q_1, \ldots q_f, \ldots p_1, p_f, t)$$

such that the probability that a system is found in the interval $dp_1 \ldots dq_f\, dp_1 \ldots dp_f$ at time $t$ is

$$\rho\,(dq_1 \ldots dq_f, dp_1 \ldots dp_f)$$

The quantum analogue of the classical density function is known as *the density operator* and its representation in the matrix form is known as the *density matrix.*

Consider an ensemble consisting of $N$ systems in the normalised states $\psi_\alpha l$; $\alpha = 1, 2, 3, \ldots N$. The expectation value of an operator $f$ in this representation is given by

$$<f> = \int \psi_\alpha^* f\, \psi_\alpha\, dq \qquad \ldots(1)$$

If $\phi_n$'s represent the orthonormal eigen functions, than a pure state $\psi_\alpha$ may be represented as the linear combination of functions $\phi$'s

$$\psi_\alpha = \sum_n C_n\, \phi_n;$$

where $C_n$ are the coefficients of expansion of $\psi_\alpha$

then $$\psi_\alpha^* = \sum_n C_m^*\, \phi_m^* \qquad \ldots(2)$$

so that equation (1) takes the form

$$<f> = \sum_m \sum_n C_m^*\, C_n \int \phi_m^* f\, \phi_n\, dq$$

$$= \sum_m \sum_n C_m^*\, C_n <m\,|\,f\,|\,n>. \qquad \ldots(3)$$

If the state is not specified completely, it may be rapresented by incoherent specified superposition of a number of pure states $\psi^{(\alpha)}$ with statistical weight $p^{(\alpha)}$, to each pure state there corresponds a mean value $<f>_\alpha$; and the mean value of $f$ for the incoherent superposition is given by the grand (or ensemble) average given by

$$<\bar{f}> = \sum_\alpha p^{(\alpha)} <f>_\alpha = \sum_\alpha p^{(\alpha)} \sum \sum C_m^{*(\alpha)}\, C_n^{(\alpha)} <m\,|\,f\,|\,n>$$

$$= \sum_m \sum_n <m\,|\,f\,|\,n> \sum_\alpha p^{(\alpha)}\, C_m^{*(\alpha)}\, C_n^{(\alpha)} \qquad \ldots(4)$$

where $$0 < p^{(\alpha)} < 1 \text{ and } \sum p^{(\alpha)} = 1 \qquad \ldots(5)$$

where $p^{(\alpha)}$ represents the probability of finding the system in the state $|\,\alpha\,|>$; when a measurement is made at random on the system.

For brevity let us write

$$\sum p^{(\alpha)}\, C_m^{*(\alpha)}\, C_n^{(\alpha)} = \rho_{nm}; \qquad \ldots(6)$$

then equation (4) takes the form

$$\overline{<f>} = \sum_m \sum_n \rho_{mn} < m \mid f \mid n > \qquad \ldots(7)$$

The ensemble average of *f* is also represented by the equation

$$\bar{f} = \int_0 \int P(q, p) f(q, p)\, dq\, dp \qquad \ldots(8)$$

where *P* is termed as the normalised density of distribution.

A comparision of equation (7) and (8) shows that the integration over *q* and *p* has been replaced by a double sum over the quantum states. Thus the *matrix* $\rho_{mn}$ plays a role analogous to that of the probability *density* $P(q, p)$. *Therefore* ρ *is termed as the* **density matrix,** whose matrix elements can be defined by equation (6) as

$$\rho_{nm} = \sum_\alpha p^{(\alpha)} C_m^{*(\alpha)} C_n^{(\alpha)}$$

so that equation (7) gives

$$<f> = \sum_m \sum_n \rho_{nm} f_{mn} = \sum_n (\rho f)_{nn}$$

$$= \text{trace}\, (\rho f) \qquad \ldots(9)$$

where Trace stands for the sum of the diagonal elements of the matrix (ρ*f*). It is convenient to regard the density matrix as defined by equation (9) rather than by equation (6)

**Limitation on density matrix:**

(i) The condition that the expectation value of *f* is real for every Hermitian operator *f*, requires that ρ must also be hermitian

$$\rho_{nm} = \rho^*_{mn} \qquad \ldots(10)$$

(ii) The condition that the unit operator 1 has the expectation value 1, requires that

$$\text{Trace}\, (\rho f) = \text{Trace}\, (\rho\, 1) = \text{Trace}\, (\rho) = \sum_n \rho_{nn} = 1 \qquad \ldots(11)$$

(iii) The condition that every operator with negative eigen values has a non-negative mean value, requires that ρ must be definitely positive. This means

$$\rho_{nn} \geq 0 \qquad \ldots(12)$$

(iv) The Hermitian matrix ρ by means of unitary transformations may be reduced to diagonal from

$$\rho_j \delta_{jj'} = \sum_n \sum_m U_{jn}\, \rho_{nm}\, U^{-1}_{mj'} \qquad \ldots(13)$$

The conditions given by (11) and (12) require that

$$\sum_j \rho_j^2 \leq \left(\sum_j \rho_j\right)^2 = [\text{Trace}\, (\rho)]^2 = 1$$

Thus we have in general $\quad \text{Trace}\, (\rho^2) = \sum_n \sum_m |\rho_{nm}|^2 \leq 1 \qquad \ldots(14)$

This limits the value of every single element of the density matrix.

## 8.10 Time Dependence of Density Matrix

**Quantum mechanical analogue of Liouville's theorem.** Time dependent Schrödinger equation is

$$\frac{i\hbar\, \partial \psi_\alpha}{\partial t} = H \psi_\alpha \text{ where } \hbar = \frac{h}{2\pi} \qquad \ldots(1)$$

using

$$\psi_\alpha = \sum_k C_k(\alpha)\, \phi_\kappa \qquad \ldots(2)$$

We may write equation (1) as

$$i\hbar \frac{\partial}{\partial t}\left(\sum_k C_k^{(\alpha)} \phi_\kappa\right) = H \sum_k C_k^{(\alpha)} \phi_\kappa$$

Multiplying above equation by $\phi_m^*$ and integrating over *q* we get

$$i\hbar \sum \frac{\partial}{\partial t} \int C_k^{(\alpha)} \phi_m^* \phi_\kappa\, dq = \sum_k C_k^{(\alpha)} \int \phi_m^* H \phi_\kappa\, dq$$

*i.e.*

$$i\hbar \frac{\partial}{\partial t} C_k^{(\alpha)} \delta_{mk} = \sum_k C_k^{(\alpha)} H_{mk}$$

where

$$\int \phi_m^* \phi_k\, dq = \delta_{mk}$$

and

$$\int \phi_m^* H \phi_\kappa\, dq = H_{mk} = < m \mid H \mid k >$$

*i.e.*

$$i\hbar \frac{\partial C_m^{(\alpha)}}{\partial t} = \sum_k C_k^{(\alpha)} H_{mk} \qquad \ldots(3)$$

The complex conjugate of above equation is written as

$$-i\hbar \frac{\partial C_m^{(\alpha)*}}{\partial t} = \sum_k C_k^{*(\alpha)} H_{mk}^* \qquad \ldots(4)$$

From definition of density-matrix in $\phi_\kappa$ representation

$$\rho_{nm} = \sum_\alpha p^{(\alpha)} C_m^{*(\alpha)} C_n^{(\alpha)} \qquad \ldots(5)$$

Differentiating above equation with respect to time, we get

$$\frac{\partial \rho_{nm}}{\partial t} = \sum_\alpha p^{(\alpha)} \left( C_m^{*(\alpha)} \frac{\partial C_n^{(\alpha)}}{\partial t} + C_n^{(\alpha)} \frac{\partial C_m^{*(\alpha)}}{\partial t} \right)$$

or

$$i\hbar \frac{\partial \rho_{nm}}{\partial t} = \sum_\alpha p^{(\alpha)} \left\{ C_m^{*(\alpha)} \left( i\hbar \frac{\partial C_n^{(\alpha)}}{\partial t} \right) + C_n^{(\alpha)} \left( i\hbar \frac{\partial C_m^{*(\alpha)}}{\partial t} \right) \right\}$$

Using (3) and (4), above equation takes the form

$$i\hbar \frac{\partial \rho_{nm}}{\partial t} = \sum_k p^{(\alpha)} \left\{ C_m^{*(\alpha)} \sum_k C_k^{(\alpha)} H_{nk} - C_n^{(\alpha)} \sum_k C_k^{*(\alpha)} H^*_{mk} \right\}$$

$$= \sum_n H_{nk} \sum_\alpha p^\alpha C_m^{*(\alpha)} C_k^{(\alpha)} - \sum_k \sum_\alpha p^{(\alpha)} C_n^{(\alpha)} C_k^{*(\alpha)} H^*_{mk}$$

$$= \sum_k (H_{nk}\, \rho_{mk} - \rho_{nk} H^*_{mk})$$

As *H* is hermitian, $\quad \therefore H^*_{km} = H_{km}$

$$\therefore \quad i\hbar \frac{\partial \rho_{nm}}{\partial t} = -\sum_k \left( \rho_{nk} H_{km} - H_{nk}\, \rho_{km} \right) = -(\rho H - H\rho)_{nm}$$

Using $(\rho H - H\rho) = [\rho, H]$; the time dependence of density matrix is given by

$$i\hbar \frac{\partial \rho}{\partial t} = -[\rho, H]. \qquad \ldots(6)$$

This equation is analogous to Liouville's theorem in classical statistical mechanics

## 8.11 Density Matrix in Microcanonical, Canonical and Grand Canonical Ensembles.

Let an ensemble consist of systems in the states

$$\psi_\alpha, \alpha = 1, 2, 3, \ldots N.$$

If the system is closed and isolated, then the function $\psi_\alpha$ can be taken to be energy eigen functions

$$H\psi_\alpha = E_\alpha \psi_\alpha \qquad \ldots(1)$$

The time dependence of density matrix is given by

$$i\hbar \frac{\partial \rho}{\partial t} = -[\rho, H] \qquad \ldots(2)$$

If systems are independent, then $\frac{\partial \rho}{\partial t} = 0$; so that $[\rho, H] = 0$:

This means $\rho$ and $H$ commute. Therefore, the density matrix $\rho$ is associated with some constant of motion of the system. One class of posssibilities is that $\rho$ is some function of $H =$ *i.e.* $\rho = \rho(H)$, where $\rho(H)$ may be expanded as a power series in $H$. We restrict overselves to this class only.

The density matrix, when we choose energy eigen functions as basic vectors, is given by

$$\rho_{nm} = \int \psi_n^* \rho(H)\, \psi_n\, dq \qquad \ldots(3)$$

If $\rho(H)$ is chosen as a power series in $H$ as

$$\rho(H) = a_0 + a_1 H + a_2 H^2 + \ldots$$

and using equation (1), we get

$$\rho(H)\, \psi_n = \rho(E_n)\, \psi_n \qquad \ldots(4)$$

and equation (3) reduces to

$$\rho_{mn} = \rho(E_n) \int \psi_m^* \psi_n\, dq = \rho(E_n)\, \delta_{nm} \qquad \ldots(5)$$

As $\delta_{nm} = \begin{cases} 1 \text{ for } m = n \\ 0 \text{ for } m \neq n \end{cases}$ : hence in the energy language any $\rho(H)$ is a diagonal matrix. Now $\rho(E_n)$ is the probability of observing the eigen value $E_n$ if a measurement of energy is made on a system chosen at random from the ensemble. This means that

$$\rho(E_n) = \omega_n \qquad \ldots(6)$$

From this equation it follows that in the case of degenerate level say with $n = n_1 = n_2 = \ldots$, all the basic state vectors $\psi_m$ have the same probability *i.e.*

$$\omega_{n_1} = \omega_{n_2} = \ldots\ldots = \rho(E_n) \qquad \ldots(7)$$

Now if system has energy $E$ within a small range $\delta E << E$, then the state of system may be represented by the superposition of basic vectors $\psi_m$ belonging to eigen value, $E_m$ is the range $E < E_m < E_m + \delta E$

As the *microcanonical ensemble represents a closed and isolated thermodynamic system*, so that equations (5) and (6) for this case take the form,

$$\left.\begin{aligned} \rho_{nm} &= \delta_{nm}\, \omega_n \\ &= \frac{1}{\Omega}, E \leq E_n \leq E + \delta E \\ &= 0, \text{ otherwise,} \end{aligned}\right\} \qquad \ldots(8)$$

where $\delta E$ is very small range in $E$ and $\Omega$ is the number of basic states $\psi_n$ belonging to eigen values $E_n$ in the range $E < E_n \leq E + \delta E$.

The constant $\frac{1}{\Omega}$ results from the normalization condition

$$\Sigma\, \omega_n = 1. \qquad \ldots(9)$$

Equation (8) implies that for a system having energy value between $E$ and $E + \delta E$, *all states belonging to the set* $(E, \delta E)$ *have the same probability* $\omega_n$. *This is equivalent to the postulate of a priori probabilities.*

To study the implication of equation (7), we note that constants $C^S$ being complex numbers, can be written as

$$C_n^{(\alpha)} = a_n^{(\alpha)}\, e^{i\theta_n^{(\alpha)}} \qquad \ldots(10)$$

where $a_n^{(\alpha)}$ are real numbers and $\theta_n^{(\alpha)}$ are phase angles.

Density matrix

$$\begin{aligned} \rho_{nm} &= \Sigma\, p^\alpha C_m^{*(\alpha)} C_n^{(\alpha)} \\ &= \sum_\alpha p^{(\alpha)} a_m^{*(\alpha)} a_n^{(\alpha)} e^{i(\theta_n^{(\alpha)} - \theta_m^{(\alpha)})} \\ &= \sum_\alpha p^{(\alpha)} a_m^{*(\alpha)} a_n^{(\alpha)} [\cos(\theta_n^{(\alpha)} - \theta_m^{(\alpha)}) + i \sin(\theta_n^{(\alpha)} - \theta_m^{(\alpha)})] \\ &= \sum_\alpha p^\alpha a_m^{(\alpha)} a_n^{(\alpha)} [\cos(\theta_n^{(\alpha)} - \theta_m^{(\alpha)}) + i \sin(\theta_n^{(\alpha)} - \theta_m^{(\alpha)})] \qquad \ldots(11) \end{aligned}$$

(since $a_m^{(\alpha)*} = a_m^{(\alpha)} =$ real).

This equation will agree with equation (8) only if we have

$$\begin{aligned} C_n^{(\alpha)2} &= \frac{1}{\Omega} \text{ for } n \text{ belonging to set } (E, \delta E) \qquad \ldots(12) \\ &= 0, \text{ otherwise} \end{aligned}$$

If we want to reduce $\rho_{nm} = \rho_0\, \delta_{mn}$, then, we must have

$$\left.\begin{aligned} a_m a_n \cos(\theta_n^{(\alpha)} - \theta_m^{(\alpha)}) = 0 \\ a_m a_n \sin(\theta_n^{(\alpha)} - \theta_m^{(\alpha)}) = 0 \end{aligned}\right\} \text{for } m \neq n. \qquad \ldots(13)$$

Equation (12) must hold for $\rho_{nm}$ to be diagonal. This is easily achieved if we assume that the phases $\theta_m^{(\alpha)}$ and $\theta_n^{(\alpha)}$ are *random*. Then the sine and cosine terms will give positive and negative values equally often and the average will be zero. This is the postulate of *random phase. The postulates of* **equal a priori probabilities** *and* **random phase** *given by equations (8) and* (12) *are the basic postulates of quantum statistical mechanics.*

**Density matrix for canonical and grand canonical ensembles.** The density matrix for canonical distribution is given by

$$\rho_{nm}=\omega_n\delta_{nm}=\frac{e^{-E_n/kT}}{\Sigma e^{-E_n/kT}}\,\delta_{nm} \qquad \ldots(14)$$

Let us consider the expansion of the operator $e^{-H/kT}$ in powers on $H$, *i.e.*,

$$e^{-H/kT}=1-\frac{H}{kT}+\frac{1}{2!}\left(\frac{H}{kT}\right)^2-\ldots=\sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{H}{kT}\right)^n \qquad \ldots(15)$$

which by virtue of (1) satisfy

$$e^{-H/kT}\psi_\alpha=e^{-E_\alpha/kT}\psi_\alpha. \qquad \ldots(16)$$

Therefore, the density matrix is a function of $H$ and can be written as

$$\rho(H)=\frac{e^{-H/kT}}{\text{canonical Trace } e^{-H/kT}}$$

Therefore, from the definition of partition function

$$\rho(H)=\frac{e^{-H/kT}}{Z}, \text{ we have}$$

$$Z\text{ (canonical)}=\text{Trace } e^{-H/kT}=\sum_\alpha [e^{-H/kT}]_\alpha$$

$$=\sum_\alpha\int\psi_\alpha^* e^{-H/kT}\psi_\alpha\, dq=\sum_\alpha e^{-E_\alpha/kT} \qquad \ldots(18)$$

Therefore, if $H$ is known, any thermodynamical property of the system can be evaluated immediately.

By analogy, the *density matrix for the grand canonical ensmble* is given by

$$\underset{\text{(grand canonical)}}{\rho(H)}=\frac{e^{-(n\mu-H)/kT}}{\text{Trace } e^{-(n\mu-H)/kT}} \qquad \ldots(19)$$

So, the partition function for the grand canonical ensemble is

$$Z\text{ (grand canonical)}=\text{Trace } e^{-(n\mu-H)/kT} \qquad \ldots(20)$$

## 8.12 Bose Einstein Statistics : Bose Einstein Distribution Law

This statistics is obeyed by identical, indistinguishable particles of integral spin (bosons) that have symmetrical wave functions and is so named as it was devised by Bose for light quanta and generalised by Einstein.

Bose utilised Planck's hypothesis of quantum theory, according to which the radiation in a temperature enclosure is composed of light quanta or particles of energy $h\nu$, where $\nu$ is the frequency of the quantum. According to present views regarding matter and energy, a light quantum has dynamical mass $h\nu/c^2$ and momentum $h\nu/c$, where $c$ is the speed of light. *The light quanta in the enclosure are indistingnishable and the number of light quanta is not necessarily unchangeable* unlike in classical statistics where the number of particles is considered to be fixed. Because in every emission process in an atom, a new light quantum is formed and if a quantum of frequency $\nu$ is absorbed by the wall of the enclosure, it can be replaced by the emission of several quanta of frequencies $\nu_1$, $\nu_2$ in accordance with the principle of conservation of energy, provided

$$h\nu=h\nu_1+h\nu_2+\ldots,$$

*i.e.*,

$$\nu=\nu_1+\nu_2+\ldots.$$

Indistinguishable

In the kinetic theory of monoatomic gas Einstein assumed that the molecules of the gas are like light quanta, indistinguishable from one another : but in the light quantum case, the number of molecules is conserved.

In classical statistics where the number of possible microscopic states of a system can be infinite, the phase space of the system can be divided into an infinite number of cells of constant energy. But in quantum statistics where only certain definite values of energy are permitted, so that the number of possible microscopic states of a system is finite, the phase space is divided into infinite elementary regions (*i.e.*, quantum groups or sheets) of constant energy and each of these elementary regions is partitioned into still smaller cells of finite size, a cell representing the smaller phase spece can contain any representative point. A change in the energy of any system is represented by its representative point jumping from one quantum state to another without occupying positions intermediate between the states. In accordance with *Heisenberg's uncertainty princple*, *i.e.*, the positions and momentum of a particle can not be more exactly defined than is consistent with the relation $dp_x\,dx\approx h$, each elementary phase cell has finite size of magnitude $h^3$ as in classical statistics since each particle has three pairs of conjugate co-ordinates (*i.e.*, three position co-ordinates and three momentum co-ordinates).

**Bose Einstein Distribution Law**

Consider a system having $n$ indistinguishable particles. Let these particles be divided into quantum groups or levels such that there are $n_1, n_2 \ldots, n_i \ldots\ldots$ number of particles in groups whose approximate constant energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i \ldots\ldots$ respectively. Let $g_i$ be the number of eigen states (*i.e. degeneracy or statistical weight*) of the ith level (for a non-degenerate case $g_i=1$).

Now we have to ascertain the distribution of $n_i$ indistinguishable particles in $g_i$ eigen states or sub levels.

Permutation

In Bose-Einstein statistics the conditions are :

(i) The particles are indistinguishable from each other, so that there is no distinction between the different ways in which $n_i$ particles can be chosen.

(ii) Each eigen state (*i.e.*, sub-level or cell) of ith quantum state may contain 0, 1, 2,... upto $n_i$ indentical particles.

(iii) The sum of energies of all the particles in the different quantum groups taken together constitutes the total energy of the system.

For finding Bose-Einstein distribution consider a box divided into $g_i$ sections (or cells) and $n_i$ indistinguishable particle are to be distributed amoung these sections. The choice that which of the sections will head the sequence and be made in $g_i$ ways. Once this has been done, the total number or permutation of $n_i$ particles *and the remaining* $(g_i-1)$ *sections* is $(n_i+g_i-1)!$ *Thus, the total number of possible ways in which* $n_i$ *particles can be distributed in* $g_i$ *sections is*

$$g_i\,[(n_i+g_i-1)]\,! \qquad \ldots(1)$$

Since the particles are indistinguishable, the permutations of particles among themselves will not give rise to indistinguishable arrangements. Obviously, there are $n_i\,!$ such permutations, hence expressions (1) must be divided by $n_i\,!$.

Further, the distributions which arise by mere permutation of sections among themselves do not produce different states.

Obviously, there are $g_i$ such permutations hence expression (1) must also be divided by $g_i\,!$.

Thus, the required number of ways in which $n_i$ particles are *to be distributed among* $g_i$ *sub-levels of* ith *quantum group is*

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

This result is in agreement with the postulate of equal *a priori probability* which states that the number of eigen states for a given energy $\varepsilon_i$ is equal to the degeneracy $g_i$ for $n_i = 1$:

Similarly, expression can be found for various other quantum states. Considering all the available quantum groups, with $n_1$ particles in first group of energy $\varepsilon_1$, $n_2$ particles in second group of energy $\varepsilon_2$ and so on, *the total number of distinguishable arrangements is given by*

$$G = \frac{(n_1+g_1-1)!}{n_1!(g_1-1)!} \cdot \frac{(n_2+g_2-1)!}{n_2!(g_2-1)} \cdot \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}$$

$$= \prod_i \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!} \qquad \text{...(2a)}$$

As $n_i$ and $g_i$ are large numbers, we may neglect one in above expression, therefore equation (2*a*) may be written as

$$\therefore G = \prod_i \frac{(n_i+g_i)!}{n_i!(g)!} \qquad \text{...(2b)}$$

In accordance with the postulate of equal a probability of states, the probability $\Omega$ of the system for occurring with the specified distribution is proportional to *the total number of eigen states, i.e.*

$$\Omega = \prod_i \frac{(n_i+g_i)!}{n_i!\,g_i!} \times \text{constant}. \qquad \text{...(3)}$$

The distribution law of Bose-Einstein statistics can now be obtained by determining the *most probable distribution* as in classical statistics.

Taking log of equation (3), we have

$$\log \Omega = \log\left[\prod_i \frac{(n_i+g_i)!}{n_i!\,g_i!} \times \text{constant}\right]$$

$$= \sum_i [\log (n_i+g_i)! - \log n_i! - \log g_i!] + \text{constant}. \qquad \text{...(4)}$$

As $n_i$ and $g_i$ are very large numbers, we can use Stirling approximation.

$$\log n! = n \log n - n.$$

So we get

$$\log \Omega = \sum_i (n_i+g_i) \log (n_i+g_i) - n_i \log n_i - g_i \log g_i] + \text{constant} \qquad \text{...(5)}$$

Remembering that $g_i$ is not subject to variation and $n_i$ varies continuously, the differentiation of above equation gives

$$\delta (\log \Omega) = \sum_i \left[ (n_i+g_i) \times \frac{1}{(n_i+g_i)} \delta n_i + \log (n_i+g_i)\, \delta n_i - n_i \times \frac{1}{n_i} \delta n_i - \log n_i\, \delta n_i \right]$$

$$= \sum_i (\log (n_i+g_i) - \log n_i)\, \delta n_i$$

$$= -\sum_i \left\{ \log \frac{n_i}{n_i+g_i} \right\} \delta n_i. \qquad \text{...(6)}$$

For most probable distribution $\Omega_{\max}$, we have $\delta (\log \Omega_{\max}) = 0$. Thus the condition of most probable distribution gives

$$\sum_i \left\{ \log \frac{n_i}{n_i+g_i} \right\} \delta n_i = 0. \qquad \text{...(7)}$$

The two subsidiary conditions are

(i) Total number of particles of the system is constant *i.e.*,

$$n = \sum_i n_i = \text{constant}. \qquad \text{...(8)}$$

*i.e.* $\delta n = \Sigma\, \delta n_i = 1$

(ii) Total energy of the system is constant *i.e.*

$$E = \sum_i n_i \varepsilon_i = \text{constant}.$$

*i.e.*, $\delta E = \sum_i \varepsilon_i\, \delta n_i = 0. \qquad \text{...(9)}$

Now we shall apply the Lagrangian method of undetermined multipliers. For this we multiply equation (8) by $\alpha$, equation (9) by $\beta$ and add the resulting expressions to equation (7): so that we get

$$\sum_i \left[ \log\left( \frac{n_i}{n_i+g_i} \right) + \alpha + \beta\varepsilon_i \right] \delta n_i = 0. \qquad \text{...(10)}$$

As the variation $\delta n_i$ are independent of each other, we get

$$\log\left( \frac{n_i}{n_i+g_i} \right) + \alpha + \beta\varepsilon_i = 0.$$

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

*i.e.* $\dfrac{n_i+g_i}{n_i} = e^{\alpha+\beta\varepsilon_i}$

*i.e.*, $1 + \dfrac{g_i}{n_i} = e^{\alpha+\beta\varepsilon_i}$

*i.e.* $\dfrac{g_i}{n_i} = e^{\alpha+\beta\varepsilon} \in_i - 1$

*i.e.* $n_i = \dfrac{g_i}{e^{\alpha+\beta\varepsilon_i} - 1} \qquad \text{...(11)}$

This equation represents the most probable distribution of the particles amont various energy levels for a system obeying Bose-Einstein statistics and is therefore known as *Bose-Einstein's distribution law*.

## 8.13 Fermi-Dirac Statistics : Fermi Dirac Distribution Law

This statistics is obeyed by indistinguishable particles of half-integral spin that have anti-symmetric wave function and obey Pauli exclusion principle.

Consider a system having $n$ indistinguishable particles. Let these particles be divided into quantum groups or levels such that there are $n_1, n_2 \ldots n_i \ldots\ldots$ number of particles in groups whose approximate constant energies are $\varepsilon_1, \varepsilon_2, \ldots \varepsilon_i, \ldots\ldots$ respectively. Let $g_i$ denote the *dengeneracy or statistical weight* (*i.e.*, number of sub-levels) of $i^{th}$ level.

Now the problem is to find the Fermi-Dirac distribution law *i.e.*, assertain the distribution of $n_i$. Fermi particles in $g_i$ eigen states (or sub-levels).

In Fermi-Dirac statistics the conditions are :

(i) The particles are indistinguishable from each other so that there is no distinction between the different ways in which $n_i$ particles are chosen.

(ii) The particles obey Pauli's exclusion principle according to which each sub level or cell may contain 0 or 1 particle. Then obviously $g_i$ must be greater than or equal to $n_i$.

(iii) The sum of energies of all the particles in the different quantum groups taken together constitutes the total energy of the system.

Now the distribution of $n_i$ particles in $g_i$ states can be done in the following ways.

Since due to Pauli's principle no cell can occupy more than one particle, therefore among $g_i$ cells only $n_i$ cells are occupied by one particle each and the remaining $(g_i - n_i)$ cells are empty. The possible number of such a distribution is given by $g_i\,!$ corresponding to the permutations of the $g_i$ cells. But as the particles are indistinguishable, therefore all the occupied $n_i$ cells are similar to each other. Hence $n_i\,!$ permutations of occupied cells will not give rise to indistinguishable arrangements. Further $(g_i - n_i)\,!$ permutations of empty cells among themselves also give rise to indistinguishable arrangements. Hence the number of distinguishable arrangements of $n_i$ particles in $g_i$ cells

and
$$\frac{g_i\,!}{n_i\,!\,(g_i - n_i)\,!} \qquad \text{...(1)}$$

Similar expressions can also be found for various other quantum states. Considering all the available quantum groups, with $n_i$ particles in first group of energy $\varepsilon_1$, $n_2$ particles in second group of energy $\varepsilon_2$ and so on and keeping in mind that due to indistinguishability of particles, the division of total number of $n$ particles into groups of $n_1, n_2, \ldots n_i$ particles can be done in only one way; the total number of eigen states for the whole system is given by

$$G = \prod_i \frac{g_i\,!}{n_i\,!\,(g_i - n_i)\,!} \qquad \text{...(2)}$$

In accordance with the postualate of equal a priori probability of states, the probability $\Omega$ of the system for occurring with the specified distribution is proportional to the total number of eigen states *i.e.*,

$$\Omega = \prod_i \frac{g_i\,!}{n_i\,!\,(g_i - n_i)\,!} \times \text{constant.} \qquad \text{...(3)}$$

The *Fermi-Dirac distribution law can* now be obtained by determining the *most probable distribution*.

Taking log of equation (3), we get

$$\log \Omega = \log \left\{ \prod_i \frac{g_i\,!}{n_i\,!\,(g_i - n_i)\,!} \times \text{constant} \right\}.$$

$$= \sum_i \left[\log g_i\,! - \log n_i\,! - \log (g_i - n_i)\,!\right] + \text{constant.} \qquad \text{...(4)}$$

As $n_i$ and $g_i$ are large numbers, therefore using Stirling approximation, eqn. (4) reduces to

$$\log \Omega = \sum_i \left[g_i - \log g_i - \log n_i + n_i - (g_i - n_i) \log (g_i - n_i) + (g_i - n_i)\right] + \text{constant}$$

$$= \sum \left[(n_i - g_i) \log (g_i - n_i) + g_i \log g_i - n_i \log n_i\right] + \text{constant.} \qquad \text{...(5)}$$

Remembering that $g_i$ is not subject to variation and $n_i$ varies continuously, the differentiation of above equation gives

$$\delta (\log \Omega) = \Sigma \{\log (g_i - n_i) - \log n_i\}\, \delta n_i$$

$$= -\sum_i \left\{ \log \frac{n_i}{g_i - n_i} \right\} \delta n_i. \qquad \text{...(6)}$$

For most probable distribution $\Omega = \Omega_{\max}$, so $\delta (\log \Omega_{\max}) = 0$. Thus the *conditions of most probable distribution* gives

$$\sum_i \left\{ \log \frac{n_i}{g_i - n_i} \right\} \delta n_i = 0. \qquad \text{...(7)}$$

The two subsidiary conditions are

(i) The total number of particles of the system is constant

*i.e.* $\quad n = \sum_i n_i = \text{constant}$

*i.e.* $\quad \delta n = \Sigma\, \delta n_i = 0 \qquad$ ...(8)

(ii) Total energy of the system is constant

*i.e.* $\quad E = \sum_i n_i \varepsilon_i = \text{constant}$

*i.e.* $\quad \delta E = \sum_i \varepsilon_i\, \delta n_i = 0. \qquad$ ...(9)

Now to apply the Lagrangian method of undetermied multipliers, we multiply equation (8) by $\alpha$ and equation (9) by $\beta$ and adding the resulting expressions to equation (7); so that we get

$$\sum_i \left\{ \log \left( \frac{n_i}{g_i - n_i} \right) + \alpha + \beta \varepsilon_i \right\} \delta n_i = 0. \qquad \text{...(10)}$$

As the variation $\delta n_i$ are independent of each other, we get

$$\log \frac{n_i}{g_i - n_i} + \alpha + \beta \varepsilon_i = 0.$$

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

*i.e.*
$$\frac{g_i - n_i}{n_i} = e^{\alpha + \beta \varepsilon_i}$$

*i.e.*
$$\frac{g_i}{n_i} - 1 = e^{\alpha + \beta \varepsilon_i}$$

*i.e.*
$$\frac{g_i}{n_i} = e^{\alpha + \beta \varepsilon_i} + 1$$

*i.e.*
$$n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + 1} \qquad \text{...(11)}$$

This equation represents the most probable distribution of the particles among various energy levels for a system obeying Fermi-Dirac statistics and is therefore known as *Fermi-Dirac Distribution law.*

## 8.14 Maxwell-Boltzmann Statistics : Maxwell's Boltzmann's Distribution Law

In classical mechanics the state of an individual particle is specified by giving a set of generalised co-ordinates and momenta, while in quantum mechanics it is specified by the quantum state $\phi_n(q)$ in which it is. In quantum statistical mechanics the classical assumption that equal regions in the phase space are a priori equally prabable is replaced by the assumption that *each quantum state is a priori equally probable.* Now to derive the Maxwell-Boltzmann distribution law instead of talking about cells, we talk about quantum states.

Consider a system having $n$ distinguishable particles. Let these particles be divided into quantum groups such that $n_1, n_2 \ldots, n_i, \ldots$ particles lie in groups having approximate energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i, \ldots$ respectively. Let $g_i$ denote the statistical weight of $i$th quantum group.

In Maxwell-Boltzmann statistics the conditions are :

(i) The particles are distinguishable and there are no symmetry restrictions.

(ii) Each eigen state of $i$th quantum group may contain 0, 1, 2 upto $n_i$ particles.

(iii) The total number of particles in the entire system is always constant, *i.e.,*

$$n = n_1 + n_2 + \ldots n_i + \ldots = \sum_i n_i = \text{constant}.$$

(iv) The sum of energies of all the particles in the different quantum groups taken together constitutes the total energy of the system.

Now the distribution of $n_i$ particles in $g_i$ eigen states can be done as follows :

For each group or level there are $g_i$ elementary wave functions available. Since there are no symmetry restrictions any number of particles in a particular group may be associated with a wave function of the group. Considering the $i$th group, the particles are accommodated in $g_i$ different sub-groups due to distinguishability of the particles each particle in the $i$th group can lie itself with any of the $g_i$ sub-groups, independently of the fate of the other particles. Therefore each particle of the $n_i$ particles has $g_i$ different possible choices. Consequently total number of choices for $n_i$ particles in $g_i$ sub-groups is $g_i^{n_i}$. Keeping in mind the distiguishability of particles the division of total number of $n$ particles into groups of $n_1, n_2, \ldots, n_i \ldots$ particles can be made in $n!$ ways by permuting the particles among themselves.

Thus the total number of eigen states for the whole system is

$$n!\, g_1^{n_1} g_2^{n_2} \ldots g_i^{n_i} \ldots\ldots$$

However, because particles within a group or level are indistinguishable from the macroscopic state point of view, their permutations among themselves do not produce any new eigen state.

Therefore, the total number of different eigen states of the whole system is

$$G = \frac{n!\, g_1^{n_1} g_2^{n_2} \ldots g_i^{n_i} \ldots}{n_1!\, n_2! \ldots n_i! \ldots}$$

$$= n! \frac{g_1^{n_1} g_2^{n_2}}{n_1!\, n_2!} \ldots \frac{g_i^{n_i}}{n_i!}$$

$$= n! \prod_i \frac{g_i^{n_i}}{n_i!} \qquad \ldots(1)$$

So, the probability of the given state is

$$\Omega = n! \prod_i \frac{g_i^{n_1}}{n_i!} \times \text{constant}. \qquad \ldots(2)$$

Taking log of above equation, we get

$$\log \Omega = \log n! + \sum_i (n_i \log g_i - \log n_i!) + \text{constant}. \qquad \ldots(3)$$

Using Stirling approximation, above equation reduces to

$$\log \Omega = n \log n - n + \sum_i (n_i \log g_i - n_i \log n_i + n_i) \; : \; \left(\text{since } \sum_i n_i = n\right)$$

$$= n \log n + \sum_i (n_i \log g_i - n_i \log n_i) + \text{constant} \qquad \ldots(4)$$

Remembering that $n$ and $g_i$ are not subject to variations and $n_i$ varies constinuously, the differentiation of equation (4) gives.

$$\delta (\log \Omega) = 0 + \sum_i \left[\log g_i\, \delta n_i - n_i \times \frac{1}{n_i} \delta n_i - \log n_i\, \delta n_i\right] + 0 = \sum_i [\log g_i - \log n_i - 1]\, \delta n_i$$

$$= -\sum_i \left\{ \log \frac{n_i}{g_i} + 1 \right\} \delta n_i. \qquad \ldots(5)$$

For most probable distribution

$$\Omega = \Omega_{\max}, \text{ so } \delta (\log \Omega_{\max}) = 0.$$

Thus, the condition of most probable distribution or maximum probability gives

$$\sum_i \left\{ \log \frac{n_i}{g_i} + 1 \right\} \cdot \delta n_i = 0. \qquad \ldots(6)$$

If we apply the condition that the total number of particles is constant

$$n = \sum_i n_i = \text{constant}$$

$$\Rightarrow \qquad \sum_i \delta n_i = 0 \qquad \ldots(7)$$

Then equation (6) gives

$$\sum_i \log \frac{n_i}{g_i} = 0 \qquad \ldots(8)$$

Now, we introduce auxiliary condition of conservation of total energy of the system, *i.e.,*

$$E = \sum_i \varepsilon_i n_i = \text{constant}$$

$$\Rightarrow \qquad \delta E = \sum_i \varepsilon_i\, \delta n_i = 0. \qquad \ldots(9)$$

Applying the method of Lagrangian undermine multipliers *i.e.,* multiplying equation (7) by $\alpha$, equation (9) by $\beta$ and adding the resulting expressions to equation (8), we get

$$\sum_i \left\{ \log \frac{n_i}{g_i} + \alpha + \beta\varepsilon_i \right\} . \delta n_i = 0. \qquad \ldots(10)$$

As the variation $\delta n_i$ are independent of each other, we get

$$\log \frac{n_i}{g_i} + \alpha + \beta\varepsilon_i = 0$$

*i.e.,*

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

*i.e.,*

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

*i.e.,*

$$n_i = \frac{g_i}{e^{\alpha + \beta\varepsilon_i}} \qquad \ldots(11)$$

This result is called *Maxwell-Boltzmann distribution law.*

## 8.15 Evaluation of the Constants α and β

The quantities α and β occur in the final expressions of all the three statistics. In all three cases $\beta = \frac{1}{kT}$ which can be seen as follows :

In all the three statistics the expression for log Ω may be written as

$$\log \Omega = \sum_i f(n_i), \qquad \ldots(1)$$

where

$$f(n_i) = \begin{cases} n_i \log g_i - n_i \log n_i + \text{constant} \\ \qquad \textbf{Maxwell-Boltzmann statistics} \\ (g_i + n_i)\log(n_i + g_i) - n_i \log n_i - g_i \log g_i + \text{constant} \\ \qquad \textbf{Bose-Einstein statistics} \\ (n_i - g_i)\log(g_i - n_i) - n_i \log n_i + g_i \log g_i + \text{constant} \\ \qquad \textbf{(Fermi-Dirac statistics)} \end{cases}$$

The condition of maximum probability gives

$$\delta(\log \Omega) = \Sigma \frac{\delta f}{n_i}\,\delta n_i = 0. \qquad \ldots(2)$$

The auxiliary conditions of conservation of total number of particles and the energy of the system yield

$$\delta n = \sum_i \delta n_i = 0, \qquad \ldots(3)$$

and

$$\delta E = \sum_i \varepsilon_i\,\delta n_i = 0. \qquad \ldots(4)$$

Combining equations (2), (3) and (4) by the method of Lagrangian undetermined multipliers, we may write

$$\delta(\log \Omega) = \alpha \sum_i \delta n_i + \beta \sum_i \varepsilon_i\,\delta n_i = 0. \qquad \ldots(5)$$

This equation holds good under the equilibrium conditions when both $\alpha \sum_i \delta n_i$ and $\beta \sum_i \varepsilon_i\,\delta n_i$ are zero as $n$ and $E$ are constants. It may be extended to the quasi-static process, where the external conditions change so slowly that the system may be considered to be in equilibrium at any instant.

If the total number of particles in the system is kept constant, the two auxiliary conditions become

$$\sum_i \delta n_i = 0, \qquad \ldots(6)$$

and

$$\delta E = \sum_i n_i\,\delta\varepsilon_i + \sum_i \varepsilon_i\,\delta n_i. \qquad \ldots(7)$$

The physical interpretation of the two terms in δE is as follows :

The *first term represents the work done in the expansion.* Thus

$$\sum_i n_i\,\delta\varepsilon_i = \sum_i n_i \frac{\partial \varepsilon_i}{\partial V}\,\delta V = -p\,\delta V, \qquad \ldots(8)$$

where

$$p = -\sum_i n_i \frac{\partial \varepsilon_i}{\partial V} \qquad \ldots(9)$$

Obviously, here $p$ denotes the pressure as the sum of forces $-\frac{\partial \varepsilon_i}{\partial V}$ of the particles in different states.

*The second term* $\sum_i \varepsilon_i\,\delta n_i$ *represents the change in the internal energy* corresponding to the arrangement of the particles with respect to different states. This change in internal energy is produced by *quantum transitions* due to the heat energy δQ supplied to the system, *i.e.*,

$$\delta Q = \sum_i \varepsilon_i\,\delta n_i. \qquad \ldots(10)$$

Thus equation (7) may be written as

$$\delta E = -p\,dV + \delta Q \qquad \ldots(11)$$

which is the mathematical representation of the first law of thermodynamics.

Now, keeping conditions (6) and (7) in mind, equation (5) may be written as

$$\delta(\log \Omega) = \beta \sum_i \varepsilon_i\,\delta n_i,$$

*i.e.*, $$\delta(\log \Omega) = \beta\,\delta Q \qquad \text{[using (10)]}. \qquad \ldots(12)$$

This shows that β δQ is a perfect differential and β is the integrating factor of the heat supplied to the system. Thus, statistical theory automatically leads to an analog of the second law of thermodynamics which states

$$\delta S = \frac{\delta Q}{T}. \qquad \ldots(13)$$

As δS is perfect differential, therefore, $1/T$ is the integrating factor of δQ.

From thermodynamics we know that all integrating factors for δQ differ only by a constant of probability. Therefore, we must have

$$\beta \propto \frac{1}{T}$$

*i.e.*, $$\beta = \frac{1}{kT} \qquad \ldots(14)$$

where $k$ is any constant.

Comparing equations (12) and (13), we have

$$\delta S = \frac{\delta Q}{T} = \frac{\delta \log \Omega}{\beta T}$$

$$= k\delta(\log \Omega) \text{ using (14)},$$

*i.e.*, $$\boxed{S = k \log \Omega.} \qquad \ldots(15)$$

which is well known Boltzmann's relation. *Therefore constant k is equation (14) is identified as Boltzmann's constant*

The factor α is determined by the condition $\Sigma\, n_i = n$ in different cases of interest.

## 8.16 Results and Comparision of Three Statistics :

The expressions for the most probable distributions in the three statistics are :

**(i) Maxwell-Boltzmann Statistics :**

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

*i.e.*, $$\frac{g_i}{n_i} = e^{\alpha + \beta\varepsilon_i} \qquad \ldots(1)$$

**(ii) Bose-Einstein Statistics :**

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

*i.e.* $$\frac{g_i}{n_i} + 1 = e^{\alpha + \beta\varepsilon_i} \qquad ...(2)$$

**(iii) Fermi-Dirac Statistics :**

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

*i.e.,* $$\frac{g_i}{n_i} - 1 = e^{\alpha + \beta\varepsilon_i} \qquad ...(3)$$

It is to be noted that if $g_i/n_i$ is very large in comparison to unity, we may write

$$\frac{g_i}{n_i} \approx \frac{g_i}{n_i} + 1 \approx \frac{g_i}{n_i} - 1,$$

*i.e.,* for large values $g_i/n_i$ Bose-Einstein and Fermi-Dirac distributions approach the Maxwell-Boltzmann distribution. This is the case for normal existence of gases when the temperature is not too low and pressure is not too high. Hence classical statistics is capable of describing their behaviour quite adequately. Only under certain extreme conditions the classical statistics fails. The examples of these cases are radiation, liquid Helium II and electron gas inside metals. In all such cases it is essential to use the respective distribution law.

## SOLVED EXAMPLES

**Ex. 1.** *Which of the statistics will you use for the systems having : (i) electrons, (ii) photons, (iii) mesons, (iv) oxygen molecules, (v) phonons, (vi) holes, (vii) neutrons, (viii) protons, (ix)* He$^4$ *atom at low temperature, (x) α-particle, (xi) positron.* ***(Rohilkhand 2005, 1993, Agra 2000)***

**Solution. (i) Electron, Proton, Neutron, Positron and holes** are spin half particles. They are, therefore, *fermions* and hence obey *Fermi-Dirac statistics.*

**(ii) Photons, phonons, mesons, α-particle and Helium atom at low temperature** are particles of integral spin. therefore, they are *Bosons* and Obey *Bose-Einstein statistics.*

**(iii) Oxygen molecules** are classical particles, they obey *Maxwell-Boltzmann statistics.*

**Ex. 2.** *Classify the following particles according to B-E and F-D statistics :*

*Proton, neutron, electron, photon, α-particle, Hydrogen atom, Hydrogen molecule, positron, lithium ion* ($^{6}_{3}$Li$^{++}$). ***(Kanpur 1992)***

**Solution.** The atoms or molecules having an **even number of fundamental particles have integral** spin value and are called **Bosons**. Similarly, the atoms or molecules having **odd number** of fundamental particles have **half integral spin** value and are called **Fermions**. Accordingly, the classification of particles is given below :

**Proton, Neutron, electron and positron** are fundamental particles having half spin value. Hence they all are **Fermions.**

**Photon** has spin 1 and hence it is **Boson**

α-particle ($_2$He$^4$) = $2p + 2n$ → Even → Boson
Hydrogen-atom = $1p + 1n + 1e$ → old → Fermion
Hydrogen-molecule = $2p + 2n + 2e$ → Even → Boson

Positron = $e^+$ → odd → Fermion
Lithium ion ($^{7}_{3}$Li$^{++}$) = $3p + 4n + e^-$ → Even → Boson

**Ex. 3.** *Four identical particles can be in any of five states. What are the number of possible ways of distributing them in various states according to Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics.* ***(Mumbai 2004)***

**Solution.** Number of states $g_i = 5$

Number of particles $n_i = 4$

(a) Number of ways according to Maxwell-Boltzmann statistics is

$$\Omega_{mB} = (g_i)^{n_i} = (5)^4 = 625$$

(b) Number of ways according to Bose-Einstein statistics is

$$\Omega_{BE} = \frac{g_i (n_i + g_i - 1)!}{n_i! g_i!} = \frac{5 \times (4 + 5 - 1)!}{4!5!}$$

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

(c) Number of Ways according to Fermi-Dirac statistics is

$$\Omega_{FD} = \frac{g_i!}{n_i!(g_i - n_i)!} = \frac{5!}{4!(5-4)!}$$

$$= \frac{5!}{4! \times 1!} = 5$$

**Ex. 4.** *Three particles ~~are~~ to be distributed in four energy states a, b, c and d. Write down all the possible ways for such a distribution if the particles are*

*(i) Fermions (b) Bosons (c) Classical particles.*

**Sol. (i) Fermions :** The Fermions are identical and indistinguistable and half-integral spin particles. Each energy state can contain zero or 1 particle. The number of possible ways of distribution of three particles in four energy states *a, b, c* and *d* being

$$\frac{g_i!}{n_i!(g_i - n_i)!} = \frac{4!}{3!(4-3)!} = 4$$

These four ways are given below

| | a | b | c | d |
|---|---|---|---|---|
| 1. | • | • | • | |
| 2. | • | • | | • |
| 3. | • | | • | • |
| 4. | | • | • | • |

**(ii) Bosons :** The bosons are identical and indistinguistables and integral spin particles. Each energy state can contain any number of particels. The number of possible ways in which three bosons may be distributed in four possible states *a, b, c* and *d* being

$$\frac{g_i (n_i + g_i - 1)!]}{n_i! g_i!} = \frac{4(4 + 3 - 1)!}{3!4!} = \frac{4 \times (6)!}{3!4!} = \frac{4 \times 5 \times 6}{2 \times 3} = 20$$

These 20 ways are given below :

| | a | b | c | d |
|---|---|---|---|---|
| 1 | ● ● ● | | | |
| 2 | | ● ● ● | | |
| 3 | | | ● ● ● | |
| 4 | | | | ● ● ● |
| 5 | ● ● | ● | | |
| 6 | ● ● | | ● | |
| 7 | ● ● | | | ● |
| 8 | ● | ● ● | | |
| 9 | | ● ● | ● | |
| 10 | | ● ● | | ● |
| 11 | ● | | ● ● | |
| 12 | | ● | ● ● | |
| 13 | | | ● ● | ● |
| 14 | ● | | | ● ● |
| 15 | | ● | | ● ● |
| 16 | | | ● | ● ● |
| 17 | ● | ● | ● | |
| 18 | ● | ● | | ● |
| 19 | ● | | ● | ● |
| 20 | | ● | ● | ● |

Thus there are twenty possible ways in which three bosons can be distributed in four energy states.

**(iii) Classical Particles :** The classical particles are identical but distinguishable. Each energy state can contain any number of particles. Let the particles be denoted by $p$, $q$, $r$ which are to be distributed in four energy states $a$, $b$, $c$ and $d$. The number of possible ways being $g_i^{n_i} = (4)^3 = 64$

These 64 ways are given below :

| | a | b | c | d |
|---|---|---|---|---|
| 1 | pqr | | | |
| 2 | | pqr | | |
| 3 | | | pqr | |
| 4 | | | | pqr |
| 5 | pq | r | | |
| 6 | pq | | r | |
| 7 | pq | | | r |
| 8 | qr | p | | |
| 9 | qr | | p | |
| 10 | qr | | | p |
| 11 | pr | q | | |
| 12 | pr | | q | |
| 13 | pr | | | q |
| 14 | r | pq | | |
| 15 | | pq | r | |
| 16 | | pq | | r |
| 17 | p | qr | | |
| 18 | | qr | p | |
| 19 | | qr | | p |

| | | | | |
|---|---|---|---|---|
| 20 | q | pr | | |
| 21 | | pr | q | |
| 22 | | pr | | q |
| 23 | r | | pq | |
| 24 | | r | pq | |
| 25 | | | pq | r |
| 26 | p | | qr | |
| 27 | | p | qr | |
| 28 | | | qr | p |
| 29 | q | | pr | |
| 30 | | q | pr | |
| 31 | | | pr | q |
| 32 | r | | | pq |
| 33 | | r | | pq |
| 34 | | | r | pq |
| 35 | p | | | qr |
| 36 | | p | | qr |
| 37 | | | p | qr |
| 38 | q | | | pr |
| 39 | | q | | pr |
| 40 | | | q | pr |
| 41 | p | q | r | |
| 42 | p | q | | r |
| 43 | p | r | q | |
| 44 | p | r | | q |
| 45 | p | | q | r |
| 46 | p | | r | q |
| 47 | q | p | r | |
| 48 | q | p | | r |
| 49 | q | r | p | |
| 50 | q | r | | p |
| 51 | q | r | | p |
| 52 | q | | p | r |
| 53 | r | p | q | |
| 54 | r | p | | q |
| 55 | r | q | p | |
| 56 | r | q | | p |
| 57 | r | | p | q |
| 58 | r | | q | p |
| 59 | | p | q | r |
| 60 | | p | r | q |
| 61 | | q | p | r |
| 62 | | q | r | p |
| 63 | | r | p | q |
| 64 | | r | q | p |

## 8.17 Black-Body Radiation and the Planck Radiation Law

This example is an application of Bose-Einstein statistics to photons. Radiation from a black body at absolute temperature $T$, and in thermal equilibrium is supposed to consist of light quanta or photons of energy content $h\nu$, moving in all possible directions with speed of light $c$ and therefore, possesses the momentum $h\nu/c$.

Some of the important properties of the photons are :

(i) Photons are particles of zero rest mass.

(ii) Photons are indistinguishable from one another the their number in a system is not necessarily constant; because in every emission process in an atom a new light quantum is formed and if a photon of frequency $\nu$ is absorbed by the wall of the enclosure, it can be replaced by the emission of several photons of frequencies $\nu_1, \nu_2 \ldots$, provided the total energy of the system is constant *i.e.*

$$h\nu = h\nu_1 + h\nu_2 + \ldots$$

Thus is this case, we have

$$\Sigma\, \delta n_i \neq 0 \qquad \ldots(1)$$

Hence we must drop the auxiliary condition $\sum_i \delta n_i = 0$, and therefore, the undetermined multiplier $\alpha$ is equal to zero.

(iii) The photons are Bose particles with spin 1, having two modes of propagation.

According to quantum idea, each allowed eigen state of a quantum mechanical system has a volume $h^3$ in the phase space.

The volume of each allowed eigen state, (*i.e.* each elementary cell) in the phase space can be written as

$$d\tau = dx\, dy\, dz\, dp_x\, dp_y\, dp_z = h^3. \qquad \ldots(2)$$

Let us now split the phase space into the position space and the momentum space. If we go on increasing the range of position co-ordinates, till they embrance the whole volume $V$ of the enclosure, then the particles can be found anywhere in the enclosure. So according to Heisenberg's uncertainty relation an element of volume in the momentum space can be written as

$$\sigma_p = \frac{h^3}{V} \qquad \ldots(3)$$

As $\sigma_p$ denotes the size of an elementary cell in the momentum space, only a single value of momentum can be recognised within a cell. Therefore, this represents an eigen state. If we take an arbitrary portion of the momentum space, only finite values of momentum, (*i.e.* eigen states) can occur in it. At any instant all photons having their momenta between $p$ and $p + dp$ will lie within a spherical shell described in momentum space with radii $p$ and $p + dp$. The volume of this shell is $4\pi p^2\, dp$. Therefore, the total number of eigen states between momenta $p$ and $p + dp$ is given by

$$g(p)\, dp = \frac{4\pi p^2\, dp}{\dfrac{h^3}{V}} = \frac{4\pi p^2\, V}{h^3}\, dp. \qquad \ldots(4)$$

For a photon,

$$p = \frac{h\nu}{c} \text{ or } dp = \frac{h\, d\nu}{c}.$$

Substituting these values in equation (4), the total number of eigen states between frequencies $\nu$ and $\nu + d\nu$ is given by

$$g(\nu)\, d\nu = 4\pi\, V \cdot \frac{\nu^2}{c^3}\, d\nu \cdot \qquad \ldots(5)$$

Taking into acount the doubling of the states due to polarisation of the photons, (*i.e.* two modes of propagation for each photon) the total number of eigen states available for the photons in the frequency range $\nu$ and $\nu + d\nu$ is given by

$$g(\nu)\, d\nu = 8\pi\, V \cdot \frac{\nu^2}{c^3}\, d\nu \cdot \qquad \ldots(6)$$

Introducing this result in Bose-Einstein's distribution law, we get

$$n(\nu)\, d\nu = \frac{g(\nu)\, d\nu}{e^{\alpha + \beta\varepsilon} - 1} \qquad \ldots(7)$$

In this case $\alpha = 0$, $\beta = \frac{1}{kT}$ and $\varepsilon = h\nu$ (the energy of a photon), therefore, using (6) above equation may be written as

$$n(\nu)\, d\nu = 8\pi\, V \cdot \frac{\nu^2}{c^3}\, \frac{d\nu}{e^{h\nu/kT} - 1}$$

*i.e.*

$$\frac{n(\nu)\, d\nu}{V} = \frac{8\pi\nu^2}{c^3} \cdot \frac{d\nu}{e^{h\nu/kT} - 1}. \qquad \ldots(8)$$

This equation represents the number of photons per unit volume lying in the frequency range $\nu$ and $\nu + d\nu$.

The *energy density* of radiation of frequencies between $\nu$ and $\nu + d\nu$ can now be found by multiplying equation (8) with the energy of the photon $h\nu$. Therefore, if $u(\nu)\, d\nu$ represents the energy density of radiation within the specified frequency range, then we get the energy distribution law

$$u(\nu)\, d\nu = \left(\frac{n(\nu)\, d\nu}{V}\, h\nu\right) = \frac{8\pi\nu^2\, d\nu}{c^3} \cdot \left(\frac{h\nu}{e^{h\nu/kT} - 1}\right)$$

*i.e.*

$$u(\nu)\, d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{d\nu}{e^{h\nu/kT} - 1}. \qquad \ldots(9)$$

This is well known *Planck's law of radiation in terms of frequency.*

Equation (9) in terms of wave-length $\lambda$ becomes

$$\left(\text{Since } \nu = \frac{c}{\lambda} \text{ and } d\nu = -\frac{c\, d\lambda}{\lambda^2}\right)$$

$$u(\lambda)\, d\lambda = \frac{8\pi h}{\lambda^3} \cdot \frac{(-c\, d\lambda/\lambda^2)}{e^{hc/\lambda kT} - 1}$$

negative sign occurs because when $\nu$ increases, $\lambda$ decreases

*i.e.* terms of modulus

$$|\, u(\lambda)\, d\lambda \,| = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{hc/\lambda kT} - 1} \qquad \ldots(10)$$

This is well known *Planck's law of radiation in terms of wavelength.*

Hence the Bose-Einstein statistics while confirming the validity of Planck's radiation law, has the merit of using only photons and no other-hypothetical resonators in the deduction of the law governing the black-body radiation.

## 8.18 Grand Canonical Ensemble and Quantum Statistics (Bose-Einstein and Fermi-Dirac Grand Partition Functions)

For indistinguishables particles we cannot specify which particle is in which state. We can only state that a certain number of particles occupy a given particular state. Let $\varepsilon_i$ be the energy of $i$th quantum state occupied by $n_i$ particles. Then the total number of particles $n$ and the total energy $E$ are given by

$$n = \sum_i n_i \qquad \text{...(1)}$$

$$E = \sum_i \varepsilon_i n_i. \qquad \text{...(2)}$$

The canonical partition function for the system is

$$Z = \sum_{\{n_i\}} \exp. \left(-\beta \sum_i \varepsilon_i n_i\right) \text{ with } \beta = 1/kT \qquad \text{...(3)}$$

Here $\{n_i\} = (n_1, n_2, \ldots)$ represents an allowed set of the numbers $n_i$ under conditions of (1) and (2). The summation runs over all such sets.

The grand partition function is

$$Z = \sum_{n=0}^{\infty} \exp. (\beta n\mu)\, Z_n = \sum_{n=0}^{\infty} \exp. (\beta n\mu) \sum_{\{n_i\}} \exp. \left(-\beta \sum \varepsilon_i n_i\right)$$

$$= \sum_{n=0}^{\infty} \sum_{\{n_i\}} \exp. \left\{\beta \sum_i (\mu - \varepsilon_i)\, n_i\right\} \sum_{n=0}^{\infty} \sum_{\Sigma n_i = n} \exp. \left\{\beta \sum_i (\mu - \varepsilon_i)\, n_i\right\}. \qquad \text{...(4)}$$

The sum over $\{n_i\}$ includes only those values of $n_i$'s for which $\sum_i n_i = n$. But in the grand canonical ensemble the limitation of constant $n$ is removed as is obvious in the summation $\sum_{n=0}^{\infty}$, therefore, we must forget the condition $\sum n_i = n$ in the grand canonical ensemble. Then $n$ can take unrestricted values and therefore, we can sum over $n_i$ independently, so that

$$Z = \sum_{n_1} \sum_{n_2} \ldots \sum_{n_i} \ldots\ldots \exp \left\{\beta \sum_i (\mu - \varepsilon_i)\, n_i\right\}$$

$$= \sum_{n_1} \exp \{\beta (\mu - \varepsilon_1)\, n_1\} \sum_{n_2} \exp \{\beta (\mu - \varepsilon_2) n_2\} \ldots \sum_{n_i} \exp \{\beta (\mu - \varepsilon_i)\, n_i\} \ldots$$

$$= \prod_i \sum_i^{n_i} \exp \{\beta (\mu - \varepsilon_i)\, n_i\}. \qquad \text{...(5)}$$

For simplicity we have assumed that all the energy levels are now-degenerate *i.e.*, $g_i = 1$. In carrying out the summation in equation (5), we have to take into account the nature of statistics, so, we shall now find the summation in Bose Einstein and Fermi-Dirac statistics independently.

**(a) Bose-Einstein grand partition function and distribution law :** For bosons (*i.e.* particles of zero or integral spin) the wave function is symmetrical and there is no limit to the number of particles in a state; therefore, $n_i$ can take on all values from 0 to ∞. Therefore,

$$Z_{B.E.} = \prod_i^{\infty} \sum_{n_i=0}^{\infty} \exp \{\beta (\mu - \varepsilon_i)\, n_i\}$$

Now using $(1-x)^{-1} = \sum_{n=0}^{\infty} x^n$ for $|x| < 1$, we get

$$Z_{B.E.} = \prod_i [1 - \exp. \{\beta (\mu - \varepsilon_i)\}]^{-1}. \qquad \text{...(6)}$$

This equation represents *Bose-Einstein grand partition function.* It is obvious that the Bose-Einstein grand partition function separates into factors $[1 - \exp. \{\beta (\mu - \varepsilon_i)\}]^{-1}$, one for each particle state, rather than for each particle.

The *Bose-Einstein grand potential* $\Omega_{B.E.}$ in now given by

$$\Omega_{B.E.} = -kT \log Z_{B.E.}$$

$$= -kT \sum_i \log [1 - \exp. \{\beta (\mu - \varepsilon_i)\}]^{-1}$$

$$= kT \sum_i \log [1 - \exp. \{\beta (\mu - \varepsilon_i)\}] = \sum_i \Omega_i \qquad \text{...(7)}$$

where $\quad \Omega_i = kT \log [1 - \exp. \{\beta (\mu - \varepsilon_i)\}].$

where $\Omega_i$ is the *grand potential for $i^{th}$ state,*

Therefore, $\quad n = -\left(\dfrac{\partial \Omega}{\partial \mu}\right)_{V, B} = \sum_i \overline{n_i} \qquad \text{...(9)}$

where $\overline{n}_i$ the ~~average~~ *number of bosons* ~~in the~~ $i^{th}$ state, is given by

$$\overline{n}_i = -\frac{\partial \Omega_i}{\partial \mu} = -kT \frac{\partial}{\partial \mu} \log (1 - \exp. \{\beta (\mu - \varepsilon_i)\}$$

$$= \beta kT \frac{\exp. \{\beta (\mu - \varepsilon_i)\}}{1 - \exp. \{\beta (\mu - \varepsilon_i)\}}$$

$$= \frac{1}{\exp. \{\beta (\varepsilon_i - \mu)\} - 1} \text{ (since } \beta = 1/kT). \qquad \text{...(10)}$$

Equation (10) represents the *Bose-Einstein distribution law.*

If we include the degeneracy term $g_i$. Bose-Einstin distribution law becomes

$$\overline{n}_i = \frac{g_i}{\exp. \{\beta (\varepsilon_i - \mu)\} - 1} \qquad \text{...(11)}$$

But the Bose-Einstein distribution law in terms of constants α and $\left(\beta = \dfrac{1}{kT}\right)$ is

$$\overline{n}_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i - 1}} \qquad \text{...(12)}$$

Camparing eqn. (11) and (12), we get

$$\alpha = -\frac{\mu}{kT} \text{ and } \beta = \frac{1}{kT}. \qquad \text{...(13)}$$

**(b) Fermi-Dirac grand partition function and the distribution law.**

For fermions (*i.e.*, particles of half integral spin), obeying Pauli-exclusion principle, the wave function is antisymmetric and so the number of particles in a state is restricted to 0 or 1. Thus $n_i$ can take values 0 or 1 only.

Therefore, *Fermi-Dirac grand partition function* is

$$Z_{FD} = \prod_i \sum_{n_i = 0 \text{ or } 1} \exp. \{\beta(\mu - \varepsilon_i) n_i\}$$

$$= \prod_i [1 + \exp\{\beta(\mu - \varepsilon_i)\}] \qquad \ldots(14)$$

Obviously Fermi-Dirac grand function partition like Bose-Einstein grand partition function separates into factors

$$[1 + \exp. \{\beta(\mu - \varepsilon_i)\}],$$

one for each particle state.

The Fermi-Dirac grand potential $\Omega_{FD}$ is given by

$$\Omega_{FD} = -kT \log Z_{FD}$$

$$= -kT \sum_i \log [1 + \exp\{\beta(\mu - \varepsilon_i)\}] = \sum_i \Omega_i \qquad \ldots(15)$$

where $$\Omega_i = -kT \log [1 + \exp. (\beta(\mu - \varepsilon_i))] \qquad \ldots(16)$$

is the *Fermi-Dirac grand potential for $i^{th}$ state.*

Therefore,

$$n = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,B} = -\sum_i \frac{\partial \Omega_i}{\partial \mu} = -\sum_i \bar{n}_i. \qquad \ldots(17)$$

where $\bar{n}_i$, the average *number of fermions in $i^{th}$ quantum state, is* given by

$$\bar{n}_i = -\frac{\partial \Omega_i}{\partial \mu} = kT \frac{\partial}{\partial \mu} [\log (1 + \exp. \{\beta(\mu - \varepsilon_i)\}]$$

$$= \frac{1}{\exp. \{\beta(\varepsilon_i - \mu)\} + 1} \qquad \ldots(18)$$

If we include the degeneracy term $g_i$ the above expression becomes

$$\bar{n}_i = \frac{g_i}{\exp\{\beta(\varepsilon_i - \mu)\} + 1} \qquad \ldots(19)$$

This equation represents the *Fermi-Dirac distribution law.*

The Fermi-Dirac distribution law in terms of constants α and $\beta\left(= \frac{1}{kT}\right)$ is

$$\bar{n}_i = \frac{g_i}{e^{\alpha + \beta\varepsilon_i} + 1}. \qquad \ldots(20)$$

Comparing equations (19) and (20) we get

$$\alpha = -\frac{\mu}{kT} \text{ and } \beta = \frac{1}{kT} \qquad \ldots(21)$$

It is obvious that equations (13) and (21) give the same values of α and β.

## 8.19 Bose-Einstein Gas

It may be pointed out that Bose-Einstein and Fermi-Dirac distributions need not be used for ordinary atomic or molecular gases; since these gases are in practice always described with sufficient accuracy by the Boltzmann distribution. An assembly of bosons (*i.e.* indistinguishable elementary particles of zero or integral spin) is termed as *Bose-Einstein gas.*

Consider a pefect Bose-Einstein gas of *n* bosons. Let these particles be distributed among quantum groups or states such that these are $n_i, n_2, \ldots, n_i, \ldots$ number of particles in quantum states whose approximate constant energies are $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i, \ldots$ respectively.

As the gas is assumed to be perfect, the interaction between its particles is negligible so that the energy may be regarded as entirely translational in character. Therefore the result obtained in this case will be particularly applicable to the mono-atomic gas.

If $g_i$ is the *degeneracy* or *statistical weight of $i^{th}$* quantum state then according to Bose-Einstein distribution law, the *most probable distribution* is given by

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

where $$\alpha = -\frac{\mu}{kT} \text{ and } \beta = \frac{1}{kT}$$

Equation (1*a*) may be written as

$$n_i = \frac{g_i}{\frac{1}{A} e^{\beta\varepsilon_i} - 1} \qquad \ldots(1b)$$

where $$A = e^{-\alpha}. \qquad \ldots(2)$$

As the number of particles in a state cannot be negative, we must always have $n_i \geq 0$. This requires

$$e^{\alpha + \beta\varepsilon_i} = \frac{1}{A} \cdot e^{\beta\varepsilon_i} \geq 1. \qquad \ldots(3)$$

If the ground state (or lowest energy state) is taken to be at zero energy, then

$$e^{\alpha} = e^{-\mu/kT} = \frac{1}{A} \geq 1. \qquad \ldots(4)$$

*i.e.* $$\alpha \geq 0; \mu \leq 0, 0 \leq A \leq 1. \qquad \ldots(5)$$

The constant α can be determined by the condition

$$n = \sum_i n_i = \sum \frac{g_i}{e^{\alpha + \beta\varepsilon_i} - 1}$$

$$= \sum_i \frac{g_i}{\frac{1}{A} e^{\beta\varepsilon_i} - 1} \qquad \ldots(6)$$

It is known that for the particles in a box of normal size, the *translational levels are spaced closely enough so that we can integrate over phase instead of summing over particles states,*

The number of particle states $g(p)\,dp$ lying between momentum $p$ and $p + dp$ is given by

$$g(p)\,dp = g_s \frac{4\pi p^2\,dp}{h^3/V} \text{ as in section (8.14),} \qquad \ldots(7)$$

where $g_s$ is the *spin degeneracy factor* caused by the particle spin *s*.

For simplicity, let us take $s = 0$, *i.e.* $g_s = 1$, then equation (7) becomes

$$g(p)\,dp = \frac{4\pi V}{h^3} p^2\,dp. \qquad \ldots(8)$$

According to equation (1) for most probable distribution the number of particles in the momentum range $p$ and $p+dp$ is given by

$$n(p)\,dp = \frac{g(p)\,dp}{e^{\alpha+\beta\varepsilon_i}-1} \qquad \text{—(9)}$$

Now, remembering that for perfect gas (non-integrating) particles

$$\varepsilon = \frac{p^2}{2m} \qquad \text{...(10)}$$

and using equation (8) we get

$$n(p)\,dp = \frac{4\pi V}{h^3}\cdot\frac{p^2\,dp}{e^{\alpha+p^2/2mkT}-1}\left(\text{since } \beta = \frac{1}{kT}\right) \qquad \text{...(11)}$$

Using equation (10) and (11) the number of particles lying between energy range $\varepsilon$ and $\varepsilon+d\varepsilon$ may be written as

$$n(\varepsilon)\,d\varepsilon = \frac{\frac{4\pi V}{h^3}\cdot(2m\varepsilon)\left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon}{e^{\alpha+\varepsilon/kT}-1}$$

$$= \frac{4\pi m V}{h^3}\sqrt{(2m)}\,\frac{\varepsilon^{1/2}\,d\varepsilon}{e^{\alpha+\varepsilon/kT}-1} \qquad \text{...(12)}$$

Now, let us substitute

$$x = \frac{\varepsilon}{kT} \quad \text{or} \quad dx = \frac{d\varepsilon}{kT} \qquad \text{...(13)}$$

So that equation (12) may be expressed as

$$n(\varepsilon)\,d\varepsilon = \frac{4\pi m V}{h^3}(2m)^{1/2}\frac{(kT\,x)^{1/2}\,(kT\,dx)}{e^{\alpha+x}+1}$$

$$= \frac{V}{h^3}(2\pi mkT)^{3/2}\,\frac{2}{\sqrt{\pi}}\,\frac{x^{1/2}\,dx}{e^{\alpha+x}-1} \qquad \text{...(14)}$$

Now, keeping in mind the closely space legels in this case, *the total number* of particles is given by

$$n = \int n(\varepsilon)\,d\varepsilon$$

$$= \frac{V}{h^3}(2\pi mkT)^{3/2}\cdot\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}\,dx}{e^{\alpha+x}-1}$$

$$= \frac{V}{h^3}(2\pi mkT)^{3/2} f_1(\alpha), \qquad \text{...(15)}$$

where

$$f_1(\alpha) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}\,dx}{e^{\alpha+x}-1} \qquad \text{...(16)}$$

The *total energy* of the system is given by

$$E = \int \varepsilon\, n(\varepsilon)\,d\varepsilon = \int kTx\,.\,n(\varepsilon)\,d\varepsilon \;[\text{using (13)}]$$

$$= \frac{V}{h^3}(2\pi mkT)^{3/2}\,.\,kT\cdot\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{3/2}\,dx}{e^{\alpha+x}-1} \;[\text{using (14)}]$$

$$= \frac{3}{2}\cdot\frac{V}{h^3}(2\pi mkT)^{3/2}\,.\,kT\,f_2(\alpha). \qquad \text{...(17)}$$

where

$$f_2(\alpha) = \frac{4}{3\sqrt{\pi}}\int_0^\infty \frac{x^{3/2}\,dx}{e^{\alpha+x}-1} \qquad \text{...(18)}$$

For $A<1$ the integral functions $f_1(\alpha)$ and $f_2(\alpha)$ may be evaluated by expanding the series as follows :

$$f_1(\alpha) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}\,dx}{e^{\alpha+x}-1} = \frac{2}{\sqrt{\pi}}\int_0^\infty x^{1/2}\left(\frac{e^x}{A}-1\right)^{-1} dx$$

$$= \frac{2}{\sqrt{\pi}}\int_0^\infty x^{1/2} A e^{-x}(1-Ae^{-x})^{-1}\,dx$$

$$= \frac{2}{\sqrt{\pi}}\int_0^\infty x^{1/2} A e^{-x}(1+Ae^{-x}+A^2e^{-2x}+\ldots)\,dx.$$

$$= \frac{2}{\sqrt{\pi}}\left[A\int_0^\infty x^{1/2}e^{-x}\,dx + A^2\int_0^\infty x^{1/2}e^{-2x}\,dx+\ldots\right]$$

$$= \frac{2}{\sqrt{\pi}}\left[\frac{\sqrt{\pi}}{2}\left(A+\frac{A^2}{2^{3/2}}+\frac{A^3}{3^{3/2}}+\ldots\right)\right]$$

$$= A+\frac{A^2}{2^{3/2}}+\frac{A^3}{3^{3/2}}+\ldots = \sum_{r=1}^{\infty}\frac{A^r}{r^{3/2}} \qquad \text{...(19)}$$

Similarly, we can write

$$f_2(\alpha) = A+\frac{A^2}{2^{5/2}}+\frac{A^3}{3^{5/2}}+\ldots = \sum_{r=1}^{\infty}\frac{A^r}{r^{5/2}} \qquad \text{...(20)}$$

Therefore, the expressions for total number of particles and total energy of perfect Bose-Einstein gas become

$$n = \frac{V}{h^3}(2\pi mkT)^{3/2}\sum_{r=1}^{\infty}\frac{A^r}{r^{3/2}}$$

$$= \frac{V}{h^3}(2\,\pi mkT)^{3/2}\left(A+\frac{A^2}{2^{3/2}}+\frac{A^3}{3^{3/2}}+\ldots\right) \qquad \text{...(21)}$$

$$E = \frac{3}{2}\frac{V}{h^3}(2\pi mkT)^{3/2}\cdot kT\sum_{r=1}^{\infty}\frac{A^r}{r^{5/2}}$$

$$= \frac{3}{2}\frac{V}{h^3}(2\pi mkT)^{3/2}\cdot kT\left(A+\frac{A^2}{2^{5/2}}+\frac{A^3}{3^{5/2}}+\ldots\right) \qquad \text{...(22)}$$

Dividing equation (22) by (21), we get

$$\frac{E}{n} = \frac{3}{2}kT\left(A+\frac{A^2}{2^{5/2}}+\frac{A^3}{3^{5/2}}+\ldots\right)\left(A+\frac{A^2}{2^{3/2}}+\frac{A^3}{3^{3/2}}\ldots\right)^{-1}$$

$$= \frac{3}{2}kT\left[1+\frac{A}{2^{5/2}}+\frac{A^2}{3^{5/2}}+\ldots\ldots\right]\left[1-\frac{A}{2^{3/2}}-\frac{A^2}{3^{3/2}}\ldots\right]$$

i.e.,
$$E=\frac{3}{2}nkT\left[1-\frac{A}{2^{3/2}}+\frac{A}{2^{5/2}}-\dots\right] \qquad \dots(23)$$

The value of $\alpha$ or $A$ can be determined by equation (15) or (21), *i.e.*,

$$f_1(\alpha)=\frac{n}{V}\frac{h^3}{(2\pi mkT)^{3/2}}. \qquad \dots(24)$$

Obviously, $f_1(\alpha)$ is proportional to the particle density $\frac{n}{V}$ and inversely proportional to $T^{3/2}$.

For $A << 1, f_1(\alpha)=A$, so equation (19) gives

$$A=e^{\alpha}=\frac{n}{V}\frac{h^3}{(2\pi mkT)^{3/2}} \qquad \dots(25)$$

Obviously, $A$ would be small for high temperatures or low density (or classical limit). However, the general value of $A$ or $\alpha$ can be obtained by inverting the series for $f_1(\alpha)$

$$f_1(\alpha)=A+2^{-3/2}A^2+3^{-3/2}A^3+\dots,$$

or
$$A=e^{-\alpha}=f_1(\alpha)-2^{-3/2}f_1^{\,2}(\alpha)+(2^{-3/2}-3^{-3/2})f_1^{\,3}(\alpha). \qquad \dots(26)$$

This equation represents value of $A$ as a function of $f_1(\alpha)$.

## 8.19 (a) Maxwell-Boltzmann Distribution as a Limiting Case of Bose-Einstein Distribution :

For $A << 1, e^{\alpha+\beta\varepsilon_i}$, *i.e.*, $\frac{1}{A}e^{\beta\varepsilon_i}$ becomes very large in comparison to 1, so that Bose-Einstein distribution

$$n_i=\frac{g_i}{e^{\alpha+\beta\varepsilon_i}-1} \text{ may be written as}$$

$$n_i\approx\frac{g_i}{e^{\alpha+\beta\varepsilon_i}}$$

which is Maxwell-Boltzmann distribution, refer eqn. (11) of section 8.14. Thus in the limiting case of $A << 1$, the Bose-Einstein distribution law reduces to Maxwell-Boltzmann distribution.

When $A << 1$, higher order terms in $A$ may be neglected and then

$$f_1(\alpha)=f_2(\alpha)=A.$$

So that we may write equations (21) and (22) as

$$n=\frac{V}{h^3}(2\pi mkT)^{3/2}A, \qquad \dots(27)$$

$$E=\frac{3}{2}\cdot\frac{V}{h^3}(2\pi mkT)^{3/2}kTA. \qquad \dots(28)$$

Dividing equation (28) by (27), we get

$$\frac{E}{n}=\frac{3}{2}kT, \text{ i.e., } E=\frac{3}{2}nkT, \qquad \dots(29)$$

which is well-known results of *Classical* (Maxwell-Boltzmann) *Statistics*.

## 8.19 (b) Degeneracy and Bose-Einstein Condensation

From Equation (25) the approximate value of $A$ is

$$A=e^{-\alpha}\approx\frac{n}{V}\frac{h^3}{(2\pi mkT)^{3/2}} \qquad \dots(3)$$

If the density of particles is increased and/or the temperature is decreased, the value of $A$ increases (or $\alpha=-\mu/kT$ decreases). Then the behaviour of the perfect gas departs farther and farther from that of the classical perfect gas due to the fact that the velocities of the particles are subject to quantum statistics and not to classical statistics. The gas under this condition is said to be *degenerate* and the parameter $A$ is called the *degeneracy parameter.*

As the expression for $A$ contains three variables, *viz.*, $m$ the mass of the particle, $n/V$ the particle density, *i.e.*, the number of particles per unit volume and $T$ the absolute temperature of the gas. obviously the criterion of *degeneracy* will be based on the magnitude of $\frac{(n/V)}{(mT)^{3/2}}$. Hence, the *degree of degeneracy will be large when temperature is low, particle density is large and the mass of each boson is small.* On account of the above three factors, the gas can become degenerate in three different ways :

For low energy values the maximum admissible value of $A$ is 1 [refer eqn. (5)] and consequently $\alpha$ can never be negative. Thus for low energy values the limiting case of highest degeneracy in Bose-Einstein gas reaches when $A=1, \alpha=0$. Then the maximum value of $f_1(\alpha)$ will be given by

$$[f_1(a)]_{\max}=f_1(0)=1+\frac{1}{2^{3/2}}+\frac{1}{3^{2/2}}+\dots=2{\cdot}612. \qquad \dots(31)$$

So the maximum value of particle density $n/V$ will be given by

$$\left(\frac{n}{V}\right)_{\max}=\frac{(2\pi mkT)^{3/2}}{h^3}(2{\cdot}612). \qquad \dots(32)$$

Since equation (32) corresponds to the limiting case of the Bose-Einstien degeneration, on solution of equation (15) can exist for

$$\frac{n}{V}>\frac{(2\pi mkT)^{3/2}}{h^3}\cdot 2{\cdot}612 \qquad \dots(33)$$

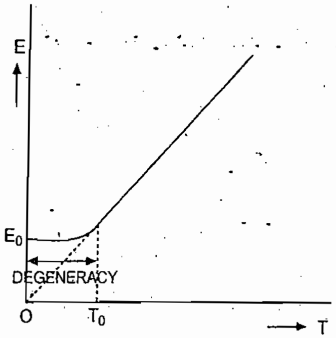
because this would involve $A>1$.

The fact that no value of $n/V$ can be greater than that given by equation (32) can be alternatively expressed in terms of the *critical temperature* $T_0$. defined as

$$\frac{n}{V}=\frac{(2\pi mkT_0)^{3/2}}{h^3}\cdot 2{\cdot}612, \qquad \dots(34a)$$

i.e.,
$$T_0=\frac{h^3}{2\pi mk}\left(\frac{1}{2{\cdot}612}\cdot\frac{n}{V}\right)^{2/3} \qquad \dots(34b)$$

Thus the critical temperature $T_0$ is the lowest temperature for which a solution of equation (15) is possible, *i.e.* there is one solution of equation (15) for $T<T_0$. $T_0$ is therefore the temperature at which the degeneracy of energy levels starts. If we plot a graph between the energy $E$ and the



(Fig. 8.2)

temperature $T$ of the gas a curve of the type shown in Fig. 8.2 is obtained. Below the critical temperature $T_0$ 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. $E_0$ is termed as *zero point energy* which will be undersood in the application of Fermi-Dirac statistics. The critical temperature $T_0$ is 5K for helium gas. Now, the question arises why there is no solution of equation (15) for $T < T_0$. The reason is that while arriving at Bose-Einstein distribution, because of the closeness of energy levels, we have assumed the continuous distribution in place of discrete distribution, and hence have replaced the summation by integration; while at low temperatures, the number of particles begin to crowd into lower energy levels and a large number of particles may occupy the ground state $\varepsilon_0 = 0$. This means that at low temperatures we must be careful in replacing the summation into integration.

Now, from equation (12) the number of particles lying between energy range $\varepsilon$ and $\varepsilon + d\varepsilon$ is given by

$$n(\varepsilon)\, d\varepsilon = \frac{g(e)\, d\varepsilon}{e^{\alpha + \varepsilon/kT'}} \qquad \ldots(35)$$

where

$$g(\varepsilon) = \frac{4\pi mV}{h^3}(2m\varepsilon)^{1/2}. \qquad \ldots(36)$$

It may be now noted that for ground state $\varepsilon = \varepsilon_0 = 0$, $g(\varepsilon) = 0$, while actually it should be unity $g(0) = 1$ as there is one state at $\varepsilon = 0$ Therefore, the above distribution [eqn. (35)] gives incorrect result for ground state, while this state is very important at low temperature. We further note at $\varepsilon \neq 0$, $g(\varepsilon) \neq 0$ and therefore the above distribution holds good.

Consequently, the distribution (35) can still be applied for all states except ground state which should be treated separately.

For a single state, we have

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

For ground state $\varepsilon_i = \varepsilon_0 = 0$ and $g_i = 1$. Therefore, the number of particles in the gound state is given by

$$n \to n_0 = \frac{1}{e^{\alpha} - 1} \qquad \ldots(37)$$

Therefore, the total number $n$ of particles for the degenerate case may be expressed as

$$n = n_0 + \int n(\varepsilon)\, d\varepsilon = n_0 + \int_0^{\infty} \frac{4\pi mV}{h^3} \frac{(2m\varepsilon)^{1/2}}{e^{\alpha + \varepsilon/kT} - 1} d\varepsilon$$

$$= n_0 + n'. \qquad \ldots(38)$$

where

$$n' = \frac{4\pi mV}{h^3} \cdot \sqrt{(2m)} \int_0^{\infty} \frac{\varepsilon^{1/2}\, d\varepsilon}{e^{\alpha + \varepsilon/kT} - 1} \qquad \ldots(39)$$

$$= \frac{V}{h^3}(2\pi mkT)^{3/2} f_1(\alpha) \quad \text{[using (16)]}$$

$$= n\left(\frac{T}{T_0}\right)^{3/2} \frac{f_1(\alpha)}{f_1(0)} \qquad \ldots(40)$$

[using (34*a*) as $f(0) = 2{\cdot}612$]

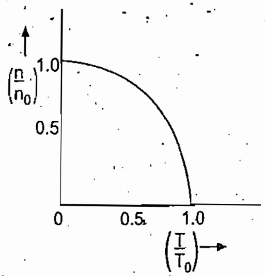
As $f_1(\alpha) < f_1(0)$, therefore $n'$ given by equation (40) acquires its maximum value when $\alpha = 0$. Thus the maximum number of particles ($n'$) occupping states above the ground state is given by

$$n' = n\left(\frac{T}{T_0}\right)^{3/2} \quad (\text{for } T < T_0). \qquad \ldots(41)$$

Therefore the rest of particles, given by

$$n_0 = n - n' = n\left[1 - \left(\frac{T}{T_0}\right)^{3/2}\right] \qquad (\text{for } T < T_0) \ldots(42)$$

must *condense* into the ground state.



(Fig. 8.3)

From equation (42), it is obvious that when the temperature of a Bose-Einstein gas is lowered below the critical temperature $T_0$, the number of particles in the ground state rapidly increases. *This rapid increase in the population of the ground state below the critical temperature* $T_0$ *for a Bose-Einstein gas is called the* **Bose-Einstein condesation**. It is obvious from equation (34*b*) that the critical temperature $T_0$ at which the Bose-Einstein condensation starts depends upon the particle density $n/V$ of the gas.

Equation (42) is plotted in Fig. 8.3 which represents the fraction of particles condensed in the ground state for $T \leq T_0$. At the ground state $\varepsilon = 0$, *the partiles of a Bose-Einstein degenerate gas condensed in the ground state do not contribute to the energy.*

For temperature above $T_0$, $\alpha \neq 0$, the number of particles is given by equation (15) with the negligible number of particles in the ground state and the gas is said to be the *classical* or *non-degenerate*.

In the case of Helium in liquid state $T_0$ can be calculated to have the value 3·12 K. Therefore the degeneration and condensation of Helium must start at 3·12 K. But experimental observation of the lambda point transition in liquid helium show that the condensation of helium starts at 2·19 K which is close to the calculated value. Below this temperature the liquid helium exhibits the remarkable physical properties of a superfluid. It is generally believed that the *lambda point transition observed in liquid helium at 2·19 K is essentially a Bose-Einstein condensation.*

## 8.20 Fermi-Dirac Gas

An assembly of Fermions (*i.e.*, indistinguishable particles of half integral spin obeying Pauli exclusion principle) is known as *Fermi-Dirac Gas*.

Consider a parfect Fermi-Dirac of $n$ fermions, Let these particles be distributed among quantum groups or states such that there are $n_1, n_2, \ldots, n_i, \ldots$ number of particles in quantum states whose approximate constant energies $\varepsilon_1, \varepsilon_2, \ldots \varepsilon_i, \ldots$ respectively.

If $g_i$ is the degeneracy or statistical weight of $i^{th}$ quantum state, then according to Fermi-Dirac distribution law the most *probable distribution is given by*

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

where $$\alpha = \frac{\mu}{kT}$$

Equation (1*a*) may be written as

$$n_i = \frac{g_i}{(1/A)\, e^{\beta \varepsilon_i} + 1} \qquad \ldots(1b)$$

where $$A = e^{-\alpha} \qquad \ldots(2)$$

As in the denominator of equation (1) a positive sign appears before one, α need not be restricted to positive values as in Bose-Einstein case; but may be positive or negative. The number of particles states lying between momentum $p$ and $p + dp$ is given by

$$g(p)\, dp = g_s \cdot \frac{4\pi p^2\, dp}{h^3/V} = g_s \cdot \frac{4\pi V p^2\, dp}{h^3} \qquad \ldots(3)$$

where $g_s$ is the spin degeneracy factor caused by the particles of spin $s$ and given by

$$g_s = (2s + 1) \qquad \ldots(4)$$

Since $\varepsilon = \dfrac{p^2}{2m}$ or $dp = \left(\dfrac{m}{2\varepsilon}\right)^{1/2} d\varepsilon$, the number of states between energy ε and $\varepsilon + d\varepsilon$ is given by

$$g(\varepsilon)\, d\varepsilon = g_s \cdot \frac{4\pi V (2m\varepsilon)\left(\dfrac{m}{2\varepsilon}\right)^{1/2} d\varepsilon}{h^3} \qquad \ldots(5)$$

For a gas of fermions at temperature $T$ in a volume $V$, the mean number of fermions in the energy range between ε and $\varepsilon + d\varepsilon$ is given by

$$n(\varepsilon)\, d\varepsilon = g_s \cdot \frac{4\pi m V}{h^3} \sqrt{(2m)} \cdot \frac{\varepsilon^{1/2}\, d\varepsilon}{e^{\alpha + \varepsilon/kT} + 1} \qquad \ldots(6)$$

As the gas is assumed to be perfect, the interaction between its particles is negligible, so that the energy may be regarded as entirely translation in character.

Further, in a box of normal size the translational levels are spaced closely enough so that we can integrate over phase space instead of summing over particles states.

Therefore the total number of particles in Fermi-Dirac gas is given by

$$n = \Sigma\, n(\varepsilon)\, d\varepsilon = \int n(\varepsilon)\, d\varepsilon$$

$$= g_s \frac{4\pi m V}{h^3} \sqrt{(2m)} \cdot \int_0^\infty \frac{e^{1/2}\, d\varepsilon}{e^{\alpha + \varepsilon/kT} + 1} \qquad \ldots(7)$$

and the total internal energy is given by

$$E = \int_0^\infty \varepsilon\, n(\varepsilon)\, d\varepsilon = g_s \cdot \frac{4\pi m V}{h^3} \sqrt{(2m)} \cdot \int_0^\infty \frac{\varepsilon^{3/2}\, d\varepsilon}{e^{\alpha + \varepsilon/kT} + 1} \qquad \ldots(8)$$

Now substituting $$x = \frac{\varepsilon}{kT} \quad \text{or} \quad dx = \frac{d\varepsilon}{kT} \qquad \ldots(9)$$

equations (7) and (8) take the form

$$n = g_s \cdot \frac{V}{h^3} (2\pi m k T)^{3/2} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}\, dx}{e^{\alpha + x} + 1}$$

$$= g_s \cdot \frac{V}{h^3} (2\pi m k T)^{3/2} f_1(\alpha). \qquad \ldots(10)$$

where $$f_1(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}\, dx}{e^{\alpha + x} + 1} = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}\, dx}{\frac{1}{A} e^x + 1} \qquad \ldots(11)$$

and $$E = \frac{3}{2} g_s \cdot \frac{V}{h^3} (2\pi m k T)^{3/2} \cdot kT \cdot \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}\, dx}{e^{\alpha + x} + 1}$$

$$= \frac{3}{2} \cdot g_s \cdot \frac{V}{h^3} (2\pi m k T)^{3/2} \cdot kT f_2(\alpha) \qquad \ldots(12)$$

where $$f_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}\, dx}{e^{\alpha + x} + 1} = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}\, dx}{\frac{1}{A} e^x + 1} \qquad \ldots(13)$$

The integrals $f_1(\alpha)$ and $f_2(\alpha)$ must be evaluated for both positive and negative values of α.

It is often convenient to introdce the *Fermi-distribution function* $f(\varepsilon)$ defined by

$$f(\varepsilon) = \frac{n(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{\alpha + \varepsilon/kT} + 1} = \frac{1}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} \qquad \ldots(14)$$

where α in terms of chemical potential μ or *Fermi-energy* $\varepsilon_F(T)$ *at temperature* $T$ is given by

$$\alpha = -\frac{\mu}{kT} = -\frac{\varepsilon_F(T)}{kT} \qquad \ldots(15)$$

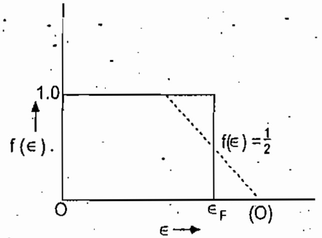
At $T = 0$K

$$\left.\begin{aligned} f(\varepsilon) &= 1 \text{ for } \varepsilon < \varepsilon_F(0) \\ &= 0 \text{ for } \varepsilon > \varepsilon_{(F)}(0) \end{aligned}\right\} \qquad \ldots(16)$$

This is shown in fig. 8.4 by solid line

At any temperature $T$,

$$f(\varepsilon) = \frac{1}{2} \text{ for } \varepsilon = \varepsilon_F.$$



**(Fig. 8.4) Plot of Fermi-Dirac distribution function at $T = 0$K (solid line) and at low temperature $\dfrac{kT}{\varepsilon_F} << 1$**

The value of $\varepsilon_F$ is determined by the condition that the total number of particles is constant at a given temperature $T$.

The expression for the number of fermions with energy between ε and $\varepsilon + d\varepsilon$ is written as

$$n(\varepsilon)\, d\varepsilon = f(\varepsilon)\, g(\varepsilon)\, d\varepsilon = g_s \cdot \frac{4\pi m V}{h^3} \sqrt{(2m)} \frac{\varepsilon^{1/2}\, d\varepsilon}{e^{\varepsilon - \varepsilon_F/kT} + 1} \qquad \ldots(17)$$

Thus at absolute zero all states with $0 < \varepsilon \le \varepsilon_F(0)$ are completely filled and all states with $\varepsilon > \varepsilon_F(0)$ are empty. The value $\varepsilon_F(0)$ of $\varepsilon_F$ at $T = 0$K is determined by

$$n = \int_0^\infty n(\varepsilon)\, d\varepsilon = \int_0^\infty g(\varepsilon) f(\varepsilon)\, d\varepsilon = \int_0^{\varepsilon_F(0)} g(\varepsilon)\, d\varepsilon$$

$$=\int_0^{\varepsilon_F(0)} g_s \cdot \frac{4\pi mV}{h^3}(2m)^{1/2}\varepsilon^{1/2}d\varepsilon = g_s \cdot \frac{4\pi mV}{h^3}(2m)^{1/2} \cdot \frac{2}{3}[\varepsilon_F(0)]^{3/2}$$

*i.e.,*
$$\varepsilon_F(0) = \frac{h^2}{2m}\left[\frac{3n}{4\pi Vg_s}\right]^{2/3} = \mu_F. \qquad \text{...(18)}$$

This represents the energy of the highest level occupied at $T = 0$K.

For particles of spin $\frac{1}{2}$ (*e.g.*, electrons, protons, etc.) the spin degeneracy factor $g_s$ is 2. This means that each level can be occupied by two particles one with spin up and the other with spin down (↑ ↓).

If $\rho = \left(\frac{mn}{V}\right) kg/m^3$ is the density of the gas, then numerically,

$$\varepsilon_F(0) = \mu_F = \begin{cases} 0{\cdot}625 \times 10^{-17}\rho^{2/3} \text{ joules or } 39\,\rho^{2/3} \text{ eV for electrons.} \\ 0{\cdot}227 \times 10^{-20}\rho^{2/3} \text{ joules or } 1{\cdot}42\,\rho^{2/3} \text{ eV for protons.} \end{cases} \qquad \text{...(19)}$$

For conduction electrons in metals $\rho \approx 0{\cdot}1$ kg/m$^3$. Thus Fermi-Dirace gas possesses appreciable energy at absolute zero, while both Bose-Einstein and classical statistics predict zero value of energy at 0K. This is because $n_i$ can have 0 or 1 only in Fermi-Dirac statistics.

As the temperature increases above 4K, the Fermi-Dirac distribution function near $\varepsilon_F(0)$ takes the shape of dotted line in fig. 8.4.

Let us now define a temperature $T_F$ called *Fermi-temperature*, by

$$T_F = \frac{\varepsilon_F(0)}{k} = \frac{\mu_F}{k} = \frac{h^2}{2mk}\cdot\left(\frac{3n}{4\pi Vg_s}\right)^{2/3} = \frac{h^2}{2m^{5/2}k}\left(\frac{3\rho}{4\pi g_s}\right)^{2/3} \qquad \text{...(20)}$$

When $T << T_F$ or $kT << \varepsilon_F(0)\ (= kT_F)$, then the distribution is called **strongly degenerate**. When $T > T_F$ or $kT > \varepsilon_F(0)$, then the distribution is called **slightly** or **weekly degenerate**. When $T >> T_F$ or $kT >> \varepsilon_F(0)$, then we get the classical limit and the distribution is **non degenerate**.

The value of $\alpha$ is negative in the case of strongly degenerate systems and positive for non-degenerate and slightly degenerate systems. Due to equation (16) this means that $\varepsilon_F > 0$ at low temperatures and $\varepsilon_F < 0$ at high temperatures.

## 8.20 (a) Degeneracy

(i) **Weak degeneracy :** At $T > T_F$ (*i.e.*, at intermediate temperatures) the Fermi gas is said to be slightly degenerate. In this case $kT > \varepsilon_F(0)$, then $\varepsilon_F$ is negative or $\alpha$ is positive and $A < 1$.

For $A < 1$, we can write

$$\frac{1}{\frac{1}{A}e^x + 1} = \left(\frac{1}{A}e^x + 1\right)^{-1} = Ae^{-x}(1 + Ae^{-x})^{-1}$$

$$= Ae^{-x}(1 - Ae^{-x} + A^2e^{-2x} - \dots).$$

Therefore
$$f_1(\alpha) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}dx}{\frac{1}{A}e^x + 1}$$

$$= \frac{2}{\sqrt{\pi}}\left[A\int_0^\infty e^{-x}x^{1/2}dx - A^2\int_0^\infty e^{-2x}x^{1/2}dx + A^3\int_0^\infty e^{-3x}x^{1/2}dx - \dots\right]$$

$$= A - \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} - \dots \qquad \text{...(21)}$$

Similarly
$$f_2(\alpha) = A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} - \dots \qquad \text{...(22)}$$

Using these values of $f_1(\alpha)$ and $f_2(\alpha)$, equations (10) and (12) take the form

$$n = g_s \cdot \frac{V}{h^3}(2\pi mkT)^{3/2}\left[A - \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} - \dots\right] \qquad \text{...(23)}$$

$$E = \frac{3}{2}g_s \cdot \frac{V}{h^3}(2\pi mkT)^{3/7}\cdot kT\left[A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} - \dots\right] \qquad \text{...(24)}$$

Dividing equation (24) by (23), we get

$$\frac{E}{n} = \frac{3}{2}kT\left[A - \frac{A^2}{2^{5/2}} + \frac{A^3}{3^{5/2}} - \dots\right]\left[A - \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}}\right]^{-1}$$

*i.e.,*
$$E = \frac{3}{2}kT\left[1 + \frac{A}{2^{5/2}} - \frac{A^2}{3^{5/2}} + \dots\right] \qquad \text{...(25)}$$

To the first approximation we can write

$$n = g_s \cdot \frac{V}{h^3}(2\pi mkT)^{3/2}A$$

$$E = \frac{3}{2}g_s \cdot \frac{V}{h^3}(2\pi mkT)^{3/2}\cdot kT\,A$$

*i.e.*
$$\frac{E}{n} = \frac{3}{2}kT \quad \text{or} \quad E = \frac{3}{2}nkT; \qquad \text{...(26)}$$

which is well known relation for a perfect gas in classical statistics.

A comparison of equations (25) and (26) shows that ideal Fermi-Dirac gas deviates from a perfect gas behaviour and this deviation, as we know, is called *degeneracy*. It is obvious that degeneracy is the function of $A$ (or $e^{-\alpha}$ or $e^{\mu/kT}$). Greater is the value of $A$, more marked will be the degeneracy. Hence for $A < 1$ or $T > T_F$, the Fermi gas is *slightly degenerate*.

**Case (ii) Strong degeneracy.** When $\alpha$ is large and negative, $A = e^{-\alpha} >> 1$. As degeneration increases will increase of $A$, therefore in this case degeneracy becomes more prominent. Further to the first approximation, from en. (23), we have

$$A \approx \frac{1}{g_s}\cdot\frac{n}{V}\frac{h^3}{(2\pi mkT)^{3/2}} \qquad \text{...(27)}$$

This equation shows that the gas will be strongly degenerate at low temperatures and high particle densities $\frac{n}{V}$. The evaluation of integrals $f_1(\alpha)$ and $f_2(\alpha)$ under these conditions is complicated.

We shall discuss this case of strong degeneracy at two temperature ranges :

(a) at absolute zero *i.e.*, when $T = 0$,

(b) when $T$ is above absolute zero, but $A >> 1$.

**Case (a). At absolute zero *i.e.*, when $T = 0$,** $A \to \infty$. In this case the Fermi-Dirac gas is *completely degenerate*.

At $T = 0$, we have

$$f(\varepsilon) = \frac{1}{\frac{1}{A} e^{\varepsilon/kT} + 1} = \frac{1}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} \begin{cases} = 1 \text{ for } 0 \le \varepsilon \le \varepsilon_F(0) \\ = 0 \text{ for } \varepsilon > \varepsilon_F(0) \end{cases}$$

So that

$$n(\varepsilon)\, d\varepsilon \begin{cases} = g_s \left(\frac{4\pi m V}{h^3}\right) . (2m)^{1/2} \varepsilon^{1/2} d\varepsilon \text{ for } \le \varepsilon \le \varepsilon_F(0) \\ = 0 \qquad \text{for } \varepsilon > \varepsilon_F(0) \end{cases}$$

where $\varepsilon_F(0)$ is given by eqn. (18).

**Now the total internal energy of perfect Fermi-Dirac gas at $T = 0$ *i.e.*, zero point energy of Fermi gas is**

$$E_0 = \int_0^{\varepsilon_F(0)} \varepsilon\, n(\varepsilon)\, d\varepsilon = g_s . \left(\frac{4\pi m V}{h^3}\right) (2m)^{1/2} \int_0^{\varepsilon_f(0)} \varepsilon^{3/2} d\varepsilon$$

$$= g_s \left(\frac{4\pi m V}{h^3}\right) (2m)^{1/2} . \left[\frac{\varepsilon^{5/2}}{5/2}\right]_0^{\varepsilon_F(0)}$$

$$= \frac{2}{5} g_s . \left(\frac{4\pi m V}{h^3}\right) (2m)^{1/2} [\varepsilon_F(0)]^{5/2}.$$

Using equation (18), above equation gives

$$E_0 = \frac{3nh^2}{10m}\left[\frac{3n}{4\pi V g_s}\right]^{2/3} = \frac{3}{5} n\, \varepsilon_F(0). \qquad \text{...(28)}$$

Now the pressure at $T = 0$ (*i.e., zero point pressure*) is given by

$$P_0 = \frac{2}{3}\frac{E_0}{V} \quad \left[\text{since } P = -\left(\frac{\partial E}{\partial T}\right)_{T, S} = \frac{2}{3}\frac{E}{V}\right]$$

$$= \frac{1}{5}\frac{nh^2}{Vm}\left(\frac{3n}{4\pi g_s V}\right)^{2/3} \qquad \text{...(29)}$$

From equations (28) and (29) it is obvious that a *strongly degenerate Fermi-Dirac gas possesses energy and exerts a pressure even at* 0 K, quite unlike a Bose-Einstein and classical gases where the energy and pressure at absolute zero are zero.

**Case (b). At temperature above absolute zero; but A >> 1 or T << T$_F$.**

In this case the Fermi-gas is strongly degenerate at low temperature and $\varepsilon$ is still positive.

From equation (17) the number of particles lying in the energy range between $\varepsilon$ and $\varepsilon + d\varepsilon$ is given by

$$n(\varepsilon)\, d\varepsilon = f(\varepsilon)\, g(\varepsilon)\, d\varepsilon = g_s . \frac{4\pi m V}{h^3} (2m)^{1/2} \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}$$

$$\boxed{= \frac{3}{2}\frac{n}{[\varepsilon_F(0)]^{3/2}} . \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}} \qquad \text{...(30)}$$

Therefore, the *total number of particles* is

$$n = \int_0^\infty n(\varepsilon)\, d\varepsilon = \frac{3}{2}\frac{n}{[\varepsilon_F(0)]^{3/2}} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} \qquad \text{...(31)}$$

and the *total integral energy* is

$$E = \int_0^\infty \varepsilon\, n(\varepsilon)\, d\varepsilon = \frac{3}{2} . \frac{n}{[\varepsilon_F(0)]^{3/2}} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} \qquad \text{...(32)}$$

To solve the integrals in equations (31) and (32), let us consider the general integral of the type

$$I \equiv \int_0^\infty \frac{\phi(\varepsilon)\, d\varepsilon}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} \qquad \text{...(33)}$$

where $\phi(\varepsilon)$ is a simple function of $\varepsilon$ such that $\phi(\varepsilon) = 0$ when $\varepsilon = 0$.

The integral of equation (33) can be expanded using the method of Taylor's series expansion,

$$I = \int_0^\infty \frac{\phi(\varepsilon)\, d\varepsilon}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} = \int_0^{\varepsilon_F} \phi(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(kT)^2 [\phi']_{\varepsilon = \varepsilon_F} + \frac{7\pi^4}{360}(kT)^4 [\phi''']_{\varepsilon = \varepsilon_F} + \ldots \qquad \text{...(34)}$$

where $\phi'$, $\phi'''$ etc. denote the first, third etc. differentials of the function $\phi$.

Now, for $\phi(\varepsilon) = \varepsilon^{1/2}$,

$$\left.\begin{aligned} \int_0^{\varepsilon_F} \phi(\varepsilon)\, d\varepsilon &= \frac{2}{3}(\varepsilon_F)^{3/2} \\ \phi'(\varepsilon) = \left(\frac{\partial \phi}{\partial \varepsilon}\right)_{\varepsilon = \varepsilon_F} &= \frac{1}{2}\varepsilon_F^{-1/2} \\ \phi''(\varepsilon) = -\frac{1}{4}\varepsilon_F^{-3/2}, \ \phi'''(\varepsilon) &= \frac{3}{8}\varepsilon_F^{-5/2} \end{aligned}\right\} \qquad \text{...(35)}$$

Then

$$n = \frac{3}{2}\frac{n}{[\varepsilon_F(0)]^{3/2}} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}$$

$$= \frac{3}{2}\frac{n}{[\varepsilon_F(0)]^{3/2}} \left[\frac{2}{3}\varepsilon_F^{3/2} + \frac{\pi^2}{6}(kT)^2 . \frac{1}{2}\varepsilon_F^{-1/2} + \frac{7\pi^4}{360}(kT)^4 . \frac{3}{8}\varepsilon_F^{-5/2} + \ldots\right]$$

or

$$1 = \frac{\varepsilon_F^{3/2}}{[\varepsilon_F(0)]^{3/2}}\left[1 + \frac{1}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2 + \frac{7}{640}\left(\frac{\pi kT}{\varepsilon_F}\right)^4 + \ldots\right]$$

or

$$\frac{\varepsilon_F}{\varepsilon_F(0)} = \left[1 + \frac{1}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2 + \frac{7}{640}\left(\frac{\pi kT}{\varepsilon_F}\right)^4 + \right]^{-2/3} \qquad \text{...(36)}$$

Remembering that $kT << \varepsilon_F$, we can take into account only the first two terms in the bracketed expression and write

$$\frac{\varepsilon_F}{\varepsilon_F(0)} = \left[1 + \frac{1}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right]^{-2/3} \approx 1 - \frac{1}{12}\left(\frac{\pi kT}{\varepsilon_F}\right)^2. \qquad \text{...(37)}$$

This gives

$$\varepsilon_F^2 = [\varepsilon_F(0)]^2\left[1 - \frac{1}{12}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right]^2 \approx [\varepsilon_F(0)]^2\left[1 - \frac{1}{6}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right]$$

$$\frac{1}{\varepsilon_F^2} \approx \frac{1}{[\varepsilon_F(0)]^2}\left[1+\frac{1}{6}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right] \qquad \text{...(38)}$$

Now we make the crude approximation by putting $\varepsilon_F = \varepsilon_F(0)$ in the second term of above expression, we get

$$\frac{1}{\varepsilon_F^2} \approx \frac{1}{[\varepsilon_F(0)]^2}\left[1+\frac{1}{6}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right]. \qquad \text{...(39)}$$

Now using equation (39), equation (37) gives

$$\varepsilon_F = \varepsilon_F(0)\left[1-\frac{1}{12}(\pi kT)^2 . \frac{1}{\varepsilon_F^2(0)}\left\{1+\frac{1}{6}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right\}\right]$$

$$\Rightarrow \qquad \varepsilon_F(T) \approx \varepsilon_F(0)\left[1-\frac{1}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right] \qquad \text{...(40)}$$

For

$$\phi(\varepsilon) = \varepsilon^{3/2}.$$

$$\left.\begin{aligned} &\int_0^{\varepsilon_F} \phi(\varepsilon)\, d\varepsilon = \frac{2}{5}\varepsilon_F^{5/2} \\ &[\phi'(\varepsilon)]_{\varepsilon=\varepsilon_F} = \frac{3}{2}\varepsilon_F^{1/2}, [\phi''(\varepsilon)]_{\varepsilon=\varepsilon_F} = \frac{3}{4}\varepsilon_F^{-1/2} \\ &[\phi'''(\varepsilon)]_{\varepsilon=\varepsilon_F} = -\frac{3}{8}\varepsilon_F^{-3/2} \end{aligned}\right\} \qquad \text{...(41)}$$

$$\therefore \qquad E = \frac{3}{2} . \frac{n}{[\varepsilon_F(0)]^{3/2}}\int_0^\infty \frac{\varepsilon^{3/2}\, d\varepsilon}{\varepsilon^{(\varepsilon-\varepsilon_F)/kT}+1}$$

$$= \frac{3}{2} . \frac{n}{\varepsilon_F^{3/2}(0)}\left[\frac{2}{5}\varepsilon_F^{5/2} + \frac{1}{6}(\pi kT)^2 . \frac{3}{2} . \varepsilon_F^{1/2} - \frac{7}{360}(\pi kT)^4 . \frac{3}{8}\varepsilon_F^{-3/2} + \ldots\right]$$

$$= \frac{3}{5}n . \left[\frac{\varepsilon_F}{\varepsilon_F(0)}\right]^{3/2} . \varepsilon_F\left[1+\frac{5}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2 - \frac{7}{384}\left(\frac{\pi kT}{\varepsilon_F}\right)^4 + \ldots\right]$$

$$\approx \frac{3}{5}n\,\varepsilon_F(0)\left(\frac{\varepsilon_F}{\varepsilon_F(0)}\right)^{5/2}\left[1+\frac{5}{8}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right]$$

Now using equations (39) and (40), we get

$$E \approx \frac{3}{5}n\,\varepsilon_F(0)\left[1-\frac{1}{12}\left(\frac{\pi kT}{\varepsilon_F}\right)^2\right]^{5/2}\left[1+\frac{5}{8}(\pi kT)^2 . \frac{1}{\varepsilon_F^2(0)} \times \left\{1+\frac{1}{6}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right\}\right]$$

$$\approx \frac{3}{5}n\,\varepsilon_F(0)\left[1-\frac{5}{24}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right]\left[1+\frac{5}{8}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right]$$

$$\approx \frac{3}{5}n\,\varepsilon_F(0)\left[1+\frac{5}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right] \qquad \text{...(42)}$$

The corresponding pressure is

$$P = \frac{2}{3}\frac{E}{V} \simeq \frac{2}{5}\left(\frac{n\,\varepsilon_F(0)}{V}\right)\left[1+\frac{5}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right]. \qquad \text{...(43)}$$

Equations (42) and (43) represent the approximate energy and pressure of a strongly degenerate gas.

## 8.21. Thermodynamic Properties of Degenerate Fermi-Dirac Gas :

(i) The *total energy* of ideal strongly degenerate Fermi-Dirac gas is given by

$$E = \frac{3}{5}n\,\varepsilon_F(0)\left[1+\frac{5}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right]. \qquad \text{...(1)}$$

[refer equation (42) of section 8·20]

(ii) *The pressure* of ideal strongly degenerate Fermi-Dirac gas is given by

$$P = \frac{2}{5}\frac{n\,\varepsilon_F(0)}{V}\left[1+\frac{5}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right] \qquad \text{...(2)}$$

[Refer equation (43) of section 8·20]

(iii) *The specific heat* $C_v$ of ideal strongly degenerate Fermi-Dirac gas is given by

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[\frac{3}{5}n\,\varepsilon_F(0)\left\{1+\frac{5}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right\}\right]_V$$

$$= \frac{3}{5}n\,\varepsilon_F(0)\left[0+\frac{5}{6}\left(\frac{\pi k}{\varepsilon_F(0)}\right)^2 . 2T\right]$$

$$= \frac{1}{2}\frac{n k^2 \pi^2}{\varepsilon_F(0)}T$$

$$= \lambda T, \qquad \text{...(3)}$$

whre $\lambda\left(=\dfrac{nk^2\pi^2}{2\,\varepsilon_F(0)}\right)$ is a constant quantity independent ot temperature, *i.e.*,

$$C_V \propto T.$$

Thus, the specific heat of ideal strongly degenerate Fermi-Dirac gas is proportional to the absolute temperature. We have already seen that the Fermi gas is strongly degenerate at low temperature, therefore, this result holds at very low temperatures.

(iv) *The entropy S of Fermi gas* at low temperature is given by

$$S = \int_0^T \frac{C_V}{T}\,dT = \int_0^T \frac{1}{2}\frac{n\pi^2 k^2}{\varepsilon_F(0)}\,dT$$

$$= \frac{1}{2}\frac{nk^2\pi^2}{\varepsilon_F(0)}T. \qquad \text{...(4)}$$

(v) *Helmholtz's free energy F* of degenerate Fermi gas is given by

$$F = E - TS = \frac{3}{5}n\,\varepsilon_F(0)\left[1+\frac{5}{12}\left\{\frac{\pi kT}{\varepsilon_F(0)}\right\}^2\right] - \frac{1}{2}\frac{nk^2\pi^2}{\varepsilon_F(0)} . T^2$$

$$= n\,\varepsilon_F(0)\left[\frac{3}{5}-\frac{1}{4}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right] \qquad \text{...(5)}$$

## 8.22. Electron Gas is Metals :

A metal can be considered to be composed of a system of fixed positive nuclei and a number of mobile electrons. These mobile electrons are assumed to move freely in the metal like the particles of a gas and constitute a perfect gas known as *electron gas*. On this assumption the classical statistics could explain to a certain extent the various properties of metals dependent on the motion of free electrons in metals such as electrical and thermal conductivities, thermoelectricity, themionic emission, magnetic properties of metals and photoelectric effect etc.

But in certain cases, the chief among them being the specific heat of metals, very serious difficulties were encountered in the use of classical statistics. That is why the theory of the *electron gas* was discredited to some extent.

Sommerfeld, in 1928, however, revived the electron theory of metals on the basis of the new quantum statistics. According to him, the electrons in metals are not completely free but only partially so, in the sense that though they are not bound to any particular atomic system, yet are bound to the metal as a whole. Therefore, the interior of the metal is to be conceived as a region of uniform potential, positive relative to free space, so that work is required to be done to extract an electron from the metal. The electrons in metals connot, therefore, be compared to the free particles of a gas obeying the classical statistics. Moreover due to their light mass and dense packing, the electrons in the metals should be assimilated to the particles of a gas under very high compression, hence to a degenerate gas. Further since these electrons are assumed to obey Pauli's exclusion principle, they should obey the Fermi-Dirac statisitics. Therefore to study the properties of the electrons in metals at low temperatures, we shall make use of the last section.

For electrons $s=\frac{1}{2}$ so that $g_s = 2s+1 = 2$.

Therefore from eqn. (18) of section (8.20) the Fermi energy at 0 K is.

$$\varepsilon_F(0) = \frac{h^2}{2m}\left[\frac{3n}{4\pi V g_s}\right]^{2/3} = \frac{h^2}{2m}\left[\frac{3n}{4\pi V.2}\right]^{2/3}$$

$$= \frac{h^2}{8m}\left(\frac{3n}{\pi V}\right)^{2/3} = 0{\cdot}625\times10^{-17}\,\rho^{2/3}\text{ joule or }39\,\rho^{2/3}\,eV, \qquad ...(1)$$

where $\rho = \left(\frac{mn}{V}\right)^{2/3}$ kg/m$^3$ is the density of the electron gas. For conduction electrons in metals $\rho \approx 0{\cdot}1$ kg/m$^3$.

The **Fermi temperature $T_F$ for electron gas is**

$$T_F = \frac{\varepsilon_F(0)}{k} = \frac{h^2}{8mk}\left(\frac{3n}{\pi V}\right)^{2/3} = (4{\cdot}52\times10^5\,\rho^{2/3})\,K. \qquad ...(2)$$

For $\rho = 0{\cdot}1$ kg/m$^3$, $T_F = 10^5$ K.

Thus electron gas below $10^5$ K temperature is degenerate.

The **degeneracy factor of an clectron gas, from eqn. (27) of section 8.20 is**

$$A = \frac{1}{g_s}\cdot\frac{n}{V}\frac{h^3}{(2\pi mkT)^{3/2}} = \frac{1}{2}\frac{n}{V}\frac{h^3}{(2\pi mkT)^{3/2}}$$

As $T \to 0, A \to \alpha$, therefore $\frac{1}{e^{\alpha+x}+1} = \frac{1}{\frac{1}{A}e^x+1} \to 1,$

so that for low temperatures

$$n = g_s\frac{V}{h^3}(2\pi mkT)^{3/2}\cdot\frac{2}{\sqrt{\pi}}\int_0^\infty x^{1/2}\,dx \text{ from (10)}$$

$$= \frac{4V}{\sqrt{\pi}}\cdot\frac{(2\pi mkT)^{3/2}}{h^3}\int_0^A x^{1/2}\,dx.$$

Here we have put $g_s = 2$ and have replaced the upper limit by $A$ at low temperatures near absolute zero since $A \to \infty$, when $T \to 0$

or
$$n = \frac{4V}{\sqrt{\pi}}\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{A^{3/2}}{\frac{3}{2}},$$

*i.e.,*
$$A = \frac{h^2}{2mkT}\left(\frac{3n}{8\pi V}\right)^{2/3} = \frac{h^2}{2m^{5/2}.kT}\left(\frac{3\rho}{8\pi}\right)^{2/3}. \qquad ...(3)$$

This equation represents the degeneracy factor of electron gas at low temperature near absolute zero.

Now substituting $h = 6{\cdot}6\times10^{34}$ joule sec, $m = 9\times10^{-31}$ kg. $k = 1{\cdot}38\times10^{-23}$ joule/deg and $\rho = 0{\cdot}1$ kg/m$^3$,

$$A = \frac{4{\cdot}66\times10^5}{T} \qquad ...(4)$$

This mean that *at low temperatures the electron gas is strongly degenerate.*

**Zero point energy of the elctron gas, from eqn. (28) is**

$$E_0 = \frac{3nh^2}{10m}\left(\frac{3n}{4\pi V g_s}\right)^{2/3} = \frac{3nh^2}{10m}\left(\frac{3n}{4\pi V.2}\right)^{2/3}$$

$$= \frac{3nh^2}{40m}\left(\frac{3n}{\pi V}\right)^{2/3} = \frac{3}{5}n\,\varepsilon_F(0). \qquad ...(5)$$

**Zero point pressure of the elctron gas, from eqn. (29), is**

$$P_0 = \frac{1}{5}\cdot\frac{nh^2}{Vm}\left(\frac{3n}{4\pi g_s V}\right)^{2/3} = \frac{1}{5}\cdot\frac{nh^2}{Vm}\left(\frac{3n}{8\pi V}\right)^{2/3}.$$

$$= \frac{nh^2}{20mV}\left(\frac{3n}{\pi V}\right)^{2/3} \qquad ...(6)$$

At normal temperatures the pressure of the elctron gas comes out to be sufficiently high of the order of $\approx 10^5$ atmosphere.

**The electronic contribution to the specific heat of metals at low temperatures is given by**

$$C_V = \left(\frac{\partial E}{ET}\right)_V = \frac{\partial}{\partial T}\left[\frac{3}{5}n\,\varepsilon_F(0)\left\{1+\frac{5}{12}\left(\frac{\pi kT}{\varepsilon_F(0)}\right)^2\right\}\right]_V$$

$$= \frac{1}{2}nk\pi^2\left(\frac{kT}{\varepsilon_F(0)}\right) \qquad ...(7)$$

$$= \lambda T$$

where $\lambda = \frac{nk^2\pi^2}{2\,\varepsilon_F(0)}$ is constant quantity, independent of temperature.

i.e., $$C_V \propto T.$$

Thus *the electronic contribution to the specific heat is proportional to the absolute temperature and vanishes at the absolute zero.*

## SOLVED EXAMPLES

**Ex. 4.** *Show that mean energy of free-electron at absolute zero of* $\frac{3}{5}$ *times of Fermi energy at absolute zero.*

**Ans. Mean Free-electron Energy at Absolute Zero**

The number of electrons in an electron-gas having energies between $\varepsilon$ and $\varepsilon + d\varepsilon$ is given by

$$n(\varepsilon)\,d\varepsilon = \frac{8\sqrt{2}\,\pi V m^{3/2}}{h^3}\,\frac{\varepsilon^{1/2}\,d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1}, \qquad \text{...(i)}$$

where $m$ is the mass of electron and $V$ is the volume of the electron-gas.

If $N$ is the total number of electrons, then the Fermi energy $\varepsilon_F$ is given by

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

or $$(\varepsilon_F)^{3/2} = \frac{h^3}{2\sqrt{2}\,m^{3/2}}\,\frac{3N}{8\pi V}$$

or $$\frac{8\sqrt{2}\,\pi V m^{3/2}}{h^3} = \frac{3N}{2}(\varepsilon_F)^{-3/2}.$$

Making this substitution in eq. (i), we get

$$n(\varepsilon)\,d\varepsilon = \frac{3N}{2}(\varepsilon_F)^{-3/2}\,\frac{\varepsilon^{1/2}\,d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1}.$$

At $T = 0$, all of the electrons have energies less than or equal to $\varepsilon_F$ (*i.e.* $\varepsilon \le \varepsilon_F$), so that at $T = 0$, we have

$$e^{(\varepsilon-\varepsilon_F)/kT} = e^{-\infty} = 0.$$

Therefore, at absolute zero

$$n(\varepsilon)\,d\varepsilon = \frac{3N}{2}(\varepsilon_F)^{-3/2}\,\varepsilon^{1/2}\,d\varepsilon.$$

Now, let us first find the total energy $E_0$ at absolute zero, which is

$$\begin{aligned} E_0 &= \int_0^{\varepsilon_F} \varepsilon\; n(\varepsilon)\,d\varepsilon \\ &= \frac{3N}{2}(\varepsilon_F)^{-3/2}\int_0^{\varepsilon_F}\varepsilon^{3/2}\,d\varepsilon \\ &= \frac{3N}{2}(\varepsilon_F)^{-3/2}\left(\tfrac{2}{5}\,\varepsilon_F^{5/2}\right) \\ &= \frac{3}{5}N\varepsilon_F. \end{aligned}$$

The average energy $\bar{\varepsilon}_0$ is this total energy divided by the total number $N$ of electrons. Thus

$$\bar{\varepsilon}_0 = \frac{E_0}{N} = \frac{3}{5}\varepsilon_F.$$

**Ex. 5.** *Calculate the Fermi energy in electron volts for sodium assuming that it has one free electron per atom. Given density of sodium = 0·97 g cm$^{-3}$, atomic weight of sodium = 23.* ***(Agra 2005)***

**Solution.** The Fermi energy is given by

$$\varepsilon_F(0) = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} = \frac{h^2}{8m}\left(\frac{3n}{\pi}\right)^{2/3}.$$

Assuming one electron per sodium atom, the electron density $n$ is given by

$$n = \frac{N_0\,\rho}{W}$$

where

Avogardo Number $N_0 = 6 \times 10^{26}$ atoms/kg. mole.

Density of sodium $\rho = 0{\cdot}97\ \text{g cm}^{-3} = 0{\cdot}97 \times 10^3\ \text{kg/m}^3$

Atomic weight of sodium, $W = 23$

$$\therefore \text{ Electron density, } n = \frac{(6\times10^{26}\ \text{atoms/kg. mole})\,(0{\cdot}97\times10^3\ \text{kg}/m^3)}{23}$$

$$= 2{\cdot}52 \times 10^{23}\ \text{electrons}/m^3.$$

Also Planck's canstant, $h = 6{\cdot}62 \times 10^{-34}$ joule-second

Mass of the electron, $m = 9{\cdot}1 \times 10^{-31}$ kg.

Therefore the Fermi energy $\varepsilon_F(0)$ is given by

$$\begin{aligned} \varepsilon_F(0) = \frac{h^2}{8m}\left(\frac{3n}{\pi}\right)^{2/3} &= \frac{(6{\cdot}62\times10^{-34}\ \text{joules-sec})^2}{8\times(9\times10^{-31}\text{kg})} \times \left[\frac{3}{3{\cdot}14}(2{\cdot}52\times10^{23}\ \text{electrons}/m^3)\right]^{2/3} \\ &= 5{\cdot}032\times10^{-19}\ \text{joule} \\ &= \frac{5{\cdot}032\times10^{-19}}{1{\cdot}6\times10^{-19}}\ \text{eV} = 3{\cdot}145\ \text{eV}, \end{aligned}$$

**Ex. 6.** *There are* $2{\cdot}54 \times 10^{22}$ *free electrons per* cm$^3$ *in sodium. Calculate its Fermi energy, Fermi velocity and Fermi temperature. ($h = 6{\cdot}63 \times 10^{-34}$ joule-sec, $m = 9{\cdot}11 \times 10^{-31}$ kg, $k = 1{\cdot}38 \times 10^{-23}$ joule/K, $1eV = 1{\cdot}6 \times 10^{-19}$ joule).*

**Solution.** The Fermi energy of a metal is given by

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

where $m$ is the mass of electron and $N$ is the number of free electrons in a volume $V$ of the metal.

Here

$$\frac{N}{V} = 2{\cdot}54 \times 10^{22}/\text{cm}^3 = 2{\cdot}54 \times 10^{28}/\text{metre}^3.$$

Substituting this and the values of $m$ and $h$, we get

$$\varepsilon_F = \frac{(6{\cdot}63 \times 10^{-34} \text{ joule-sec})^2}{2 \times (9{\cdot}11 \times 10^{-31} \text{ kg})} \left( \frac{3 \times 2{\cdot}54 \times 10^{28}/\text{m}^3}{8 \times 3{\cdot}14} \right)^{2/3}$$

$$= 5{\cdot}0 \times 10^{-19} \text{ joule} = \mathbf{3{\cdot}1\ eV}.$$

This is the (maximum) kinetic energy of the free electron at absolute zero. If $v_F$ be the Fermi velocity, then

$$\tfrac{1}{2} m v_F^{\,2} = 5{\cdot}0 \times 10^{-19} \text{ joule}.$$

$$\therefore \quad v_F = \sqrt{\frac{2 \times 5{\cdot}0 \times 10^{-19} \text{ joule}}{9{\cdot}11 \times 10^{-31} \text{ kg}}}$$

$$= \mathbf{1{\cdot}05 \times 10^6\ m/s}.$$

The Fermi temperature $T_F$ is defined by

$$T_f = \frac{\varepsilon_F}{k} = \frac{5{\cdot}0 \times 10^{-19} \text{ joule}}{1{\cdot}38 \times 10^{-23} \text{ joule/K}}$$

$$= \mathbf{3{\cdot}6 \times 10^4\ K}.$$

**Ex. 7.** *The density of zinc* ($1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}\, 4s^2$) *is* 7·13 g/cm$^3$ *and its atomic weight is* 65·4. *Calculate its Fermi energy. The effective mass of a free electron in zinc crystal is* $7{\cdot}7 \times 10^{-31}$ *kg and the Avogadro's number is* $6{\cdot}02 \times 10^{23}$ *atoms/gram-atom.*

**Solution.** The electron configuration of the ground state of Zn shows that each atom has 2 valence electrons which ~~it~~ contributes to the electron gas.

The mass of 1 gram-atom of Zn is 65·4 gram, so that the volume

$$V = \frac{\text{mass}}{\text{density}} = \frac{65{\cdot}4}{7{\cdot}13} = 9{\cdot}17 \text{ cm}^3.$$

The number of Zn atoms in this volume is $6{\cdot}02 \times 10^{23}$. Therefore, the number of atoms per unit volume

$$= \frac{6{\cdot}02 \times 10^{23}}{9{\cdot}17} = 6{\cdot}56 \times 10^{22}/\text{cm}^3.$$

Since each contributes 2 valence electrons, the number of free electrons per unit volume is

$$\frac{N}{V} = 2 \times 6{\cdot}56 \times 10^{22}$$

$$= 13{\cdot}1 \times 10^{22}/\text{cm}^3 = 13{\cdot}1 \times 10^{28}/\text{metre}^3.$$

Now, the Fermi energy of the metal Zn is

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

where $m$ is the (effective) mass of the electron in zinc. Substituting the values, we get

$$\varepsilon_F = \frac{(6{\cdot}62 \times 10^{-34} \text{ joule-sec})^2}{2 \times (7{\cdot}7 \times 10^{-31} \text{ kg})} \left( \frac{3 \times 13{\cdot}1 \times 10^{28}/\text{m}^3}{8 \times 3{\cdot}14} \right)^{2/3}$$

$$= \frac{(6{\cdot}62 \times 10^{-34})^2}{2 \times 7{\cdot}7 \times 10^{-31}} (6{\cdot}25 \times 10^{18})$$

$$= 17{\cdot}78 \times 10^{-19} \text{ joule}$$

$$= \frac{17{\cdot}78 \times 10^{-19}}{1{\cdot}6 \times 10^{-19}} = \mathbf{11\ eV}.$$

**Ex. 8.** *The Fermi energy in silver is* 5·51 eV. *(a) What is the average energy of the free electrons in silver at 0 K ? (b) At what temperature a classical free particle (such as ideal gas molecule) will have this kinetic energy ? ($k = 1{\cdot}38 \times 10^{-23}$ joule/K and 1 eV = $1{\cdot}6 \times 10^{-19}$ joule).*

**Solution. (a)** The average energy of an electron in electron-gas at 0 K is

$$\bar{\varepsilon}_0 = \frac{3}{5} \varepsilon_F,$$

where $\varepsilon_F$ is the Fermi energy. Now, $\varepsilon_F = 5{\cdot}51$ eV. Therefore

$$\bar{\varepsilon}_0 = \frac{3}{5} \times 5{\cdot}51 = \mathbf{3{\cdot}306\ eV}.$$

**(b)** The kinetic energy of a classical particle at kelvin temperature $T$ is $\frac{3}{2} kT$. Then, if the particle has an energy 3·306 eV, then we have

$$\frac{3}{2} kT = 3{\cdot}306 \text{ eV} = 3{\cdot}306 \times (1{\cdot}6 \times 10^{-19}) \text{ joule},$$

where $k = 1{\cdot}38 \times 10^{-23}$ joule/K. There

$$T = \frac{2}{3} \times \frac{3{\cdot}306 \times 1{\cdot}6 \times 10^{-19} \text{ joule}}{1{\cdot}38 \times 10^{-23} \text{ joule/K}}$$

$$= \mathbf{2{\cdot}55 \times 10^4\ K}.$$

**Ex. 9.** *The Fermi energy for lithium is* 4·72 eV *at absolute zero. Calculate the number of conduction electrons per unit volume in lithium. ($h = 6{\cdot}63 \times 10^{-34}$ J-s, $m = 9{\cdot}11 \times 10^{-31}$ kg).*

**Solution.** The Fermi energy is

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

where $N$ is the number of conduction electrons in a volume $V$ of the lithium metal. The number of conduction electrons per unit volume is therefore

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

Then, with $\varepsilon_F = 4{\cdot}72 \text{ eV} = 4{\cdot}72 \times 1{\cdot}6 \times 10^{-19}$ joule, we have

$$\frac{N}{V} = \left[ \frac{2 \times 9{\cdot}11 \times 10^{-31} \text{ kg}}{(6{\cdot}63 \times 10^{-34} \text{ joule-sec})^2} \right]^{3/2} \times \frac{(4{\cdot}72 \times 1{\cdot}6 \times 10^{-19} \text{ joule})^{3/2} \times 8 \times 3{\cdot}14}{3}$$

$$= \mathbf{4{\cdot}64 \times 10^{28}/m^3}.$$

## 8.23. Specific Heat Anomaly of Metals and its Solution.

Experiments show that the specific heat of metals referred to 1 gram atom does not exceed a value of $3R$ even at very large temperatures.

Theoretically the specific heat of metals shall get contribution from the atoms as well as the free electrons *i.e.*,

$$C_V \text{ (metals)} = C_V \text{ (atomic)} + C_V \text{ (electronic)}.$$

According to the law of equipartition of energy of classical statistics, the average energy associated with each quadratic term is $\frac{1}{2}kT$. Further, according to the classical kinetic theory of matter, the atoms of a solid substance are at rest under the action of their mutual attractions and repulsions at the absolute zero of temperature. The energy of solids in this state is assumed to be zero. When the temperature is raised, the atoms are set into vibrations about their positions of equilibrium and the restoring force produced is proportional to displacement as long as the amplitude of vibration is not too large. Thus the vibrations of the atoms are simple harmonic in nature.

In the case of S.H.M., the energy of the atom along one coordinate can be represented as the sum of two quadratic terms *viz.*

$$\frac{1}{2}m\dot{x}^2 + \frac{1}{2}Kx^2.$$

where $K$ is the force constant, $x$ is the displacement of the atom from mean position and $\dot{x} = \frac{dx}{dt}$. Here the first term represents the kinetic energy and the second term represents the potential energy.

According to law of equipartition of energy, the average energy associated with the motion of an atom along one coordinate

$$= 2 \times \frac{1}{2}kT = kT.$$

As each atoms is free to vibrate along three coordinate axes, the total energy of each atom $= 3\,kT$.

The total energy of a gram atom of solid containing $N$ (= Avogrado number) atoms is given by

$$E_{atomic} = NkT = 3\,RT$$

where $R = Nk =$ gas constant for gram atom.

Therefore *atomic contribution to specific heat referred to 1 gram atom of metal is*

$$C_1 \text{ (atomic)} = \left[\frac{\partial E_{atomic}}{\partial T}\right]_V = \frac{\partial}{\partial T}(3\,RT) = 3\,R, \qquad \text{...(1)}$$

As the electrons inside the metal are assumed to be free to move along three axes, they do not possess the potential energy but possess only kinetic energy. According to law of equiparition of energy, the average energy associated with the motion

$$= 3.\frac{1}{2}kT = \frac{3}{2}kT$$

Assuming one free electron per atom in the metal, the total energy of a gram atom of solid containing $N$ atoms is

$$E_{electronic} = \frac{3}{2}NkT = \frac{3}{2}RT.$$

Therefore the electronic contribution to specific heat referred to 1 gram atom of metal is

$$C_V \text{ (electronic)} = \left[\frac{\partial E_{electronic}}{\partial T}\right]_V = \frac{\partial}{\partial T}\left(\frac{3}{2}RT\right) = \frac{3}{2}R. \qquad \text{...(2)}$$

Hence *classically the specific heat referred to 1 gram atom of metals is*

$$C_V = 3\,R + \frac{3}{2}R = \frac{9}{2}R$$

which is too high as compared to the experimental value $3\,R$. This specific heat anomaly of metals is the chief problem which the classical statistics could not solve. This specific heat anomaly was solved by Fermi-Dirac statistics in a very elegant manner.

According to Fermi-Dirac statistics the electronic contribution to the specific heat per gram atom of metals at low temperature

$$C_V \text{ (electronic)} = \frac{1}{2}\frac{Nk^2\pi^2}{\varepsilon_F(0)}T = \lambda T \qquad \text{...(4)}$$

where

$$\lambda = \frac{1}{2}\frac{Nk^2\pi^2}{\varepsilon_F(0)}. \qquad \text{...(5)}$$

Obviously *the electronic contribution to the specific heat of a metal at low temperatures is proportional to the temperature and vanishes at absolute zero* in agreement with the experimental observations. On substituting numerical values in the above relation it is found that the contribution of the electrons to the specific heat at ordinary temperatures is of about 1% of heat of the atoms. For example for silver $C_V = 0{\cdot}046$ cal per gram atom at 300 K, which is only 0·7% of the ordinary specific heat of silver at 300 K, and hardly adds anything to it. Hence we should not expect to detect the electronic specific heat in specific heat measurements at ordinary temperatures. It is only when very high temperatures of the order of 10,000 K are reached, that the light packing of the electrons gradually becomes loosended and the electrons make a noticeable contribution to the specific heat.

According to Debye's theory the specific heat at extremely low temperatures is found to be proportional to $T^3$. Hence the specific heat of metals at low temperatures can be expressed as

$$C_V = \beta\,T^3 + \lambda T. \qquad \text{...(6)}$$

where the first term refers to the atomic contribution to the specific heat according to Deby's theory and the second term refers to the electronic contribution to the specific heat according to Fermi-Dirac statistics. At very low temperatures the atomic specific heat becomes small and the electronic specific heat becomes relatively high. This has been verified by many scientists for a variety of metals. For example according to equation (6), the atomic specific heat for silver becomes small compared to its electronic specific heat below the temperature 3 K. In specific heat measurements Keesom and Cok found that in the range from 1·5 K to 3 K the specific heat varies according to equation (4) : but above 3 K, the $T^3$ term predominates. This suggests that below 3 K for silver, free electrons become the chief contributor to the specific heat. Thus the Fermi-Dirac statistics has solved the problem of specific heat of metals.

## 8.24. Thermionic Emission :

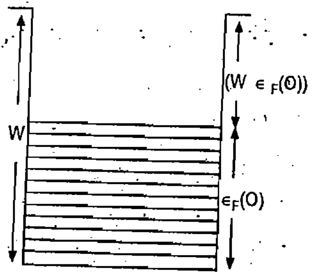
*The emission of the electrons from the metal under the effect of thermal energy is called thermionic emission. The electrons so emitted are called thermions.*

It is well known that the electrons in a metal are not completely free, but are bound to the metal surface by the attractive force of atomic nuclei. Experimental observations show that the metals do not emit electrons till their temperature is sufficiently high. This means that at ordinary temperatures the electrons do not possess sufficient energy to overcome the attractive force and to escape out the metallic surfaces.

According to Fermi-Dirac statistics *an electron at absolute zero possesses a maximum energy equal to the Fermy energy* $\varepsilon_F$ *(0), which does not change appreciably with the increase of temperature.* Thus the electrons at ordinary temperature possess the Fermi-energy $\varepsilon_F$ (0) which is not itself sufficient to escape out an electron from the metal. Further the free electron theory assumes that the potential within the metal is constant, being positive relative to free space. If this constant potential is $W$, then $W$ is the minimum energy of the electron for its emission from the metallic surface. Therefore the minimum energy to be supplied to the electron for its emission is $[W - \varepsilon_F (0)]$ and is defined as the *work function* $\phi$ of the metal.

When the metal is heated, the free electrons gain the *thermal energy* and when this thermal energy is more than $\{W - \varepsilon_F (0)\}$, the electrons are emitted from the metallic surface. The thermal energy in excess of $[W - \varepsilon_F (0)]$ will be converted into the kinetic energy of the electrons. On the other hand on the classical picture, the amount of energy to be supplied to emit an electron from the metal is $W$, (since at absolute zero all the electrons are at rest), a value much greater than indicated by experiments.

Let us now calculate the emission current density of the emitted electrons :



**(Fig. 8.5) Free electron model of a metal according to Fermi-statistics.**

In the free electron model of a metal, the electrons are free to move throughout the volume $V$. According to Fermi-Dirac statistics the number of electrons per unit volume having the momentum in the range $p$ and $p + dp$ is

$$dn = g_s \frac{4 \pi p^2 dp}{h^3} \cdot \frac{1}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}$$

For electrons $g_s = (2s + 1) = 2$. Therefore

$$dn = \frac{2}{h^3} \cdot \frac{4 \pi p^2 dp}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} \qquad \text{...(1)}$$

If $p_x, p_y, p_z$ be the components of mementum of the electron along $X$, $Y$ and $Z$ axes, such that

$$p^2 = p_x^2 + p_y^2 + p_z^2$$

then the volume in the momentum space lying between $p_x$ and $p_x + dp_x$, $p_y$ and $p_y + dp_y$, $p_z$ and $p_z + dp_z$ will be

$$dp_x \, dp_y \, dp_z = 4 \pi p^2 \, dp.$$

Since that the number of electrons per unit volume whose, momentum components lie between $p_x$ and $p_x + dp_x$, $p_y$ and $p_y + dp_y$, $p_z$ and $p_z + dp_z$ is

$$dn = \frac{dp_x \, dp_y \, dp_z}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}$$

If $v_x$, $v_y$ and $v_z$ denote the velocity components along $X$, $Y$ and $Z$–axes, we have

$$dn = \frac{2}{h^3} \frac{(m \, dv_x)(m \, dv_y)(m \, dv_z)}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} = 2 \frac{m^3}{h^3} \frac{dv_x \, dv_y \, dv_z}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}$$

This equation gives the number of electrons per unit volume having velocity components in the ranges $v_x$ and $v_x + dv_x$, $v_y$ and $v_y + dv_y$, $v_z$ and $v_z + dv_z$.

As $kT$ is of the order of 0·3 $eV$ and $(\varepsilon - \varepsilon_F)$ is at least 20 times greater than $kT$, we can neglect one in the denominater or R.H.S. and write

$$dn = 2 \frac{m^3}{h^3} \cdot e^{(\varepsilon_F - \varepsilon)/kT} \, dv_x \, dv_y \, dv_z$$

$$= 2 \frac{m^3}{h^3} \cdot e^{\varepsilon_F/kT} \cdot e^{-\frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)/kT} \, dv_x \, dv_y \, dv_z$$

since $$\varepsilon = \frac{1}{2} mv^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

or $$dn = 2. \frac{m^3}{h^3} \cdot e^{\varepsilon_F/kT} \cdot e^{-mv_x^2/2T} \, dv_x \, e^{-mv_y^2/2kT} \, dv_y \, e^{-mv_z^2/2kT} \, dv_z$$

Now, supposing that the surface of the metal lies in the $Y - Z$ plane and $X$–axis is normal to this surface, the number of electrons per unit volume in velocity range $v_x$ and $v_x + dv_x$ is given by

$$dn_x = n(v_x) \, dv_x = 2. \frac{m^3}{h^3} \cdot e^{\varepsilon_F/kT} \cdot e^{-mv_x^2/2kT} \, dv_x \int_{-\infty}^{\infty} e^{-mv_y^2/kT} \, dv_y \int_{-\infty}^{\infty} e^{-mv_z^2/kT} \, dv_z$$

$$= 2. \frac{m^3}{h^3} e^{-mv_x^2/2kT} \, dv_x \sqrt{\left(\frac{2 \pi kT}{m}\right)} \sqrt{\left(\frac{2 \pi kT}{m}\right)}$$

$$= \frac{4 \pi m^2 kT}{h^3} e^{\varepsilon_F/kT} e^{-mv_x^2/2kT} \, dv_x.$$

When the metal is heated only those electrons can escape from the surface along $X$ axis which fulfil the condition

$$\varepsilon = \frac{1}{2} mv_x^2 \geq W, \text{ i.e., } v_x \geq \sqrt{\left(\frac{2W}{m}\right)}.$$

Therefore, the number of electrons leaving unit area of the surface in unit time is

$$n_x = \int_{\sqrt{2W/m}}^{\infty} n(v_x) \, dv_x = \frac{4 \pi m^2 kT}{h^3} \cdot e^{\varepsilon_F/kT} \int_{\sqrt{(2W/m}}^{\infty} e^{-mv_x^2/kT} v_x \, dv_x \qquad \text{...(1)}$$

$$= \frac{4 \pi mk^2}{h^3} . T^2 e^{-(W - \varepsilon_F)/kT} \qquad \text{...(2)}$$

$$= \frac{4 \pi mk^2}{h^3} . T^2 e^{-\phi/kT} \qquad \text{...(3)}$$

where work function, $$\phi = W - \varepsilon_F = W - \varepsilon_F (0).$$

The emission current per unit area (*i.e., emisslon current density*) is obtained by multiplying the number of electrons leaving unit area of the surface in the unit time with the electronic charge,

*i.e.,* $$J = n.e = \frac{4 \pi mek^2}{h^3} . T^2 e^{-\phi/kT}$$

$$= AT^2 e^{-\phi/kT}. \qquad \text{...(4)}$$

where $A = \frac{4\pi mek^2}{h^3}$ is a constant independent of the nature of the metal.

Equation(4) is well known *Richardson-Dushmann equation for thermionic emission.* The equation indicates that the emission current density depends upon the work function of the metal and the square of the absolute temperature.

Since the work function is a characteristic property of the metal, the emission current will also be a characteristic property of the metal. Equation (4) is in complete agreement with experimental observations.

## 8.25. Magnetic Susceptibility of Free Electrons

Metals contain a large number free electrons. Each electron possesses a magnetic moment. When magnetic field is applied the elementary electrons bahave as magnetic dipoles which tend to orient along the direction of external magnetic field. Thus the free electrons affect the paramagnetic volume susceptibility. Langevin showed that the paramagnetic susceptibility varies as $\frac{1}{T}$ and its value is $10^{-4}$ at room temperature but experimental observations show that the paramagnetic susceptibility has a small value $10^{-6}$ and is independent of temperature. Pauli applied Fermi-Dirac statistics to explain this disagreement.

Each electron has a magnetic moment $\pm\mu_B$ along the direction of magnetic field. If there are $n$-conduction electrons per unit volume, then net magnetisation is

$$\left.\begin{aligned} M &= \mu_B (n_+ - n_-), \\ \text{with} \quad n &= n_+ + n_- \ldots \end{aligned}\right\} \qquad \ldots(1)$$

where $n_+$ is number of electrons parallel to magnetic field $\vec{H}$ and $n_-$ is the number antiparallel to $\vec{H}$. Regarding electrons as fermions forming Fermi-Dirac gas, we have

$$n_\pm = \int_0^\infty \frac{1}{2} g(\varepsilon \pm \mu_B H) f(\varepsilon)\, d\varepsilon \qquad \ldots(2)$$

where ε is total energy. The fraction $\frac{1}{2}$ is introduced because magnetic field removes spin degeneracy. We have

$$g(\varepsilon \pm \mu_B B) = \frac{2\pi V}{h^3} (2m)^{3/2} \varepsilon^{1/2} \left(1 \pm \frac{\mu_B H}{\varepsilon}\right)^{1/2}$$

$$\approx \frac{2\pi V}{h^3} (2m)^{3/2} \varepsilon^{1/2} \left(1 \pm \frac{\mu_B H}{2\varepsilon}\right) \qquad \ldots(3)$$

$$\therefore \quad \text{Magnetisation } M = \frac{\mu_B}{V} \int_0^\infty \left[\frac{1}{2} g(\varepsilon + \mu_B H) - \frac{1}{2} g(\varepsilon - \mu_B H)\right] f(\varepsilon)\, d\varepsilon$$

$$= \frac{4\pi}{h^3} (2m)^{3/2} \frac{\mu_B^2 H}{2} \int_0^\infty f(\varepsilon)\, \varepsilon^{-1/2}\, d\varepsilon \qquad \ldots(4)$$

At lower temperature all bands upto Fermi energy are filled while all the levels above Fermi energy are empty, so we can take limit of integration 0 to $\varepsilon_F$ and so

$$f(\varepsilon) \begin{cases} = 1 & \text{for } 0 < \varepsilon \le \epsilon_F \\ = 0 & \text{for } \varepsilon > \varepsilon_F \end{cases}$$

$$\therefore \quad \text{Magnetisation } M = \frac{2\pi}{h^3} (2m)^{3/2} \mu_B^2 H \int_0^{\varepsilon_F} \varepsilon^{-1/2}\, d\varepsilon$$

$$= \frac{2\pi}{h^3} (2m)^{3/2} \mu_B^2 H \left[\frac{\varepsilon^{1/2}}{1/2}\right]_0^{\varepsilon_F}$$

$$= 4\pi \left(\frac{2m}{h^2}\right)^{3/2} \mu_B^2 H \varepsilon_F^{1/2} \qquad \ldots(5)$$

We have

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

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

$$\Rightarrow \qquad \frac{2m}{h^2} = \left(\frac{3n}{8\pi}\right)^{2/3} \cdot \frac{1}{\varepsilon_F}$$

$$\therefore \qquad \left(\frac{2m}{h^2}\right)^{3/2} = \left(\frac{3n}{8\pi}\right) \cdot \varepsilon_F^{-3/2} \qquad \ldots(6)$$

Substituting this value in (5), we get

$$M = 4\pi \cdot \frac{3n}{8\pi} \varepsilon_F^{-3/2} \mu_B^2 H \varepsilon_F^{1/2} = \frac{3n\mu_B^2 H}{2\varepsilon_F}$$

Magnetic susceptibility

$$\chi_m = \frac{M}{H} = \frac{3n\mu_B^2}{2\varepsilon_F}$$

This is independent of temperature thus verifying experimental results. The physical reason of this result is that only a small fraction of electrons at the top of the Fermi distribution has a chance to turn over in the field $H$ and so only these electrons contribute is $\chi$.

## 8.26. White Dwarfs

*White dwarfs are stars which are much fainter, possess smaller diameter and are very dense as compared to other stars of the same mass.*

An ideal white dwarf has the following specifications :

Content → helium

Mass ~ $10^{30}$ kg ~ mass of sun

Density ~ $10^{10}$ kg m$^{-3}$ ≈ 10 × density of sun

Temperature $10^7$ K ~ temperature of sun

At this extremely high temperature, the helium gas gets completely ionised and so the white dwarf may be regarded as a gas composed of helium nuclei and electrons. The gas of electrons behaves as an ideal Fermi-Dirac gas of density $10^{36}$ electrons per metre$^3$, this corresponds to Fermi energy of

$$\varepsilon_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3} \approx 20\text{ MeV} \qquad \text{...(1)}$$

So that the Fermi temperature is

$$T_F \approx \frac{\varepsilon_F}{k} = \frac{20 \times 1{\cdot}6 \times 10^{-13}}{1{\cdot}38 \times 10^{-23}} \approx 10^{11}\text{ K} \qquad \text{...(2)}$$

As $\frac{T_F}{T} >> 1$, the electron gas is highly degenerate. We can regard it as an ideal Fermi gas at $T = 0$ (*i.e.* in the ground state) The effect of high electron density is to provide $T_F >> T$ and also to make the electrons **relativistic energies** due to increase of mean energy. The Fermi Dirac gas possesses zero point energy and enormous pressure $P_0$ which is balanced by the gravitational attraction.

We shall first calculate the pressure $P_0$ exerted by Fermi Dirac gas of relativistic electron in the ground state.

The single particle energy levels are given by

$$\varepsilon_{ps} = [p^2c^2 + m^2c^4]^{1/2} \qquad \text{...(3)}$$

where $p$ is momentum, $m$ is rest mass of electron and $c$ is speed of light. The states of electrons are specified by momentum $p$ and spins 's'. The ground state energy of Fermi gas is

$$E_0 = g_s \sum_{|p| < p_F} (p^2c^2 + m^2c^4)^{1/2} \qquad \text{...(4)}$$

where $p_F$ is Fermi momentum given by

$$p_F = \sqrt{2m\,\varepsilon_F} = \sqrt{2m \times \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}} \Rightarrow p_F = h\left(\frac{3N}{8\pi V}\right)^{1/3} \qquad \text{...(5)}$$

As energy levels are quite close to each other, so the summation may be replaced by integration; we have

$$g_s = g(p)\,dp = (2s+1)\frac{V.4\pi p^2 dp}{h^3}$$

$$= \frac{2.V\,4\pi p^2\,dp}{h^3} \qquad (\text{as } s = \tfrac{1}{2} \text{ for electron})$$

$$\therefore \qquad E_0 = \frac{2V}{h^3}\int_0^{p_F} (p^2c^2 + m^2c^4)^{1/2}\, 4\pi p^2\, dp \qquad \text{...(6)}$$

Now putting

$$\frac{p}{mc} = x \Rightarrow \frac{dp}{mc} = dx, \text{ we get}$$

$$E_0 = \frac{8\pi V}{h^3}\int_0^{x_F} mc^2\,[1 + x^2]^{1/2}\,(mcx)^2\,.\,mcdx$$

$$= \frac{8\pi V\, m^4c^5}{h^3}\int_0^{x_F}(1 + x^2)^{1/2}\,x^2\,dx$$

$$= \frac{8\pi V\, m^2c^5}{h^3} f(x_F) \qquad \text{...(7)}$$

where $$f(x_F) = \int_0^{x_F} x^2(1 + x^2)^{1/2}\,dx$$

$$= \begin{cases} \frac{1}{2}x_F^3\left(1 + \frac{3}{10}x_F^2 + \ldots\right); & x_F \le 1 \\ \frac{1}{4}x_F^4(1 + x_F^{-2} + \ldots); & x_F >> 1 \end{cases} \qquad \text{...(8)}$$

where $x_F << 1$ corresponds to non relativistic case and $x_F >> 1$ corresponds to the relativistic case; with $x_F = \frac{p_F}{mc}$.

$$\text{Pressure } P_0 = -\left(\frac{\partial E_0}{\partial V}\right) = -\frac{8\pi m^4c^5}{h^3}\left[f(x_f) + \frac{V\,\partial f(x_F)}{\partial x_F}\frac{\partial x_F}{\partial V}\right]$$

$$= \frac{8\pi m^4c^5}{h^3}\left[\frac{1}{3}x_F^3(1 + x_F^2)^{1/2} - f(x_F)\right]$$

$$= \begin{cases} \frac{8\pi m^4c^5}{15h^3}x_F^5 & x_F << 1 \\ \frac{2\pi m^4c^5}{3h^3}(x_F^4 - x_F^2), & x_F >> 1 \end{cases} \qquad \text{...(9)}$$

If $m$ is mass of electron, $m_p$ the mass of proton and $N$ is the number of helium atoms, then mass of star,

$$M = (m + 2m_p)\,N \approx 2m_pN \qquad (\text{because } m << m_p) \qquad \text{...(10)}$$

Radius of star is given by $V = \frac{4}{3}\pi R^3 \Rightarrow R = \left(\frac{3V}{4\pi}\right)^{1/3}$ ...(11)

$$\frac{V}{N} = \frac{\frac{4}{3}\pi R^3}{M/2m_p} = \frac{8}{3}\pi\cdot\left(\frac{m_pR^3}{M}\right)$$

Then $$p_F = h\cdot\left(\frac{3N}{8\pi V}\right)^{1/3} = h\left(\frac{3}{8\pi}\cdot\frac{3}{8\pi}\frac{M}{m_pR^3}\right)^{1/3} = \frac{h}{2\pi R}\cdot\left(\frac{9\pi}{8}\frac{M}{m_p}\right)^{1/3}$$

$$\Rightarrow \qquad x_F = \frac{p_f}{mc} = \frac{h}{2\pi mc}\left(\frac{9\pi M}{8\,m_p}\right)^{1/3} = \frac{\overline{M}^{1/3}}{\overline{R}} \qquad \text{...(12)}$$

where $$\overline{M} = \frac{9\pi}{8}\frac{M}{m_p} \text{ and } \overline{R} = \frac{R}{(h/2\pi mc)}$$

The enormons zero point pressure is balanced by the gravitational attraction to bind the star. The work done to form the star of radius $R$ from the state of infinite diluteness is given by

$$W = \int_\infty^R P_0\,.\,4\pi r^2\,dr$$

where $P_0$ is pressure of uniform $F.D$ gas

Thin work is calculated by gravitational self energy which is given by

$$U_s = -\frac{3}{5}\frac{GM^2}{R} \text{ where } G \text{ is gravitational constant}$$

$$\therefore \int_0^R P_0 4\pi r^2\, dr = -\frac{3}{5}\frac{GM^2}{R} \qquad ...(13)$$

Differentiating both sides with respect to $R$, we get equilibrium condition

$$P_0 4\pi R^2 = \frac{3}{5}\frac{GM^2}{R^2}$$

$$\Rightarrow \qquad P_0 = \frac{3}{20\pi}\frac{Gm^2}{R^4} \qquad ...(14)$$

In terms of $\overline{M}$ and $\overline{R}$ it is expressed in

$$P_0 = \frac{3}{20\pi} G\left(\frac{8\, m_p}{9\pi}\overline{M}\right)^2 \times \left(\frac{2\pi mc}{h}\right)^4 \cdot \frac{1}{R^4}$$

This is the value of equilibrium pressure in terms of $\overline{M}$ and $\overline{R}$

Using equation (9) for extreme relativistic case $x_F >> 1$, no white draft can have a mass larger than

$$M_0 = \left(\frac{8}{9\pi} m_p\right)\left(\frac{45}{64}\pi\right)^{3/2}\left(\frac{hc}{2\pi\, Gm_p^2}\right)^{3/2} \approx 10^{30}\ \text{kg}$$

$$= \text{mass of sun}$$

The refined estimate gives

$$M_0 = 1{\cdot}4 \times \text{mass of sun}$$

This mass is called the **Chandrashekhar Limit.**

## 8.27. Quantum Theory of Diatomic Molecules

When we deal with the motion of the atoms and molecules which are constituents of matter in bulk, we must use quantum mechanics rather than classical mechanics even if the quantum effects are negigible. In quantum mechanics the state of a dynamical system is specified by specifying the eigen values and the corresponding eigen functions. If a system is composed of three non-interacting particles 1, 2, 3 with identical energy levels and if the single particles wave functions and energy levels are $\phi_1, \phi_2, \ldots \phi_i, \ldots; \varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i, \ldots;$ then wave function $\psi$ and corresponding eigen value $E$ of the system are given by

$$\phi_{ijk} = \phi_i(1)\,\phi_j(2)\,\phi_k(3), \qquad ...(1)$$

and

$$E_{ijk} = \varepsilon_i(1) + \varepsilon_j(2) + \varepsilon_k(3), \qquad ...(2)$$

where the triple index $i, j, k$ donotes a single state of the system.

The canonical partition function of the system is

$$Z = \sum_{ijk} e^{-(\varepsilon_i+\varepsilon_j+\varepsilon_k)/kT} = \sum_i e^{-\varepsilon_i/kT}\sum_j e^{-\varepsilon_j/kT}\sum_k e^{-\varepsilon_k/kT} \qquad ...(3)$$

$$= [\sum_i e^{-\varepsilon_i/kT}]^3 = f^3, \qquad ...(4)$$

where

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

In analogy for a system of $n$ similar particles,

$$Z = f^n \qquad \text{(for distinguishable particles).}$$

If the particles of the gas are indistinguishable quantum mechanically, the interchange of the particles among different energy levels will not lead to any new distribution and therefore, for a perfect gas consisting of $n$ indistinguishable particles, the partition function becomes

$$Z = \frac{f^n}{n!} \qquad ...(5)$$

Here $f$ is called *the single particle partition function.*

Here we shall calculate the partition functions for translational, vibrational and rotational motions of the diatomic molecules and then evaluate the contributions due to each type of motion separately to various thermodynamic functions.

**Translation motion.** A single diatomic molecule possesses three translational degrees of freedom corresponding to the translational motion of the centre of mass of the molecule. According to quantum mechanics the allowed translational energy levels* of a molecule of mass $m$ which is constained to move in a rectangular box of edges $l_x$, $l_y$ and $l_z$ is given by

$$\varepsilon(t) = \frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right) \qquad ...(6)$$

where $n_x, n_y, n_z = 1, 2, 3, 4, \ldots$

Therefore, the translational partition function for a single molecule is

$$z_t = f_t = \sum_{n_x=1}^{\infty}\exp\left(-\frac{h^2 n_x^2}{8\, ml_x^2 kT}\right)\sum_{n_y=1}^{\infty}\exp\left(-\frac{h^2 n_y^2}{8\, ml_y^2 kT}\right)\sum_{z=1}^{\infty}\exp\left(-\frac{h^2 n_z^2}{8\, ml_z^2 kT}\right) \qquad ...(7)$$

For ordinary temperatures and large size of the box the quantity $\dfrac{h^2}{8\, ml_x^2 kT}$ is very less than 1. Hence the quantity $\dfrac{h^2 n_x^2}{8\, ml_x^2 kT}$ changes slowly as $n_x$ is varied. This means that the discrete energy levels are closely spaced; therefore, we can replace the summation by integration. Thus,

$$\sum_{n_x=1}^{\infty}\exp\left(-\frac{h^2 n_x^2}{8\, ml_x^2 kT}\right) = \int_0^{\infty}\exp\left(-\frac{h^2 n_x^2}{8\, ml_x^2 kT}\right) dn_x\ \frac{(2\pi m kT)^{1/2}}{h} l_x.$$

Similarly,

$$\sum_{n_x=1}^{\infty}\exp\left(-\frac{h^2 n_y^2}{8\, m\, l_y^2 kT}\right) = \frac{(2\pi m kT)^{1/2}}{h} l_y,$$

and

$$\sum_{n_z=1}^{\infty}\exp\left(-\frac{h^2 n_z^2}{8\, m\, l_z^2 kT}\right) = \frac{(2\pi m kT)^{1/2}}{h} l_z.$$

Therefore, the translational partition function for a single molecule takes the form

$$z_t = f_t = \frac{(2\pi m kT)^{3/2}}{h^3} l_x l_y l_z = \frac{V}{h^3}(2\pi m kT)^{3/2} \qquad ...(8)$$

where $V = l_x l_y l_z$ = Volume of the enclosure.

Now using equation (5) the partition function for a gas of $n$ indistinguishable diatomic molecules is given by

$$Z_t = \frac{f_t^n}{n!} = \frac{V^n}{h^{3n}\, n!}(2\pi m kT)^{3n/2}. \qquad ...(9)$$

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*Refer 'Advanced Quantum Mechanics' by Satya Prakash (Kedar Nath Ram Nath Meerut).

**Translational thermodynamic functions.** The total translational energy of $n$ diatomic molecule is

$$E_t = kT^2 \frac{\partial}{\partial T} \log Z_t = kT^2 \frac{\partial}{\partial T}\left(\frac{f_t^n}{n!}\right).$$

$$= kT^2 \frac{\partial}{\partial T}\left[\log\left\{\frac{V^n}{h^{3n}\, n!}(2\pi m kT)^{3n/2}\right\}\right]$$

On simplifying and using Stirling approximation, we get

$$E_t = \frac{3}{2} nkT \qquad \text{...(10)}$$

The *translational entropy of n diatomic molecules is*

$$S_t = k \log Z_t + \frac{E_t}{T} = k \log \frac{f_t^n}{n!} + \frac{3}{2} nk.$$

Using again Stirling approximation

$$S_t = nk \log\left(\frac{f_t}{n}\right) + \frac{5}{2} nk. \qquad \text{...(11)}$$

Substitution of value of $f_t$ in above equation leads to well known *Sackur-Tetrode relation for entropy.*

The specific heat at constant volume due to translational motion is

$$(C_V)_t = \left(\frac{\partial E_t}{\partial T}\right)_V = \frac{3}{2} nk. \qquad \text{...(12)}$$

Helmholtz free energy due to translational motion is

$$E_{\text{trans}} = E_t - TS_t$$

$$= \frac{3}{2} nkT - T\left[nk \log \frac{f_t}{n} + \frac{5}{2} nk\right].$$

$$= -nkT - nkT \log \frac{f_t}{n} \qquad \text{...(13)}$$

**Vibrational Motion.** A diatomic molecule has only one degree of freedom corresponding to the vibrational motion of the nuclei along the axis joining them. The vibrational energy of a diatomic molecule considering it as a harmonic oscillator is given by

$$\varepsilon(v) = \left(v + \frac{1}{2}\right) h\nu \qquad \text{...(14)}$$

where $\nu$ is the frequency of vibration and $v$ is the vibrational quantum number and can have the values 0, 1, 2 etc.

Therefore the vibrational *partition function for a single molecule* is

$$Z_v = f_v = \sum_{v=0}^{\infty} e^{-\varepsilon(v)/kT} = \sum_{v=0}^{\infty}\left[e^{-\left(v+\frac{1}{2}\right)h\nu/kT}\right]$$

$$= e^{-h\nu/2kT} \sum_{v=0}^{\infty} e^{-v h\nu/kT}$$

$$= e^{-h\nu/2kT}\left[1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \ldots\right]$$

$$= e^{-h\nu/2kT}\cdot\left[\frac{1}{1 - e^{-h\nu/kT}}\right], \qquad \text{...(15a)}$$

$$= \frac{1}{e^{h\nu/2kT} - e^{-h\nu/2kT}} = \frac{1}{2\sinh(h\nu/2kT)}. \qquad \text{...(15b)}$$

Therefore for a gas of $n$ diatomic molecules, the vibrational partition function will be

$$Z_v = (f_v)^n = [e^{-h\nu/kT}.(1 - e^{h\nu/kT})^{-1}]^n,$$

$$= e^{-nh\nu/2kT}(1 - e^{h\nu/kT})^{-n} = \frac{1}{2^n \sinh^n(h\nu/2kT)} \qquad \text{...(16)}$$

**Vibrational Thermodynamic Functions.** The *total vibrational energy of n* diatomic molecules is

$$E_v = kT^2 \frac{\partial}{\partial T} \log f_v^n = nkT^2 \frac{\partial}{\partial T} \log f_v$$

$$= nkT^2 \frac{\partial}{\partial T}[\log\{e^{-h\nu/2kT}(1 - e^{-h\nu/kT})^{-1}\}]$$

$$= nkT^2 \frac{\partial}{\partial T}\left[-\frac{h\nu}{2kT} - \log_e(1 - e^{-h\nu/kT})\right]$$

$$= nkT^2\left[\frac{h\nu}{2kT^2} + \frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}\cdot\frac{h\nu}{kT^2}\right]$$

$$= \frac{1}{2} nh\nu + \frac{nh\nu}{e^{h\nu/kT} - 1}. \qquad \text{...(17)}$$

The *contribution to entropy due to vibrational motion of n diatomic molecules Is*

$$S_v = k \log Z + \frac{E_v}{T} = k \log f_v^n + \frac{E_v}{T}$$

$$= nk \log f_v + \frac{E_v}{T}$$

$$= nk \log[e^{-h\nu/kT}(1 - e^{-h\nu/kT})^{-1}] + \left[\frac{\left\{\frac{1}{2} nh\nu + \frac{nh\nu}{e^{h\nu/kT} - 1}\right\}}{T}\right]$$

$$= nk.\left(-\frac{h\nu}{2kT}\right) - nk \log(1 - e^{-h\nu/kT}) + \frac{nh\nu}{2T} + \frac{nh\nu/T}{e^{h\nu/kT} - 1}$$

$$= -nk \log(1 - e^{h\nu/kT}) + nk\left(\frac{h\nu}{kT}\right)\left(e^{h\nu/kT} - 1\right)^{-1} \qquad \text{...(18)}$$

The *contrbution to specific heat at constant volume due to vibrational motion of n* diatomic molecules is

$$(C_V)_{vib} = \left(\frac{\partial E_v}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[\frac{1}{2} nh\nu + \frac{nh\nu}{e^{h\nu/kT} - 1}\right]$$

$$= nk\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{[e^{h\nu/kT} - 1]^2} \qquad \text{...(19)}$$

The *Helmholtz's free energy due to vibrational motion of n* diatomic molecules is

$$F_{vib} = E_v - TS_v$$

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

$$= \frac{1}{2} nh\nu + nkT \log (1 - e^{h\nu/kT}) \qquad ...(20)$$

**Rotational Motion.** The rotational energy levels of a diatomic molecule, considering it as a *rigid rotator**, are given by

$$\varepsilon (r) = \frac{j(j+1)\, h^2}{8 \pi^2 I}. \qquad ...(21)$$

where $I$ is the moment of inertia and $j$ is the *rotational quantum number* which can have the value 0, 1, 2 etc.

According to quantum mechanics there are $(2j+1)$ eigenstates corresponding to the same rotational energy $\varepsilon_j$. Thus each rotational level has a *degeneracy or statistical weight* $g_r = (2j+1)$.

Therefore the rotational partition function for a single molecule is

$$z_r = f_r = \Sigma\, g_r\, e^{-\varepsilon_r/kT} = \sum_{j=0}^{\infty} (2j+1)\, e^{-(j+1)\hbar^2/8\pi^2/IkT} \qquad ...(22)$$

In almost all the cases the difference between the rotational energies is small compared with $kT$, even at quite low temperatures. Therefore we can change the summation into integration.

Thus

$$f_r = \int_0^{\infty} (2j+1) \exp \{-j(j+1) h^2/8\pi^2 IkT\}\, dj = \frac{8\pi^2 IkT}{h^2}. \qquad ...(23)$$

Therefore for a system of $n$ diatomic molecules, the rotational partition function will be given by

$$Z_r = (f_r)^n = \left[\frac{8\pi^2 IkT}{h^2}\right]^n. \qquad ...(24)$$

This agrees with the rotational partition function calculated by classical arguments. Therefore *rotational energy* for $n$ diatomic molecules is

$$E_r = n\, kT. \qquad ...(25)$$

The *contribution to rotational entropy* of $n$ diatomic molecules is

$$S_r = k \log Z_r + \frac{E_r}{T} \qquad ...(26)$$

$$= k \log \left[\frac{8\pi^2 IkT}{h^2}\right]^n + \frac{nkT}{T}$$

$$= nk \log \frac{8\pi IkT}{h^2} + nk.$$

The *contribution to specific heat due to rotational motion* of $n$ diatomic molecules is

$$(C_V)_r = \left(\frac{\partial E_r}{\partial T}\right) = nk. \qquad ...(27)$$

The *Helmholtz free energy due to rotational motion of n diatomic molecules* is

$$F_{\text{rot}} = E_r - TS_r = nkT - T\left[nk \log \frac{8\pi IkT}{h^2} + nk\right]$$

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*Refer 'Advanced Quantum Mechanics' by Satya Prakash (Kedar Nath Ram Nath Meerut).

$$= -nkT \log \frac{8\pi IkT}{h^2} \qquad ...(28)$$

Therefore the *total partition function* of an assembly on $n$ diatomic molecules is

$$Z = Z_t Z_r Z_v = \frac{f_t^n}{n!} \cdot \left(\frac{8\pi IkT}{h^2}\right) e^{-nh\nu/2kT} (1 - e^{-h\nu/kT})^{-n} \qquad ...(29)$$

The total *mean energy of an assembly of n diatomic molecules* is

$$E = E_t + E_r + E_v = \frac{3}{2} nkT + \frac{1}{2} nh\nu + \frac{nh\nu}{e^{h\nu/kT} - 1} + n\,kT$$

$$= \frac{5}{2} nkT + \frac{1}{2} nh\nu + \frac{nh\nu}{e^{h\nu/kT} - 1}. \qquad ...(30)$$

## 8.28. Nuclear Spin Statistics : Ortho and Para Hydrogen

The nuclei of many atoms possess a resultant intrinsic angular momentum, generally referred as *nuclear spin;* the corresponding spin quantum number $s$ gives the number of units (measured in units of $\hbar$) of spin momentum of the nucleus. This nuclear spin magnitude $s$ is fixed and can not change (without great change in energy) for a given isotope of a given element. The nuclear spin of magnitiude $s$ can take $(2s+1)$ different orientations along any unique axis is space. These different orientations are distinguished from each other in that the projection of the spin along the chosen axis may take any of the $(2s+1)$ values which differ by integers from $-s$ to $+s$ inclusive, $s$ is always an integer or a half odd integer; it is integral if the atomic weight of the isotope is even and a half odd integer if the atomic weight of isotope is odd. The magnitude of the magnetic moment associated with the nuclear spin is so small that there is no appreciable energy difference between the states of different nuclear spin orientations even if the atom or molecule has itself an appreciable magnetic moment due to the other causes.

From statistical point of view the effect of the nuclear spin is only to increase the number of quantum states in every rotational level by a factor $(2s+1)$ for every atom present in the molecule. In the case of diatomic molecule the atoms of the molecule combine to yield a resulrant spin quantum number $S$. Each resultant spin is $(2S+1)$ fold degenerate; because there are $(2S+1)$ possible orientations along any unique axis in space, differing from each other by integers from $-S$ to $+S$ inclusive. Now we shall consider the effect of nuclear spin on the rotational partition functions for heteronuclear and homonuclear diatomic molecules.

**(i) Heteronuclear diatomic molecule.**. In heteronuclear diatomic molecule the two atoms are of different kinds. If the two atoms of this diatomic molecule have spins $s_1$ and $s_2$, the spin degeneracy factor for the diatomic molecule will be $(2s_1+1)(2s_2+1)$. Therefore the rotational partition function for a single hetronuclear diatomic molecule will be given by

$$f_r = (2s_1+1)(2s_2+1) \frac{8\pi^2 IkT}{h^2} \qquad ...(1)$$

in place of $\dfrac{8\pi^2 IkT}{h^2}$.

**(ii) Homonclear diatomic molecule** (like hydrogen molecule) :

In homonuclear diatomic molecule the magnitude of spin for each atom is the same (say $s$). Hydrogen molecule is a homonuclear molecule having two nuclei, each having nuclear spin $s = \frac{1}{2}$.

When $s = \frac{1}{2}$, there are two possible values of resultant nuclear spin $s$ namely *unity for parallel spins and zero for antiparallel spins.* It appears that each type of resultant spin is associated with either symmetric or antisymmetric rotational states and no transitions are possible between them. As each resultant spin is $(2S+1)$ fold degenerate, therefore when $S = 1$, there are three possible orientations whereas when $S$ is zero, there is only one orientation. Therefore the *probability* or *statistical weight* of the molecular state with parallel spins $S = 1$) is three times as great as that for the state with antiparallel spins $s = 0$. Thus it follows that the probability of the occurrence of one set of rotational states, either symmetric or antisymmetric, will be three times as great as for the other. When the spectrum of ordinary hydrogen is studied, the intense lines are observed to possess odd values of $j$ $(j = 1, 3, 5, \ldots)$. Since the lines are intense, they must correspond to the molecular state of greater probability, *i.e.*, parallel nuclear spin $(S = 1)$; while the weak lines should correspond to antiparallel spin $(S = 1)$. Also the rotational levels with odd values of $j$ are considered as *antisymmetric* and those with even values of $j$ as *symmetric*. Therefore the antisymmetric levels can be considered to be associated with $S = 1$; while symmetric levels correspond to $S = 0$. For convenience of nomenclature, the molecules whose rotational levels are present in excess at equilibrium are said to be in *ortho states* and those present in smaller amounts are in *para states*. Thus ordinary molecular hydrogen at ordinary temperature consists of three parts of orthohydrogen and one part of parahydrogen. If there were no interaction between the nuclear spins and the remainder of the molecule, the transitions between symmetric and antisymmetric levels would be completely forbidden.

The existence of ortho and para states in different properties, corresponding to symmetric and antisymmetric states, should be of general occurrence for all homonuclear diatomic molecules. If the spin of each nucleus is $s$, the resultant spin of the diatomic moleule can then be

$$2s, 2s-1, 2s-2, \ldots, 2, 1, 0, \qquad \ldots(2)$$

the maximum values being $2s$ for parallel spins and the minimum values being zero for antiparallel spins. Of this set of resultant spin values the first, third fifth etc., correspond to the set of rotational antisymmetrical levels, while the second, fourth, sixth etc. correspond to the symmetric levels. Therefore in general the resultant nuclear spin may be written as $2s - r$ where $r$ is an integer which cannot exceed $2s$, so that $(2s - r)$ is always positive. Since $r = 0, 2, 4$ etc. would give first, third, fifth etc. terms in the set (2) of resultant spin, therefore these values of $r$ should correspond to antisymmetric or orthostates. Similarly $r = 1, 3, 5$ etc. should correspond to the symmetric or para-states. As the degeneracy factor is $(2s+1)$ where $s$ is now equal to $(2s - r)$, therefore the degeneracy of any state is given by the general expression $(2s+1) = 2(2s-r)+1$. Recalling that $r$ is even for orthostates and odd for para states, it follows that

$$\frac{\text{statistical weight of ortho states}}{\text{statistical weight of para states}} = \frac{\sum\limits_{r=0,2,4\ldots} 2(2s-r)+1}{\sum\limits_{r=1,3,5\ldots} 2(2s-r)+1} \qquad \ldots(3)$$

$$= \frac{(s+1)(2s+1)}{s(2s+1)} = \frac{s+1}{s} \qquad \ldots(4)$$

This relation gives the limiting proportion of ortho form to para form at equilibrium. This relation also represents the ratio of the intensities of alternate rotational lines in the band spectrum under equilibrium conditions.

Since the hydrogen molecule $s = \frac{1}{2}$, therefore *the limiting proportion of ortho form to para form in the hydrogen gas at equilibrium* is 3 : 1.

It is now obvious that in the para states the complete statistical weight is $s(2s+1)(2j+1)$ whereas that of the levels in the orthostates is $(s+1)(2s+1)(2j+1)$. Therefore it follows that at any temperature the ratio of the number of hydrogen molecules in any ortho form to para form is

$$\frac{\text{ortho hydrogen}}{\text{para hydrogen}} = \frac{(s+1)(2s+1) \sum\limits_{j=1,3,5\ldots} (2j+1)\, e^{-\varepsilon_j/kT}}{s(2s+1) \sum\limits_{j=0,2,4\ldots} (2j+1)\, e^{-\varepsilon_j/kT}} \qquad \ldots(5)$$

Since the nuclear spin $s$ for hydrogen is $\frac{1}{2}$, it follows that

$$\frac{\text{ortho hydrogen}}{\text{para hydrogen}} = \frac{3\,[3e^{-\varepsilon_1/kT} + 7e^{-\varepsilon_3/kT} + 11e^{-\varepsilon_5/kT} + \ldots]}{[1 + 5e^{-\varepsilon_2/kT} + 9e^{-\varepsilon_4/kT} + 13e^{-\varepsilon_6/kT} + \ldots]} \qquad \ldots(6)$$

The ratio of ortho to para hydrogen can be evaluated from eqn. (6) by inserting the rotational energies of the various levels as determined from the spectrum of molecular hydrogen. The terms in both numerator and denominator are summed up as long as they contribute appreciably to the total at various temperatures. Actually $e^{-\varepsilon_j/kT}$ falls off rapidly as $j$ increases, specially at fairly low temperatures, hence the number of terms to be included in the summation is not too large. The following table gives percentage of ortho and para forms of hydrogen calculated in this manner at various temperatures.

| *Temp.* | *Ortho hydrogen* | Para hydrogen | Temp. | Ortho hydrogen | *Para hydrogen* |
|---|---|---|---|---|---|
| 20 K | 0·18% | 99·82% | 120 K | 67·13% | 32·87% |
| 40 K | 11·39% | 88·61% | 170 K | 72·01% | 27·99% |
| 60 K | 34·61% | 65·39% | 230 K | 74·58% | 25·42% |
| 80 K | 51·61% | 48·39% | 273 K | 74·87% | 25·13% |
| 100 K | 61·69% | 38·58% | 273 K to ∞ | 75·00% | 25·00% |

It is obvious that at low temperatures the hydrogen at equilibrium consists almost exclusively of the para form; this is due to lowest $(j = 1)$ rotational level and this being an even level must be a para state. As the temperature increases, higher rotational levels are occupied to an increasing extent and hence the molecules in the ortho form are present at equilibrium. At high temperatures a limiting ratio of 3 : 1 of ortho and para hydrogen is obtained. This limiting value agree with equation (4).

**Rotational partition function including nuclear spin :** In the case of homonuclear diatomic molecules, like hydrogen molecule, the rotational partition function is expressed as a mixture of the ortho and para states as follows :

$$Z_r = (s+1)(2s+1) \sum_{j=1,3,5,\ldots} (2j+1)\, e^{-\varepsilon_j/kT} + s(2s+1) \sum_{j=2,4,6,\ldots} (2j+1)\, e^{-\varepsilon_j/kT}$$

$$= (s+1)(2s+1) \sum_{j=1,3,5,\ldots} (2j+1) \exp\{-j(j+1)\, h^2/8\pi^2 IkT\}$$

$$+ s(2s+1) \sum_{j=2,4,6,\ldots} (2j+1) \exp\{-(j+1)\, h^2/8\pi^2 IkT\} \qquad \ldots(7)$$

The quantity $\frac{h^2}{8\pi^2 IkT}$ for most of the homonuclear diatomic molecules with the exception of $H_2$ and $D_2$ is found to quite small at all temperatures. Therefore we can write

$$\therefore \sum_{j=0}^{\infty}(2j+1)\exp\{-j(j+1)h^2/8\pi^2 IkT\} = \frac{8\pi^2 IkT}{h^3} \quad ...(8)$$

In the above summation all values of *j*, odd and even, are included in equal number. If we separate them, we can write

$$\sum_{j=1,3,5,\ldots}(2j+1)\exp\{-j(j+1)h^2/8\pi^2 IkT\}$$

$$= \sum_{j=2,4,6,\ldots}(2j+1)\exp\{-j(j+1)h^2/8\pi^2 IkT\}$$

$$= \frac{1}{2}\cdot(8\pi^2 IkT/h^2). \quad ...(9)$$

Substituting this value in equation (7), we get

$$Z_r = [(s+1)(2s+1)+s(2s+1)]\frac{1}{2}\frac{8\pi^2 IkT}{h^2}$$

$$= (2s+1)^2\frac{4\pi^2 IkT}{h^2} \quad ...(10)$$

## EXERCISES

### SHORT ANSWER QUESTIONS

1. What is the difference between classical and quantum statistics ?
*(Agra 2005, 2002, Kanpur 2001, Rohilkhand 2002)*
2. Distinguish between Maxwell's Boltzmann and Fermi-Dirac statistics.
*(Purvanchal 2005, 1994, Lucknow 2003)*
3. Compare the basis postulates of Maxwell's Boltzmann; Bose Einstein and Fermi-Dirac statistics : *(Mumbai 2004, Kanpur 2006, 1999, 96, Agra 2002)*
4. Differentiate between Fermi-Dirac and Bose-Einstein statistics.
*(Avadh 2001, Agra 2000, Kanpur 2002)*
5. Write Maxwell's Boltzmann's, Bose-Einstein and Fermi Dirac distribution laws. Under what condition Bose-Einstein and Fermi Dirac distribution laws reduce to classical Maxwell's Boltzmann's distribution law ? *(Delhi 2005)*
6. What do you mean by Fermi energy and Fermi temperature ?
7. Explain briefly (i) Photons obey Bose Einstein statistics and (ii) Electrons obey Fermi Dirac statistics.
8. What is the difference between a Boson and Fermion ?
9. Write translational, rotational and vibrational partition functions of a diatomic gas. Hence express total partition function of diatomic gas.
10. How does nuclear spin affect the rotational partition function of homonuclear diatomic molecules ?
11. Which distribution law will you use for the study of photon gas and why ?
12. Which gas possess zero point energy : ordinary gas or photon gas or electron gas ?

13. Which of the statistics would you use for the systems having :
(i) electrons (ii) photons (iii) mesons (iv) oxygen molecules (v) liquid $He^4$ (vi) α-particles (vii) positrons (viii) protons (ix) holes (x) phonons *(Agra 2000, Rohilkhand 2006)*
14. Classify the particles on the basis of Bose-Einstein and Fermi Dirac statistics :
Protons, neutrons, electrons, holes, α-particles, hydrogen atoms, hydrogen molecules, Lithium ions (${}^6_3Li^{++}$). *(Kanpur 1992)*
15. How does Fermi Dirac statistics explain electronic contribution to specific heat ?
16. Explain why specific heat of metals at low temperatures can be expressed as
$$C_V = \lambda T + \beta T^3$$
where λ and β are constants.
17. Two particles are to be distributed in two cells by M.B., B.E. and F.D. statistics. Give the possible distributions. *(Rohilkhand 2006)*
18. Define density matrix. How does is vary with time ?

### LONG ANSWER QUESTIONS

1. State the basic assumptions on which the classical, Fermi-Dirac and Bose-Einstein statistics are developed and deduce expressions for distribution functions in the three cases. Mention the conditions for validity of the respective distribution functions.
*(Rohilkhand 2004, 02; Meerut 2005, 03; Agra 2001)*
2. Deduce expressions for the distribution functions corresponding to B.E. and F.D. statistics. Mention with examples the conditions for the state of degeneracy of a gas.
*(Rohilkhand 1981)*
3. (a) Derive Bose-Einstein distribution law. *(Agra 1981)*
(b) How would it be used to obtain the Planck's formula for the black-body radiation ?
4. Obtain Planck's formula for the distribution of energy in the spectrum of a black-body from statistical consideration applied to an assembly of photons. Deduce Rayleigh-Jean's law using the desired expression. *(Kanpur 1986)*
5. Apply Bose-Einstein statistics to photon gas and hence derive Planck's law for the spectral distribution of energy in black-body radiation. *(Rohilkhand 2000, Mumbai 2004)*
6. Deduce Bose-Einstein distribution formula and explain the phenomenon of Bose-Einstein condensation. *(Rohilkhand 1986)*
7. Give an account of Bose-Einstein statistics and discuss its application to liquid Helium II.
*(Agra 1996)*
8. Discuss Bose-Einstein condensation and how it differs from ordinary condensation. Discuss the anomalous properties of liquid helium at the transition temperature. *(Meerut 2006, 1999)*
9. Discuss the phenomenon of Bose-Einstein condensation To what extent does this explain the properties of liquid $H_e^4$ ? *(Meerut 1999, Kanpur 2002)*
10. What do you understand by Bose-Einstein condensation ? Calculate the critical temperature at which the condensation will start. *(Meerut 1998)*

11. Derive Planck's radiation formula, using Bose-Einstein statistics. Bring out clearly the essential differences between Bose-Einstein and Fermi-Dirac statistics. *(Agra 2005)*
12. What distribution law would you use for the study of a photon gas ? Obtain the Planck's radiation law using the appropriate distribution. Obtain the free energy and the pressure of the photon gas having a volume $V$ and temyeratury $T$. *(Meerut 1998, 1995)*
13. What is Fermi energy ? Derive an expression for Fermi energy at temperature $T$. Establish a relation between mean energy of electron and Fermi energy.
14. Compare the basic postulates of the Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. Deduce the law of distribution of energy of particles according to Fermi-Dirac statistics. *(Meerut 1983, 80)*
15. Differentiate between Bose-Einstein and Fermi-Dirac statistics. Starting from basic assumptions deduce the expression for Bose-Einstein and Fermi-Dirac distribution. *(Meerut 1981)*
16. Give a clear outline of the concepts of statistical mechanics which lead to an evaluation of energy distribution in an assembly of particles. Explain the distrinction between classical. Bose-Einstein and Fermi-Dirac statistics. Discuss the energy distribution near the absolute zero of temperature for an assembly of particles obeying Fermi-Dirac statistics. *(Meerut 2001, 1987; Agra 1997)*
17. What is the difference between a Boson and Fermion. Find an expression for the energy distribution function for electron gas in a met[illegible] *(Meerut 1994)*
18. What is a degenerate gas ? How do the Bose and Fermi distributions tend to the classical distribution ? *(Meerut 1999, Mumbai 2005, Delhi 2001)*
19. What are Fermions ?Derive the Fermi-Dirac distribution formula. Discuss one application for this distribution. *(Mumbai 2004, Meerut 1997)*
20. Distinguish between gases obeying Fermi-Dirac and Bose-Einstein statistics. Obtain the distribution function for a Fermi gas. *(Agra 1992)*
21. (a) Distinguish between the classical, Bose-Einstein and Fermi-Dirac statistics.
    (b) What is Fermi gas ? Deduce an expression for the energy of a Fermi gas at absolute zero. Point out its physical significance. *(Kanpur 1990, 79; Agra 82)*
22. State the essential requirements of F-D statistics. Derive the F-D distributions and show qualitatively that it accounts for the anomaly of specific heat of electrons in metals. *(Agra 2000, 1983)*
23. Considering the free electrons is a metal to form a Fermi gas, obtain the Richardson-Dushmann equation for thermionic emission for electrons.
24. Show that the specific heat of a strongly degenerate Fermi-gas per gram atom is given by

$$C_V \simeq \frac{1}{2}\frac{N\pi^2 k^2}{\varepsilon_F(0)}T.$$

Indicate how the above result can be useful to understand the low temperrature experimental data on the specific heat of metals.

25. Derive the Fermi-Dirac distribution formula and show that the specific heat of a strongly degenerate Fermi-Dirac gas is directly proportional to its absolute temperature. Discuss the importance of this result. *(Kanpur 1988)*
26. Obtain an expression for the Fermi-Dirac distribution law. Discuss some of its applications. Briefly point out the comparative features of the three statistics. *(Rohilkhand 1987)*
27. Calculate on the basis of Fermi-Dirac statistics the electronic contribution to the specific heat of a metal like silver. How this point of the specific heat has been verified experimentally ? *(Meerut 1987)*
28. Deduce Fermi-Dirac distribution law. Hence obtain an expression for the energy of a Fermi gas at absolute zero and point out its physical significance. *(Meerut 1986)*
29. Discuss the theory of highly degenerate Fermi gas. Apply this theory to the free electrons inside a metal and obtain expressions for internal energy and specific heat of the electron gas. *(Rohilkhand 1983)*
30. How do the degeneracies of Bose-Einstein and Fermi-Dirac gas differ ? Discuss the phenomenon of condensation in momentum space and hence explain the properties of liquid He II. *(Rohilkhand 1992)*
31. Deduce an expression for Fermi energy $\varepsilon_f$. Calculate the value of zero point pressure in terms of Fermi energy. *(Meerut 1990)*
32. On the basis of quantum theory calculate (i) translational, (ii) vibrational (iii) rotational partition functions for a single diatomic molecule and hence for a gas consisting of $n$ diatomic molecules. *(Meerut 1986)*
33. Derive the expression for vibrational partition function for diatomic molecule. Calculate the vibrational energy of a gas of $n$ diatomic molecule using the vibrational partition function. *(Meerut 1994, 2005)*
34. What are ortho and para states ? Express rotational and vibrational partitions function. How nuclear spin affects the rotational partition function ?
35. What is the effect of nuclear spin on the rotational partition function of homonuclear diatomic molecule. Show that in an assembly of homonuclear diatomic molecules the ratio of ortho state to para state is $(s+1)$ where $s$ is the spin quantum number for each atom.
36. Write short notes on :
    (i) Symmetric and antisymmetric wave functions. *(Meerut 1986)*
    (ii) Quantum statistics of identical particles and the postulate of equal a priori probability in quantum statistics. *(Meerut 1981, 82)*
    (iii) Bose-Einstein statistics and Bose-Einstein condensation. *(Meerut 1985, 82; Agra 82, 61)*
    (iv) Fermi-Dirac distribution in gases. *(Rohilkhand 1986)*
    (v) Electronic specific heat of a metal. *(Rohilkhand 1988)*
    (vi) Fermi gas *(Agra 2002)*

## Numericals

1. Assuming a diatomic molecule as a rigid rotator, calculate (i) the rotational partition function, (ii) the rotational heat capacity for chlorine at 300 K. Given moment of inertia $= 114{\cdot}5 \times 10^{-14}$ kg/metre$^2$.

2. Assuming the nitrogen molecules as a simple harmonic oscillator, calculate (i) the vibrational partition function and (ii) the vibrational heat capacity at 27°C. Given vibrational frequencies $2360 \text{ cm}^{-1}$.

3. Consider silver in the metallic state, with one free (conduction) electron per atom. Calculate its Fermi energy. The density of silver is $10{\cdot}5 \text{ gram/cm}^3$ and its atomic weight is 108. The Avogadro's number is $6{\cdot}02 \times 10^{23}$ atoms/mole. ($h = 6{\cdot}63 \times 10^{-34}$ J-s, $m = 9{\cdot}1 \times 10^{-31}$ kg)
[Ans. 5·5 eV.]

4. For lithium, the Fermi energy is 4·70 eV and the density of electrons is $4{\cdot}6 \times 10^{28}/\text{m}^3$. Find the electron density for a metal with Fermi energy 2·35 eV. [Ans. $1{\cdot}6 \times 10^{28}$ per $m^3$]

## MULTIPLE CHOICE QUESTIONS : *SELECT THE RIGHT CHOICE*

1. Bose Einstein statistics applies to :
(a) electrons (b) molecules (c) photons (d) all above

2. Bose-Einstein distribution function is ($n_i =$
(a) $g_i e^{-\beta\varepsilon_i}$ (b) $g_i e^{\beta\varepsilon_i}$ (c) $\dfrac{g_i}{e^{\beta\varepsilon_i}+1}$ (d) $\dfrac{g_i}{e^{\beta\varepsilon_i}-1}$

3. Fermi-Dirac statistics applies to :
(a) electrons (b) molecules (c) photons (d) all above

4. Fermi-Dirac distribution function is ($n_i =$
(a) $g_i e^{-\beta\varepsilon_i}$ (b) $g_i e^{\beta\varepsilon_i}$ (c) $\dfrac{g_i}{e^{\beta\varepsilon_i}+1}$ (d) $\dfrac{g_i}{e^{\beta\varepsilon_i}-1}$

5. Quantum statistics approaches to classical statistics if :
(a) $\dfrac{g_i}{n_i} = 1$ (b) $\dfrac{g_i}{n_i} >> 1$ (c) $\dfrac{g_i}{n_i} << 1$ (d) never

6. In quantum statistics the particles are :
(a) identical and distinguishable (b) identical and indistinguishable
(d) molecules only (d) photons only

7. Planck's rediation law can be derived by using : ***(Rohilkhand 2006)***
(a) Maxwell's Boltzmann statistics (b) Fermi-Dirac statistics
(c) Bose-Einstein statistics (d) all above

8. Which of the following is a boson :
(a) $\alpha$-particle (b) neutron (c) positron (d) proton

9. Which of the following is suitable statistics for photons ?
(a) F.D. statistics (b) B.E. statistics (c) M.B. statistics (d) none of these

10. Fermi energy is :
(a) zero (b) energy in highest occupied level
(c) energy in lowest occupied level (d) mean energy of electrons in a metal

11. In sodium the Fermi energy is 3·1 eV. What is Fermi temperature ? ($k = 1{\cdot}38 \times 10^{-23}$ J/k).
(a) $3{\cdot}6 \times 10^4$ K (b) $3{\cdot}6 \times 10^3$ K (c) $2{\cdot}25 \times 10^{23}$ K (d) $2{\cdot}25 \times 10^{24}$ K

12. The quantum statistics under the following condition ($\rho$ = number density of particle and $\lambda$ is de Broglie wavelength),
(a) $\rho\lambda^3 = 1$ (b) $\rho\lambda^3 >> 1$
(c) $\rho\lambda^3 << 1$ (d) $\rho = 0$

13. Bose Einstein Grand partition function is ($Z =$
(a) $\sum_i [1 + e^{\beta(\mu - \varepsilon_i)}]^{-1}$ (b) $\sum_i [1 - e^{\beta(\mu - \varepsilon_i)}]^{-1}$
(c) $\prod_i [1 - e^{-\beta(\mu - \varepsilon_i)}]^{-1}$ (d) $\prod_i [1 - e^{\beta(\mu - \varepsilon_i)}]^{-1}$

14. There is no solution in the case of Bose-Einstein degeneration if
(a) $\dfrac{n}{V} > \left(\dfrac{2\pi mkT}{h^3}\right) . 2{\cdot}612$ (b) $\dfrac{n}{V} < \left(\dfrac{2\pi mkT}{h^3}\right) . 2{\cdot}612$
(c) $\dfrac{n}{V} > \left(\dfrac{2\pi mkT}{mh^3}\right)^{3/2}$ (d) $\dfrac{n}{V} < \left(\dfrac{2\pi mkT}{mh^3}\right)^{3/2}$

15. In Bose Einstein statistics, the number of particles condensing into ground state are
(a) Zero (b) all
(c) $\eta\left[1 - \left(\dfrac{T}{T_0}\right)^{3/2}\right]$ (d) $n\left[1 - \left(\dfrac{T}{T_0}\right)^{1/2}\right]$

16. The Fermi function $f(\varepsilon) = \dfrac{n(\varepsilon)}{g(\varepsilon)}$ has value $\dfrac{1}{2}$ when
(a) $\varepsilon < \varepsilon_f$ (b) $\varepsilon > \varepsilon_F$
(c) $\varepsilon = \varepsilon_F$ at absolute zero only (d) $\varepsilon = \varepsilon_F$ at any temperature

17. Which gas at absolute zero possesses energy and exerts pressure
(a) Oxygen gas (b) Photon gas (c) Electron gas (d) No gas

18. The relation of Fermi energy at absolute zero and at absolute temperature $T$ are related as
(a) $\varepsilon_F(T) = \varepsilon_F(0) = \text{constant}$ (b) $\varepsilon_F = \varepsilon_F(0)\left[1 + \dfrac{1}{12}\left(\dfrac{\pi kT}{\varepsilon_F(0)}\right)^2\right]$
(c) $\varepsilon_F(T) = \varepsilon_F(0)\left[1 - \dfrac{1}{6}\,\dfrac{\pi kT}{\varepsilon_F(0)}\right]$ (d) $\varepsilon_F = \varepsilon_F(0)\left[1 - \dfrac{1}{12}\left(\dfrac{\pi kT}{\varepsilon_F(0)}\right)^2\right]$

19. For strongly degenerate Fermi gas the specific heat
(a) is proportional to absolute temperature
(b) is proportional to square of absolute temperature
(c) is proportional to cube of absolute temperature
(d) is independent of temperature

20. According to Fermi Dirac statistics, the minimum energy to be supplied to the electron for its emission is [$W$ = constant potential energy within metal relative to free space and $\varepsilon_F(0)$ is Fermi energy at absolute zero]
(a) $W$ (b) $\varepsilon_F(0)$
(c) $W - \varepsilon_F(0)$ (d) $W + \varepsilon_F(0)$

21. The rotational partition function for *n*-diatomic molecules is

(a) $\left[ n \times \frac{8\pi^2 IkT}{h^2} \right]$ (b) $\left[ \frac{8\pi^2 IkT}{h^2} \right]^n$

(c) $\frac{V^n}{h^{3n}\, n\,!}(2\pi mkT)^{3n/2}$ (d) $\frac{1}{2\sinh(h\nu/2kT)}$

22. The ratio of statistical weights of orthostates to statistical weight of parastates of hydrogen having nuclear spins *s* is

(a) $\frac{2s+1}{2s-1}$ (b) $\frac{s+1}{s-1}$ (c) $\frac{s}{s+1}$ (d) $\frac{s+1}{s}$

**ANSWERS**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. (c) | 2. (d) | 3. (a) | 4. (d) | 5. (b) | 6. (b) | 7. (c) | 8. (a) |
| 9. (b) | 10. (b) | 11. (a) | 12. (c) | 13. (d) | 14. (a) | 15. (c) | 16. (c) |
| 17. (c) | 18. (d) | 19. (a) | 20. (c) | 21. (b) | 22. (d). | | |

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# 9

# QUANTUM THEORY OF SPECIFIC HEATS

## 9.1 Introduction : The Dulong and Petit's Law

From the study of bulk properties in the macroscopic state of solids, it has been shown that solids, in general, are characterised by the regularity of distribution of atoms, the atoms being bound together by means of a chemical bond. The atoms of an ideal solid are assumed to be non-interacting with each other and hence an ideal solid may be considered to be consisting of a space lattice of independent atoms vibrating about their mean positions.

An expression for the specific heat of solids may be obtained from the kinetic theory and the use of classical statistical mechanics. From these it is known that the atoms of a solid substance are at rest under the action of their mutual attractions and repussions at the absolute zero of temperature. The energy of the solid in this state is assumed to be zero. When the temperature is raised, each of the atoms starts vibrating about its mean position and these vibrations are transmitted from one atom to another atom throughout the crystal lattice. At low temperatures, the displacement of atoms about their mean position is very small as compared to the interatomic distances and hence the vibration of the atom can be considered to be harmonic, Thus each atom of the solid can be considered to be a harmonic oscillator and so the energy cen be considered as the sum of two squared terms of one kinetic energy and the other potential. As in the case of simple harmonic motion the average kinetic energy is equal to the average potential energy, the average energy corresponding to one vibration is equal to twice the kinetic energy corresponding to one degree of freedom. But according to the law of equipartition of energy, the kinetic energy associated with each degree of freedom is $\frac{1}{2}kT$. $k$, being Boltzmann constant. Thus the average energy associated with the motion of an atom along one co-ordinate, *i.e.*, for each vibrational mode

$$= 2 \times \frac{1}{2}kT = kT$$

As each atom can vibrate in space along any of the three co-ordinates axes, the average energy per atom is, therefore, $3kT$. Hence the total vibrational energy of a gram atom of solid containing $N$ (Avogadro number) atoms is classically given by

$$E = 3NkT = 3RT,$$

where $R$ is gas constant. Thus for a solid, the specific heat per gram atom,

$$C_V = \frac{dE}{dT} = 3R = 3 \times 1{\cdot}9856 = 5{\cdot}96 \text{ cal. degree}^{-1}\text{ mole}^{-1}.$$

This result was called the *Dulong and Petit's law* and was generalised by them in 1819, as a result of their investigations on the specific heat of elements in the solid state. The law may be stated as, *"The product of atomic weight and specific heat [called, the atomic heat] of all elements in the solid state is about the same and equal to 6·0 cals per gram atom per °C."*

According to this law specific heat of solid must be a constant quantity independent of temperature. This is however, contrary to the experimentally observed facts. It has been found by experiments that the specific heat of all substances varies with temperature. The results of the experiments of many investigators can be summarised as follows :

(i) The atomic heat at constant volume increases with increase in temperature and finally converges towards the value $3R$ at high temperature as given by Dulong and Petit's law.

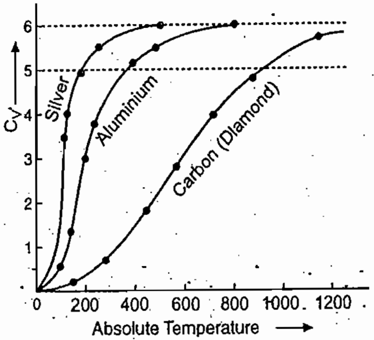
(ii) At low temperatures, the atomic heat decreases slowly with decrease of temperature and below a certain temperature, characteristics of each element, it decreases rapidly converging towards the value zero as the absolute zero of temperature is approached.

(iii) The nature of variation of atomic heat with temperature (fig. 9.1) is the same for all elements, *i.e.*, all the graphs of atomic heat and absolute temperature can be made to coincide exactly if the temperature scale is suitable adjusted. This result can be expressed in the form

$$C_V = f\left(\frac{\Theta}{T}\right),$$

where the function $f$ is the same for all substances and $\Theta$ is a constant characteristic of each substance..

The above discussions show that Dulong and Petit's law is in good agreement with experiments as the temperature decreases. Thus the validity of Dulong and Petit's law is restricted to fairly high temperatures. It fails to explain the observed rapid decrease of all specific heats at low temperatures. We are therefore, forced to look elsewhere for a satisfactory interpretation of such variations in specific heats. Einstein succeeded in obtaining a satisfactory explanation for the experimentally observed variation on the basis of modern quantum theory. A further improvement in Einstein's theory was later on made by Debye.



(Fig. 9.1)

## 9.2 Einstein's Theory of the Specific Heat of Solids

The first attempt to explain the variation of specific heat with temperature was made by Einstein, in 1907, on the basis of quantum theory, the revolutionary feature of which is that the energy of an oscillating system varies not in a continuous mannner permitting all possible values but only in definite 'packets' or 'quanta', *i.e.*, integral multiplies of an elementary quantum of energy $h\nu$, where $h$ is called *Planck's constant* and $\nu$ the natural frequency of oscillation. Einstein modified the classical results by making the following simple assumptions :

(1) The atoms in a solid are all independent and that each atom acts as a simple harmonic oscillator with a common frequency $\nu$. Thus a solid (considered as a collection of atomic vibrators) is characterised by one and the same frequency, (*i.e., monochromatic vibrations*).

(2) Each atom of a solid has three degrees of freedom like a molecule of a monoatomic gas.

(3) The mean energy per degree of freedom of an oscillator vibrating with the frequency $\nu$ is not $kT$ as given by equipartition law, but $\dfrac{h\nu}{e^{h\nu/kT}-1}$ as obtained by Planck by the application of quantum theory in connection with the theory of black-body radiation.

Hence the energy of each atom

$$= \frac{3h\nu}{e^{h\nu/kT}-1}$$

The energy content of a gram atom of the solid consisting of $N$ atoms is therefore given by

$$E = \frac{3Nh\nu}{e^{h\nu/kT}-1}$$

Hence the specific heat of a gram atom at constant volume

$$C_V = \frac{dE}{dT} = \frac{d}{dT}\left[3Nh\nu\,(e^{h\nu/kT}-1)^{-1}\right]$$

$$= 3Nh\nu\,(-1)\,(e^{h\nu/kT}-1)^{-2}\,.\,e^{h\nu/kT}\,.\left(-\frac{h\nu}{kT^2}\right)$$

$$= \frac{3Nh^2\nu^2}{kT^2}\cdot\frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}$$

$$= 3Nk\frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}\left(\frac{h\nu}{kT}\right)^2 \qquad \text{...(1)}$$

This expression can be conveniently written as

$$C_V = 3R\left[\frac{e^{\Theta/T}}{(e^{\Theta/T}-1)^2}\left(\frac{\Theta}{T}\right)^2\right], \qquad \text{...(2)}$$

where $\Theta = \dfrac{h\nu}{k}$. The value of $\nu$ giving good fit for a particular solid is represented by $\nu_E$ and called the *Einstein's frequency* for that solid, $\Theta$ corresponding to $\nu_E$ is represented by $\Theta_E$ and is called *Einstein's temperature.*

We thus have $h\nu_E = k\,\Theta_E$.

And equation (2) becomes

$$C_V = 3R\left(\frac{\Theta_E}{T}\right)^2\frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)^2} \qquad \text{...(3)}$$

This is Einstein's equation for the atomic heat of a solid at constant volume. This equation represents that the atomic heat is *a function of temperature.*

Let us now explain the experimentally observed facts on the basis of Einstein's equation.

**(1) At high temperature :** At very high temperature neglecting higher order terms $\dfrac{h\nu}{kT}$ approaches very small values and so, we have

$$(e^{h\nu/kT}-1)^2 = \left[1+\frac{h\nu}{kT}+\frac{1}{2\,!}\left(\frac{h\nu}{kT}\right)^2+\ldots-1\right]^2 \approx \left(\frac{h\nu}{kT}\right)^2$$

Therefore, from equation (1)

$$C_V = \frac{3R\left[1+\frac{h\nu}{kT}+\ldots\right]}{(h\nu/kT)^2}\left(\frac{h\nu}{kT}\right)^2$$

$$= 3R\left[1+\frac{h\nu}{kT}+\ldots\right]$$

$$= 3R \text{ as } T \to \infty,\ i.e.,\ \frac{h\nu}{kT} \to 0.$$

Thus according to Einstein's equation (1), the *atomic heat approaches* 3R which is in agrement with experiments and Dulong and Petit's law.

**(2) At very low temperature :** When $T \to 0, \frac{h\nu}{kT} \to \infty$ and hence 1 may be neglected in the expression $(e^{h\nu/kT} - 1)^2$. Equation (1), then becomes

$$C_V = 3R \frac{e^{h\nu/kT}}{(e^{h\nu/kT})^2}\left(\frac{h\nu}{kT}\right)^2$$

$$= 3R \frac{1}{e^{h\nu/kT}}\left(\frac{h\nu}{kT}\right)^2 \qquad \text{...(4)}$$

$$= 3R \frac{\left(\frac{h\nu}{kT}\right)^2}{\left[1 + \frac{h\nu}{kT} + \frac{1}{2!}\left\{\frac{h\nu}{kT}\right\}^2 + \frac{1}{3!}\left\{\frac{h\nu}{kT}\right\}^3 + \ldots\right]}$$

or

$$C_V = 3R \frac{1}{\frac{1}{\left(\frac{h\nu}{kT}\right)^2} + \frac{1}{\left(\frac{h\nu}{kT}\right)} + \frac{1}{2!} + \frac{1}{3!}\left(\frac{h\nu}{kT}\right) + \ldots}$$

$$\to 0 \text{ as } T \to 0 \text{ i.e., } \frac{h\nu}{kT} \to \infty.$$

Thus according to eqn. (1) the *atomic heat tends to zero as temperature tends to absolute zero.* Moreover eqn. (4) can be written in the form

$$C_V = 3R\left(\frac{\Theta_E}{T}\right)^2 \cdot e^{-\frac{\Theta_E}{T}} \qquad \text{...(5)}$$

which gives specific heat as proportional $e^{-\Theta_E/T}$ for $T << \Theta_E$. Thus *atomic heat decreases with decrease of temperature* due to dominator of exponential factor but the Einstein's function falls off more rapidly than it should.

(3) According to eqn. (5) the atomic heats of different elements differ only because of differences in the characteristic frequency $\nu_E$. At corresponding temperatures, such that the value of the ratio $\nu/T$ are same, atomic heat will be same for elements. Thus *the experimental curves have the same form for all substances.*

In this way, the Einstein's theory predicts the correct values of atomic heats for various elements as observed experimentally *i.e.*, the Einstein's theory is in good agreement with the experiments. However, in case of some elements like copper, aluminium, iron etc. it was observed that atomic heat at low temperatures decreases more slowly than that predicted from Einstein's theory. For silver at 14K, the value calculated from Einstein's formula is 28 times lower than the experimental value. This disagreement is due to the assumption that the vibrations of all the atoms are simple harmonic and have one and the same frequency. Another weak point in Einstein model is that $\nu$ and $\Theta$ are obtained empirically and cannot be verified from any other independent physical data. Debye improved upon Einstein's theory in order to account for these discrepencies.

## 9.3 Debye's Theory of Specific Heat of Solids

Classical mechanics leads to the Dulong and Petit's law according to which the atomic heat $C_V$ of an element in the solid state is constant and is equal to 6 calories per atom per °C. Experimental studies, however, show that the specific heat of solids decreases as the temperature is lowered and tends to zero near absolute zero. Einstein applied the quantum theory to the problem with remarkable success. His specific-heat curve agrees fairly well with the experimental data for high temperatures, but although it approaches zero at $T \to 0$, it does so too rapidly. The reason for this discrepancy should be sought in the over simplified model proposed by Einstein in supposing a single frequency $\nu$ for all the atomic vibrations. In fact the vibrational spectrum of a solid covers a wide range of frequencies because the atomic oscillators are under the field of force of a large number of other vibrating atoms and thus do not vibrate independently. The atoms rather behave collectively as a system of coupled harmonic oscillators.

Debye developed and utilized a different approach. He suggested that instead of considering each atom to oscillate with the same frequency, a distribution of frequencies should be considered. Debye assumed that a solid is capable of vibrating elastically in many different modes, the frequency varying from one mode to another, and that the number of modes of vibration are limited in number. This number is assumed to be same as the total number of degrees of freedom of the atoms of which the body is composed, there being three degrees of freedom per atom. Thus the essential difference between the Debye Model and Einstein model is that Debye considered the vibrational modes of a crystal as a whole while Einstein considered the vibration of a single atom and that too to be independent of other atoms. ~~As a matter of fact,~~ the atoms do not vibrate independently, the vibration of any individual atom will set neighbouring atoms in oscillation with the result that the free vibrations of the system as a whole are identical with the elastic vibrations of a continuous solid.

Now when a continuous solid is subjected to elastic vibrations, two kinds of vibrations are produced :

(i) Longitudinal vibrations, (ii) Transverse vibrations.

The number of modes of longitudinal vibrations per unit volume with frequencies between $\nu$ and $\nu + d\nu$

$$= \frac{4\pi\nu^2 d\nu}{c_l^3},$$

$c_l$ being the velocity of longitudinal vibrations.

The number of modes of transverse vibrations per unit volume with frequencies between $\nu$ and $\nu + d\nu$

$$= \frac{8\pi\nu^2 d\nu}{c_t^3}.$$

$c_l$ being the velocity of transverse vibration. Here the expression in the second case is double because there are two transverse modes corresponding to the two independent components of the displacement perpendicular to the direction of propagation while there is only one longitudinal mode because the displacement in that case is along the direction of propagation.

Therefore, the number of independent vibrations per unit volume with frequencies between $\nu$ and $\nu + d\nu$

$$= 4\pi\left[\frac{1}{c_l^3} + \frac{2}{c_t^3}\right]\nu^2 d\nu.$$

If $V$ is the volume of a gram-atom of the solid, the number of modes of vibrations for this amount within frequencies $\nu$ and $\nu + d\nu$

$$= 4\pi V\left[\frac{1}{c_l^3} + \frac{2}{c_t^3}\right]\nu^2 \, d\nu.$$

Debye assumes that this result holds for all the frequencies from the lowest $\nu = 0$ to the highest possible $\nu = \nu_m$, characteristic of the substance, because there can not be an infinite number of standing waves. Then the total number of independent modes of vibration of all frequencies is given by

$$4\pi V\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)\int_0^{\nu_m} \nu^2 \, d\nu = \frac{4\pi V}{3}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)\nu_m^3 \qquad \text{...(2)}$$

But this must be equal to the number of degrees of freedom of all the atoms, equal to $3N$, since there are $N$ atoms in volume $V$ of the gram-atom and each atom possesses three degrees of freedom. On this assumption

$$\frac{4\pi V}{3}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)\nu_m^3 = 3N$$

or

$$4\pi V\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right) = \frac{9N}{\nu_m^3} \qquad \text{...(3)}$$

Combining eqn. (3) and (1), we have the total number of vibrations in a volume $V$ having a frequency range between $\nu$ and $\nu + d\nu$

$$= \frac{9N\nu^2 d\nu}{\nu_m^3} \qquad \text{...(4)}$$

Debye assumes that the mean energy of each vibration has the value given by quantum theory, *viz* $\left(\frac{h\nu}{e^{h\nu/kT} - 1}\right)$. Therefore, the total energy for one gram-atom of the solid is given by

$$E = \int_0^{\nu_m} \frac{9N\nu^2 d\nu}{\nu_m^3} \cdot \frac{h\nu}{e^{h\nu/kT} - 1}$$

$$= \frac{9Nh}{\nu_m^3}\int_0^{\nu_m} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \qquad \text{...(5)}$$

Differentiating this expression for energy with respect to $T$, we obtain for $C_V$, the atomic heat at constant volume. Thus

$$C_V = \frac{dE}{dT} = \frac{9Nh}{\nu_m^3}\int_0^{\nu_m} \frac{\nu^3(-1)(-h\nu/kT^2)}{(e^{h\nu/kT} - 1)^2} e^{h\nu/kT} \, d\nu$$

or

$$C_V = \frac{9Nk}{\nu_m^3}\int_0^{\nu_m} \frac{h^2\nu^4/(kT)^2 . e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} d\nu. \qquad \text{...(6)}$$

In this expression we substitute for simplicity $\xi = \frac{h\nu}{kT}$.

and for each substance define a *Debye characteristic temperature* $\Theta$ by the relation

$$\Theta = \frac{h\nu_m}{k}$$

and put

$$\frac{\Theta}{T} = \frac{h\nu_m}{kT} = \xi_m = x.$$

so that

$$\nu = \frac{kT}{h}\xi \quad \text{and} \quad d\nu = \frac{kT}{h}d\xi.$$

Then expression (6) for specific heat becomes

$$C_V = \frac{9Nk}{x^3}\int_0^x \frac{\xi^4 e^\xi}{(e^\xi - 1)^2} d\xi. \qquad \text{...(7)}$$

This equation may be integrated by parts, for we have

$$\int_0^x \frac{\xi^4 e^\xi}{(e^\xi - 1)^2} d\xi = -\int_0^x \xi^4 \cdot \frac{d}{d\xi}(e^\xi - 1)^{-1} d\xi$$

$$= -\left[\xi^4 \frac{1}{e^\xi - 1}\right]_0^x + \int_0^x \frac{1}{e^\xi - 1}\frac{d\xi^4}{d\xi} d\xi$$

$$= -\left[\frac{x^4}{e^x - 1}\right] + \int_0^x \frac{4\xi^3}{e^\xi - 1} d\xi.$$

Using this result and remembering that $Nk = R$, equation (7) for specific heat becomes

$$C_V = 3R\left[\frac{12}{x^3}\int_0^x \frac{\xi^3}{e^\xi - 1} d\xi - \frac{3x}{e^x - 1}\right] \qquad \text{...(8)}$$

$$= 3R.D(x)$$

where $D(x)$ represents the expression within square brackets (as it is a function of $x$ alone) and is known as *Debye's* function. Since $x$ is equal to $\frac{h\nu_m}{kT} = \frac{\Theta}{T}$, the above (Debye's) expression for the atomic heat of a monoatomic solid may also be expressed by

$$C_V = 3.f\left(\frac{\Theta}{T}\right), \qquad \text{...(9)}$$

where $\Theta$ is a constant for a given substance (varies from element to element) and is called Debye's temperature whereas $f$ is the same function for all substances.

It may be noted that eqn. (9) is in accord with the important experimental results listed in section 9.1. The integral of eqn. (1) can not be evaluated in finite terms but Debye has evaluated it numerically. We shall here consider some limiting cases :

**(1) At high temperature :** When $T$ is large, $x\left(= \frac{\Theta}{T}\right)$ is small and $e^x \approx 1 + x$.

Hence

$$\frac{x}{e^x - 1} = \frac{x}{1 + x - 1} \approx 1,$$

$$\xi\left(= \frac{h\nu}{kT}\right) \text{is also small and } e^\xi \approx 1 + \xi.$$

Hence $$\int_0^x \frac{\xi^3 d\xi}{e^{\xi}-1} = \int_0^x \xi^2 d\xi = \frac{x^3}{3}$$

Therefore expression (8) for specific heat provides

$$C_V = 3R\left[\frac{12}{x^3}\cdot\frac{x^3}{3} - 3\right] \approx 3R.$$

Thus atomic heat of all substances tends to a maximum value of $3R$, the expected classical value.

**(2) At very low temperatures :** When $T$ is very small, $x$ and $\xi$ become large, so that the last term in eqn. (8) can be neglected since with increasing values of $x$ the exponential factor in the denominator increases much rapidly than the numerator. Moreover when $T$ becomes small, the denominator in the first term is large unless ν is small. Hence terms having large ν contribute very little to the total atomic heat, or in other words the *energy is concentrated in the spectrum of lower frequencies*. The upper limit $x$ in integral of (8) can therefore be replaced by ∞ with little error. We then have

$$C_V = 3R\,\frac{12}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^{\xi}-1}.$$

It is know that $\int_0^x \frac{\xi^3 d\xi}{e^{\xi}-1} = \frac{\pi^4}{15}$

Hence eqn. (8) becomes, approximately

$$C_V = 3R\,\frac{12\pi^4}{15}\left(\frac{T}{\Theta}\right)^3 = 77{\cdot}94 \times 3R\left(\frac{T}{\Theta}\right)^3$$

$$= \frac{233{\cdot}8R}{\Theta^3}T^3 = \frac{464{\cdot}4}{\Theta^3}T^3 \text{ cal/mol-K} \quad \ldots(10)$$

Since $\Theta$ is constant for the substance, *the specific heat of a solid at extremely low temperatures is proportional to the cube of the absolute temperature, i.e.,*

$$C_V \propto T^3.$$

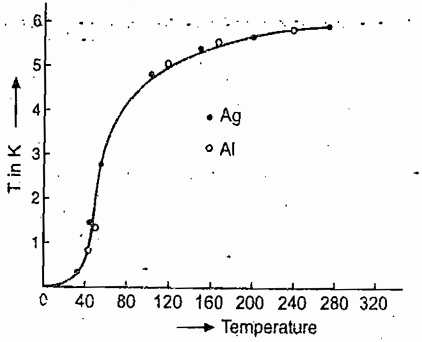
This is the famous **Debye's $T^3$ law** for the specific heat of a solid at low temperatures and has been tested experimentally for a large number of substances.

Further when $T = 0$, equation (10) gives $C_V = 0$, *i.e., the atomic heat tends to zero as temperature tends to absolute zero.*

## 9.4. Comparison of the Debye Formula with Experiments

In order to illustrate the agreement between the Debye theory and experiments, the experimentally observed specific heat values for silver and aluminium as fitted to a Debye curve are shown in fig. 9.2. Here the continuous curve corresponds to the Debye's general formula while the black and white dots represent the experimental values of $C_V$ for $Ag$ and $Al$ respectively. It is obvious from this curve that the theoretical and experimental results are in fair agreement.

It may be observed from fig. 9.2 that at absolute zero, the specific heat reduces to zero. At lower temperatures the variation is in accordance with the $T^3$ law and at high temperatures the specific heat becomes almost constant and assumes an asymptotic value (≈ $3R$) for all the solids.



(Fig. 9.2)

**The value of Debye characteristic temperature Θ** can be determined from the elastic constants of the substance. From eqn. (3) § 9.3 considering unit volume

$$\frac{1}{c_l^3} + \frac{2}{c_t^3} = \frac{9N}{4\pi V_m^3} = \frac{9N}{4\pi}\left[\frac{h}{k\Theta}\right]^3.$$

so that $$\left[\frac{1}{\Theta}\right]^3 = \frac{4\pi k^3}{9Nh^3}\left(\frac{1}{c_l^3} + \frac{2}{c_t^2}\right)$$

The velocities $c_l$ and $c_t$ can be expressed in terms of the elastic constants of the substance. From the theory of elasticity, we have

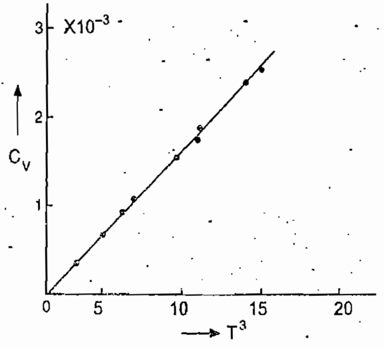
$$c_l = \sqrt{\left\{\frac{3(1-\sigma)}{(1+\sigma)\beta\rho}\right\}} \quad \text{and} \quad c_t = \sqrt{\left\{\frac{3(1-2\sigma)}{2(1+\sigma)\beta\rho}\right\}},$$

where ρ is the density, β the compressibility and σ the Poisson's ratio of the substance. All the quantities involved in these equations can be measured experimentally and hence Θ can be calculated.

Another method for determining Θ is to plot a graph between $C_V$ and $T^3$ in the equation

$$C_V = \frac{464{\cdot}4}{\Theta^3}T^3 \text{ cal/mol K}$$

Thus the slope of $C_V - T^3$ line would give the value $\frac{464{\cdot}4}{\Theta^3}$ from which Θ can be determined. Fig. 9.3 illustrates such a graph. (The $T^3$ law) for $KCl$ on the basis of results obtained by Keesom and Pearlman.



(Fig. 9.3)

The values of Debye characteristic temperature Θ obtained from measurements of specific heat at low temperatures are for several elements in close resemblance with those calculated from the elastic contants data. The values for copper, aluminium, silver and gold are given in Table below :

| *Debye Characteristic Temp.* | *Cu* | *Al* | *Ag* | *Au* |
|---|---|---|---|---|
| From specific heat | 316–327 | 402 | 214 | 170 |
| From elastic constants | 325 | 388 | 215 | 161 |

Agreement between the two sets of values for Debye characteristic temperature Θ is a testimony for the general accuracy of the Debye theory.

## 9.5. Criticism of Debye's Theory

Inspite of the great success of Debye's theory one finds it difficult to agree with its theoretical foundations. It suffers from the following defects.

(1) Debye treated the vibrations of a solid as if it were a continuous medium. Actually a solid is a collection of discrete ions which are held together by the forces of cohesion.

(2) In Deby's theory, the solid is regarded as an isotropic body whereas solids are actually composed of definite crystals, either in the form of a single crystal or minute crystals brought together by pressure. Debye's theory does not take into account the crystalline structure of solids.

(3) Debye assumed that the sound velocity is constant for all wavelengths. Actually the velocity of elastic vibrations depend upon the wavelength when the wavelength of vibration is comparable with the atomic distances-the shorter waves travelling with lesser velocities. Hence a change of velocity with frequency must be taken into account in formulating the expression for $\nu_m$ (eqn. 3 § 9.3).

(4) Debye's theory completely neglects the interatomic interactions and the electronic contribution to specific heat but it is highly observable at very low temperatures (in the vicinity of 1 K). Keesom has shown that Debye's theory almost completely breaks down in the liquid helium temperature region for many metals. At about 0·74 K, the observed specific heat for silver is found to be much larger than that predicted by Debye theory. Kessom accounts this increase in specific heat to the influence of free electrons (electronic contribution) which in this low temperature region is simply linear in $T$ *i.e.*,

$$C_V \text{ (electronic)} = \alpha T$$

where the proportionality constant $\alpha$ is relation to the density of conduction electrons in the solid.

(5) The experimental evidence for the existence of a $T^3$ region as predicted by Debye is weak. Blackman showed that the $T^3$ law should be expected to hold for the temperature region much lower than that predicted by the Debye's Theory. Infact, the Debye' theory is seriously in error concerning the temperatures at which it predics the $T^3$ region to begin.

(6) In some cases it is observed that the specific heat of solid increases with the decrease in temperature near the absolute zero. The magnetic studies on neodynium ethyl sulphate over the temperature range 0·95 K to 2·15 K provides a good example of it. The specific heat at constant magnetization $C_m$ is, infact, found to obey the relation

$$C_m = \frac{b}{T^2}$$

where $b$ is a constant at a particular temperature.

(7) The Debye characteristic temperature $\Theta$ is assumed to be constant for a given substance but in has been observed that it varies widely with temperature. As $T$ increases $\Theta$ does not remain constant because then the $T^3$ law fails to hold. In low temperature region for silver below 6 K, the value of $\Theta$ calculated from equation $C_V = \frac{464 \cdot 4}{\Theta^3} T^3$ falls off rapidly and continuously from 215 to 160. Similarly variation of $\Theta$ with temperature has been observed in case of *LiF* also.

Debye's theory has evoked adverse criticism from the renowned Indian physicists and Nobel Laureate Sir C.V. Raman while investigating reflections of *X*-rays from crystals. Dr. Raman contended that the so called Debye temperature is purely arbitrary and has no physical significance except at the lowest temperatures.

## 9.6 Improvement upon Debye's Theory (Born-Karman Theory)

Attempts have been made to modify Debye's theory and extend it to substances other than simple chemical elements. The theory has been extended by Born and others to apply to crystals and the bodies cuntaining more than one type of atoms. These theories take into account the fact that the body is not continuous but is composed of atoms separated in space arranged on a lattice.

Born and Karman have developed the *lattice theory of atomic heats* for the most general cases of crystals and chemical compounds In Debye's theory, the maximum frequency $\nu_m$ was common to both the longitudinal and the transverse vibrations. Born proposed to cut off the spectrum in such a way that the longitudinal and transverse vibrations have a *common minimum wavelength* $\lambda_m$. Then the maximum permitted frequency $\nu_m$ for longitudinal waves will be greater than $\nu_{mt}$ for the transverse waves because the longitudinal waves travel faster than transverse waves.

Since the number of modes of vibrations lying between frequencies 0 and $\nu$ in a volume $V$ is

$$\frac{4}{3}\pi\left(\frac{\nu^3}{c^3}\right)V = \frac{4}{3}\pi\left(\frac{1}{\lambda^3}\right)V$$

and each mode may contribute three vibrations (one longitudinal and two transverse). Hence the total number of vibrations is $\left(\frac{4\pi}{\lambda^3}\right)V$. Following Born we should integrate only upon a common minimum wavelength $\lambda_m$ given by the relation

$$4\pi\left(\frac{1}{\lambda_m}\right)^3 V = 3N$$

because this procedure leaves the total number of vibrational modes equal to $3N$. From it, one obtains *two Debye frequencies*, one $\nu_{ml}$ for longitudinal modes and another $\nu_{mt}$ for the transverse modes from the relations $c_l = \lambda_m \nu_{ml}$ and $c_t = \lambda_m \nu_{mt}$. This.

$$\nu_{ml} = c_l\left(\frac{3N}{4\pi V}\right)^{1/3} \text{ and } \nu_{mt} = c_t\left(\frac{3N}{4\pi V}\right)^{1/3}$$

Now we must integrate eqn. (2) § 9.3 upto $\nu_{ml}$ and $\nu_{mt}$ for the lontitudinal and transverse waves respectively rather than over a common $\nu_m$ as done by Debye and write eqn. (3) § 9.3 in the form

$$4\pi V\left[\int_0^{\nu_{ml}} \frac{1}{c_l^3}\nu^2 d\nu + \int_0^{\nu_{mt}} \frac{2}{c_t^3}\nu^2 d\nu\right] = 3N$$

It may be easily seen that these Born modifications lead to the following expression for specific heat

$$C_V = R\left[C\left\{\frac{\Theta_l}{T}\right\} + 2D\left\{\frac{\Theta_t}{T}\right\}\right]$$

where $\Theta_l = \frac{h\nu_{ml}}{k}$ and $\Theta_t = \frac{h\nu_{mt}}{k}$.

Here we have not taken into account the variation of velocity with wavelength. Hence even with these modifications, the theory is not applicable to anisotropic solids or crystals where the velocity of elastic waves varies with direction. Born and Karman therefore worked out the case a crystal extending to infinity in all directions and sought to determine the law according to which the natural vibrations are distributed between the separate frequency regions assuming that the atoms interact according to Hooke's law only with their neighbours. It was shown that there will be $3S$ natural vibrations when an elastic wave of given wavelength propagates through the crystal in some definite direction, there being $S$ particles in a unit cell of the crystal. Of these, the first three represent low frequency vibrations identical with the vibrations of an elastic continum and are termed accoustical vibrations of an elastic continuum and are termed accoustical vibrations. The remaining $(3S-3)$ vibrations have frequencies in the optical region and are termed as optical frequencies. The procedure is to represent each of the accoustical vibrations by a Debye spectrum and each of the optical vibrations by Einstein (single-line) spectrum. Thus the expression for specific heat consists of 3 Debye functions and a number of Einstein functions corresponding to $(3S-3)$ monochromatic vibrations. With these assumptions, the specific heat is represented by

$$C_V = R\left[\sum_{S=1}^{3} D\left(\frac{\Theta_S}{T}\right) + \sum_{S=4}^{3S} E\left(\frac{\Theta_S}{T}\right)\right]$$

It is however doubtful whether Born's procedure of separating Debye and Einstein function is justified for all ionic and molecular crystals. *Blackman* has extended Born's theory by taking into account the interactions between the closed neighbouring particles on the lattice and also between next nearest nighbouring particles. Forces of a quasi-elastic type were assumed and in calculations the former were taken to be twenty times that of the latter. The vibrational spectrum so obtained shows that the density of normal vibrations varies as $\nu^2$ at low frequency but rises faster than $\nu^2$ as soon as the continuum region is passed. This property of the spectrum ensures that $\frac{C_V}{T^3}$ will increase with an increase in temperature. It means that Debye's characteristic temperature ~~Θ~~ will fall the amount of which will depend upon the particular properties of the spectrum. Thus this theory shows better agreement with observations than Debye's theory.

## SOLVED EXAMPLES

**Ex. 1.** *(i) Calculate Einstein's frequency for copper for which $\theta_E = 230$ K. Given $h = 6{\cdot}6 \times 10^{-34}$ joule-sec; Boltzmann's constant $k = 1{\cdot}37 \times 10^{-23}$ joule/K.*

*(ii) Use result (i) to show that the classical thoery result $C_V = 3R$ should be valid for copper if $T > 230$°C.*

**Solution.** (i) Einstein's frequency $\nu_E$ is given by

$$\frac{h\nu_E}{k} = \theta_E$$

where $h$ is Planck's constant and $k$ is Boltzmann's constant.

We have

$$h = 6{\cdot}6 \times 10^{-34} \text{ joule/sec.}$$
$$k = 1{\cdot}37 \times 10^{-23} \text{ joule/K}$$
$$\theta_E = 230 \text{ K}$$

∴ Einstein's frequency, $$\nu_E = \frac{\theta_E k}{h} = \frac{230 \times 1.37 \times 10^{-23}}{6{\cdot}6 \times 10^{-34}} \text{ sec}^{-1}$$
$$= \mathbf{4{\cdot}79 \times 10^{12} \text{ sec}^{-1}}.$$

(ii) $C_V = 3R$ if $T >> \frac{h\nu}{k}$

$$\frac{h\nu}{k} = \frac{6{\cdot}6 \times 10^{-34} \times 4{\cdot}794 \times 10^{12}}{1{\cdot}37 \times 10^{-23}} = \mathbf{230 \text{ K}}.$$

**Ex. 2.** *(a) For copper $\nu = 2{\cdot}49 \times 10^{12}$ hertz. Calculate the characteristic temperature $\theta_E$.*

*(b) For copper the value $C_V$ is 23·8 joule/mole K while for diamond the value of $C_V$ is only 6·1 joule/mole K (both values are at $T = 300$ K). How do you account for this difference ? Given $h = 6{\cdot}6 \times 10^{-34}$ joule sec., $k = 1{\cdot}38 \times 10^{-23}$ joule/K.* ***(Rajasthan 2000)***

**Solution.** (a) The characteristic temperature $\theta_E$ is given by

$$\theta_E = \frac{h\nu}{k}.$$

Given $h = 6{\cdot}6 \times 10^{-34}$ Joule sec.

$$k = 1{\cdot}38 \times 10^{-23} \text{ joule/K}$$
$$\nu = 2{\cdot}49 \times 10^{12} \text{ hertz}$$
$$\theta_E = \frac{6{\cdot}6 \times 10^{-34} \times 2{\cdot}49 \times 10^{12}}{1{\cdot}38 \times 10^{-23}}$$
$$= \mathbf{119{\cdot}1 \text{ K}}.$$

(b) According to Einstein theory, the specific heat of solid

$$C_V = 3R\left[\frac{e^{\Theta/T}}{(e^{\Theta/T}-1)^2} \cdot \left(\frac{\Theta}{T}\right)^2\right]$$

where $\Theta = \frac{h\nu}{k}$ is called Einstein temperature and $\nu$ is Einstein frequency.

∵ For same temperature $T$, the values of $C_V$ for copper and diamond differ only due to their different values of $\nu$.

**Ex. 3.** *For copper, atomic weight = 63.5, density 8·95 gram cm$^{-3}$ and compressibility $\beta = 7.3 \times 10^{-13}$ cm$^2$ dyne$^{-1}$. Using these data and the universal constant N, k and h, deduce the following :*

*(i) mass m of copper atom.*

*(ii) the interatomic distance 'a' assuming simple cubic lattice.*

*(iii) frequency of vibration $\nu = \frac{1}{2\pi}\sqrt{\left(\frac{3a}{\beta m}\right)}$*

*(iv) Use result (iii) to show that classical theory result $C_V = 3R$ should be valid for copper if $T > 230$ K.*

**Solution.** (i) Mass of copper atom,

$$m = \frac{\text{Atomic weight}}{\text{Avogadro Number}}$$
$$= \frac{63{\cdot}5}{6{\cdot}02 \times 10^{23}} = \mathbf{1{\cdot}05 \times 10^{-22} \text{ g}}.$$

(ii) Interatomic distance, $a = \left(\frac{nA}{N\rho}\right)$

Here $n$ = lattice points per unit cell = 1 for simple cubic lattice

$A$ = atomic weight = 63·5

$N =$ Avogadro number $= 6{\cdot}02 \times 10^{23}$

$\rho =$ density of copper $= 8{\cdot}95\ \text{g cm}^{-3}$

$$\therefore \qquad a = \left( \frac{1 \times 63{\cdot}5}{6{\cdot}02 \times 10^{23} \times 8{\cdot}95} \right)^{1/2}$$

$$\log a = \frac{1}{3}[\log 63{\cdot}5 - \log 6{\cdot}02 - 23 - \log 8{\cdot}95]$$

$$= \frac{1}{3}[1{\cdot}8028 - 0{\cdot}7796 - 23 - 0{\cdot}9513]$$

$$= \bar{8}{\cdot}3572$$

$$\therefore \qquad a = 2{\cdot}281 \times 10^{-8}\ \text{cm} = \mathbf{2{\cdot}281\ Å}$$

(iii) $\nu = \dfrac{1}{2\pi} \sqrt{\left( \dfrac{3a}{\beta m} \right)}$

$$= \frac{1}{2 \times 3{\cdot}14} \sqrt{\left( \frac{3 \times 2{\cdot}281 \times 10^{-8}}{7{\cdot}3 \times 10^{-13} \times 1{\cdot}05 \times 10^{-22}} \right)}$$

$$\log \nu = -\log 2 - 3{\cdot}14 + \frac{1}{2}[\log 3 + \log 2{\cdot}81 - 8 - \log 7{\cdot}3 - 13 - \log 1{\cdot}05 + 22]$$

$$= -0{\cdot}3010 - 0{\cdot}4969 + \frac{1}{2}[0{\cdot}4771 + 0{\cdot}3581 - 8{\cdot}9633 + 13 - 0{\cdot}0212 + 22]$$

$$= 12{\cdot}6774$$

$$\nu = \mathbf{4{\cdot}757 \times 10^{12}\ cycles/sec.}$$

(iv) According to Einstein's theory of atomic heat $C_V$ approaches the value $3R$ if $\dfrac{h\nu}{kT} << 1$, *i.e.* if, $\dfrac{h\nu}{k} < T$, *i.e.* if $T > \dfrac{h\nu}{k}$.

Here $$\frac{h\nu}{k} = \frac{(6{\cdot}62 \times 10^{-24}\ \text{joule sec.}) \times (3{\cdot}75 \times 10^{12}\ \text{sec}^{-1})}{1{\cdot}38 \times 10^{-23}\ \text{joule/K}}$$

$$= 230\ \text{K}.$$

Therefore, for copper classical theory result

$$C_V = 3R \text{ is valid if } T > 230\ \text{K}.$$

**Ex. 4.** *The Debye temperature for carbon cyrstallised as diamond is 2230 K. Calculate the heat capacity for diamond at 30 K. Also compute to highest lattice frequency $\nu_m$ involved in Debye theory.*

***(Mumbai 2004)***

**Solution.** Heat capacity of diamond at (low) temperature $T$ kelvin is

$$C_V = \frac{12\pi^4}{15} \cdot (3R) \left( \frac{T}{\Theta_D} \right)^3 = 233{\cdot}8\, R \left( \frac{T}{\Theta_D} \right)^3 = 464{\cdot}4 \left( \frac{T}{\Theta_D} \right)^3$$

where $\Theta_D$ is Debye temperature

Give $T = 30$ K, $\Theta_D = 2230$ K

$$R = 1{\cdot}9856\ \text{cal/g-atom K}$$

$$\therefore \qquad C_V = 233{\cdot}8 \times 1{\cdot}9856 \times \left( \frac{30}{2230} \right)^3$$

---

$$= 464{\cdot}4 \times \left( \frac{30}{2230} \right)^3 = 464{\cdot}4 \times (1{\cdot}345 \times 10^{-2})^3$$

$$= 464{\cdot}4 \times 2{\cdot}433 \times 10^{-6} = 1{\cdot}13 \times 10^{-3}\ \text{cal/g-atom K}$$

$$\Rightarrow \qquad \mathbf{C_V = 1{\cdot}13 \times 10^{-3}\ cal/g\text{-}atom\ K}$$

Debye temperature $\Theta_D = \dfrac{h\nu_m}{k}$

$\therefore$ Highest lattice frequency $\nu_m = \dfrac{k}{h}\Theta_D$

$$= \left( \frac{1{\cdot}38 \times 10^{-23}\ \text{J/K}}{6{\cdot}63 \times 10^{-34}\ \text{J-s}} \right) \times (2230\ \text{K})$$

$$= \mathbf{4{\cdot}64 \times 10^{13}\ Hz.}$$

**Ex. 5.** *The specific heat c of a certain substance at very low temperature is found to depend on the absolute temperature T according to the relation $c = AT^3$, where A is a constant.*

*(i) If units are calories, gram and kelvin what units must the constant A have ?*

*(ii) How much heat must be added to raise the temperature of a mass m of the material from $T_1$ to $T_2$ ?*

***(Purvanchal 2002)***

**Solution.** (i) Given $c = AT^3$.

$$\therefore \qquad A = \frac{c}{T^3}.$$

The unit of specific heat $c$ is cal. per g. per kelvin and that of $T$ is kelvin. So unit of $A$ is

$$\frac{\text{cal. per g per kelvin}}{(\text{kelvin})^3} = \text{cal per g per (kelvin)}^{-4}$$

$$\text{or} \qquad \mathbf{cal\ g^{-1}\ (K)^{-4}} \quad \text{or joule kg}^{-1}\ \text{K}^{-4}$$

(ii) Heat required to raise the temperature of a mass $m$ of the material by $dT = mc\, dT$ : so heat required to raise the temperature of a mass $m$ of the material from $T_1$ to $T_2$

$$= \int_{T_1}^{T_2} mc\, dT = \int_{T_1}^{T_2} mAT^3\, dT$$

$$= mA \left[ \frac{T^4}{4} \right]_{T_1}^{T_2} = \frac{1}{4}\, \mathbf{mA\ (T_2^2 - T_1^4).}$$

## 9.7. Specific Heat of Gases

The classical agrument concerning the specific heat of gases can be interpreted in a very striking way by means of a theorem in statistical mechanics called the theorem of equipartition of energy. According to it, the total energy of a system is equally divided among the different degrees of freedom and the energy corresponding to each degree of freedom per molecule is equal to $\frac{1}{2}kT$, where $k$ is the Boltzmann constant and $T$ the absolute temperature of system. The law, first deduced by Maxwell for translational kinetic energy, was later shown by Boltzmann to be true for the energies of rotation and vibration also. Boltzmann showed that the law of distribution of particles having their motion defined by any set of $p$ and $q$, and contained within the range $q, q+dq$ and $p, p+dp$ is given by

$$f(p,q)\,dp\,dq = Ce^{-E/kT}\,dp\,dq,$$

where $E$ is the energy corresponding to the state of the particles deoted by $p$ and $q$ and is expressed as a quadratic function of $p$'s. This law enables us to calculate the specific heat of gases.

**(1) A monoatomic gas :** In a monoatomic gas, the atoms and molecules are identical and if an atom be assumed to be a structureless point, then each molecule will have three degrees of freedom because its translational motion can take place along any of the three co-ordinate axes in space. Hence $N$ molecules (in a gram molecule of the gas) will have $3N$ degrees of freedom. Considering one gram molecule of the gas, the total energy is given by

$$E = 3N \times \frac{1}{2}kT = \frac{3}{2}NkT = \frac{3}{2}RT.$$

The molar specific heat at constant volume is given by

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}R = 2{\cdot}98 \text{ cal/degree.}$$

For a perfect gas $C_P - C_V = R$ and hence

$$C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R = 4{\cdot}96 \text{ cal/degree}$$

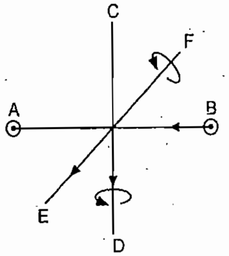
and the ratio of two specific heats is given by

$$\gamma = \frac{C_P}{C_V} = \frac{5}{3} = 1{\cdot}67$$

These theoretical conclusions have been tested for monoatomic gases like argon, helium etc. and are found to be in good agreement with the above results.

The atoms, however, are not structureless points but consist of a positively charged nuclei and shells of electrons. Such a system possesses both rotational motion and internal vibrations. But the vibrations can take place at very high temperatures and can be neglected. The energy of rotational motion of electrons can also be omitted at ordinary temperatures because the whole mass of the atom is concentrated in its nucleus which has a very small radius, thus giving an extremely small moment of inertia $\approx 10^{-47}$ kg-m$^2$.

**(2) A diatomic gas :** The molecule of a diatomic gas may be supposed to consist of two atoms at a certain distance from each other, the atoms being held together by force of attraction, forming a 'dumb bell'. Such a system cannot be stable unless the particles execute a rotatory motion about the common centre of gravity, the force of attraction providing the necessary centripetal force. Thus every diatomic molecule not only moves as a whole; but also rotates about an axis passing through the centre of gravity of the molecules. Taking the simplest possible picture of such a molecule (Fig. 9.4) the moment of inertia about any axis at right angle to $AB$ will be large compared to the moment of inertia about $AB$. Moreover the atoms are supposed to be mass points and hence the moment of inertia about $AB$, the line joining the two atoms, is almost zero and, therefore the rotation about it is not possible. As a result a diatomic molecule possesses three degrees of freedom corresponding to the translation of its centre of gravity and two of rotation about the two axes perpendicular to the line joining the atoms. In all, therefore, each molecule possesses 5 degrees of freedom and $N$ (Avogadro Number) molecules possess $5N$ degrees of freedom. In additional to them, a diatomic molecule may also have vibrational degrees of freedom but at normal temperatures the vibration of the atom along their axes does not take place and hence it is sufficient to consider only the translational and rotational degrees of freedom. Thus the total energy of a gram mole of a perfect diatomic gas is $E = 5N \times \frac{1}{2}kT = \frac{5}{2}NkT = \frac{5}{2}RT$, and the molar specific heat at constant volume



(Fig. 9.4)

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{5}{2}R = 4{\cdot}90 \text{ cal/degree.}$$

Hence $$C_P = C_V + R = \frac{5}{2}R + R = \frac{7}{2}R$$

and $$\gamma = \frac{C_P}{C_V} = \frac{7}{5} = 1{\cdot}4.$$

This agrees with the experimental values of gases like $H_2$ and $N_2$ etc.

**(3) A polyatomic gas :** The same considerations show that each molecule of a gas, whose molecules contain three or more atoms arranged in space at some fixed distance apart, has three translational degrees of freedom and three rotational *i.e.*, six degrees of freedom in all. Hence

$$E = 6N \times \frac{1}{2}kT = 3RT$$

or $$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R.$$

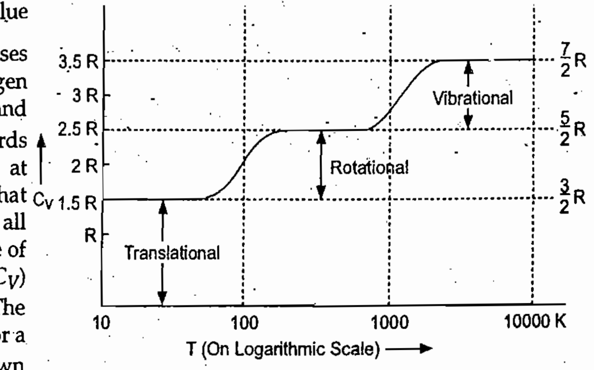
Hence $$C_P = C_V + R = 3R + R = 4R,$$

and $$\gamma = \frac{C_P}{C_V} = \frac{4}{3} = 1{\cdot}33.$$

These results are also supported by experimental evidence.

## 9.8 Variation of Specific Heat of Diatomic Gases with Temperature

It has been observed experimentally that the specific heat of diatomic gases like hydrogen ($H_2$), nitrogen ($N_2$), chlorine ($Cl_2$) and hydrogen chloride (HCl) etc. increases in value as the temperature rises and decreases with fall of temperature, finally approaching the limiting value of $\frac{3}{2}R$ ($= 2{\cdot}98$ calories) which is the value of specific heat of monoatomic gases at all temperatures. Thus for oxygen $C_V$ is 5·17 at 300°C, 5·5 at 500°C and 6·95 at 2000°C while it ends towards the limiting value of 2·98 cals. at about 40 K. We can thus conclude that at sufficiently low temperatures all diatomic gases have the same value of specific heat at constant volume ($C_V$) as that of the monoatomic gas. The variation of $C_V$ with temperature for a diatomic gas like $H_2$ has been shown in fig. 9.5



(Fig. 9.5)

An explanation for the variation of specific heat of diatomic gases can be given on the basis of classical theory. As pointed out in the last section, the diatomic molecules may, in general, have three types of motion–translation, rotation and vibration of its atoms with respect to each other. If these motions are independent of each other, the total energy of a gram molecule of a gas is the sum of three kinds of energies of individual molecules. The total energy of gram-molecule at temperature $T$ should be given by

$$E=E_t+E_r+E_v,$$

where $E_t, E_r$ and $E_v$ represent respectively the energy due to translational, rotational and vibrational motions of the molecule. In consequence, the specific heat of the gas will be due to the obtained contribution of all these energies,

*i.e.,*
$$C_V=C_t+C_r+C_v,$$

where $C_t, C_r$ and $C_v$ represent the contributions from translational, rotational and vibrational motion respectively.

At very low temperatures, the total energy of the molecules is very small and is less than the minimum energy required to set up the rotational and vibrational motion. Hence the specific heat is only due to translational motion

*i.e.,*
$$C_V=C_t=\frac{3}{2}R.$$

Consequently at very low temperatures the specific heat for all diatomic gases is equal to $\frac{3}{2}R=2{\cdot}98$ cals. It is the lowest value of specific heat for any gas

As the temperature is increased slightly, rotational motion develops progressively molecule, after molecule. As a result, the specific heat increases gradully to the value $C_t+C_r$. The rotational motion of the diatomic molecule, as pointed out in the last section, has two degrees of freedom since the two atoms rotate about a pair of axis at right angles to each other and ot the line joining the atoms. Thus the kinetic energy of rotational motion of one gram molecule is given by

$$E_r=N\times 2\times\frac{1}{2}kT=nkT=RT.$$

$$\therefore\quad C_r=\frac{dE_r}{dT}=R.$$

Hence, at low temperature, the specific heat at constant volume

$$C_V=C_t+C_r=\frac{3}{2}R+R=\frac{5}{2}R=4{\cdot}96\ \text{cal/kelvin}.$$

The specific heat remains constant at this value until, due the further rise in temperature, the oscillations of atoms also start. The atoms of the diatomic gases then vibrate with respect to each other. Assuming the motion to be simple harmonic, the energy is represented by two squared terms, *viz.,*

$$\frac{1}{2}m\dot{x}^2+\frac{1}{2}Kx^2,$$

where $K$ is the force constant.

Here the first term represents the kinetic energy and the second the potential energy. But in simple harmonic motion, average potential energy is equal to the average kinetic energy, *i.e.,* the mean total energy associated with this vibrational degree of freedom is

$$\frac{1}{2}kT+\frac{1}{2}kT=kT.$$

Thus the total energy associated with vibrational motion of 1 gram mole.

$$=NkT=RT.$$

Therefore the total energy associated with 1 gram mole of the gas is given by

$$E=E_t+E_r+E_v=\frac{3}{2}RT+RT+RT=\frac{7}{2}RT.$$

So, the specific heat per gram molecule is given by

$$C_V=\frac{dE}{dT}=\frac{7}{2}R=6{\cdot}95\ \text{cal/K}.$$

Thus at sufficiently high temperatures, the specific heat of diatomic gases finally approaches the constant value of $\frac{7}{2}R$. But this simple theory does not explain the specific heats of gases at all temperatures Moreover, it could not predict the experimentally observed variation of specific heat of gases like $Cl_2, Br_2, I_2$ etc.

Hence attempts were made to improve it and quantum theory was applied to the problem.

## 9.9 Quantization of Rotational Motion and Its Contribution to Specific Heats :

Translational kinetic energy of a molecule may vary continuosly, *i.e.,* it may change from zero to a value slighty greater than zero. Such is not the case with the rotational energy. Experimental observations depict that the rotational energy of a diatomic molecules is limited to a discrete set of values, say 0: $E_1, E_2, E_3$, etc. It has been explained theoretically on the basis of quantum theory.

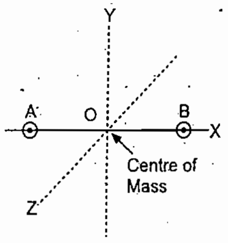
On quantum considerations it can be shown that the diatomic molecules possess only discrete values of energies due to rotation. In a diatomic molecule the rotation energy is quite significant because moment of inertia of a diatomic molecule arrangement is substantial.

A diatomic molecule can rotate about an axis passing through the common centre of mass of the two atoms. Confining ourselves first to the case when the molecule is supposed to have only one degree of rotation, we have for the rotational energy of the molecule $E_r=\frac{1}{2}Iw^2$, and since the angular momentum $J$ is given by $I=Jw$, we have

$$E_r=\frac{J^2}{2I}.$$

Now any rotation of such a molecule ($AB$) can be resolved in three mutually perpendicular directions, *viz.,* $OX$, $OY$ and $OZ$ (fig. 9.6). Here we have considered the centre of mass as the origin of the co-ordinate axes and the line joining the two masses as the $X$ – axis. If $I_x, I_y$ and $I_z$ be the moments of inertia of the molecule about $X, Y$ and $Z$ – axes respectively and $J_x, J_y$ and $J_z$ the corresponding angular momenta, than the rotation energy of the molecule is given by

$$E_r=\frac{J_x^2}{2I_x}+\frac{J_y^2}{2I_y}+\frac{J_z^2}{2I_z}$$



(Fig. 9.6)

According to quantum theory $J^2$ cannot have all possible values it can have discrete values given by

$$J^2=j(j+1)\frac{h^2}{4\pi^2},$$

where the rotational quantum number $j$ can take up all integral values including zero, *i.e.,* $j=0, 1, 2, 3, \ldots$

Now, from fig. 9.6 it may seen that $I_y = I_z = I$ (say) due to symmetry and also $I_x \ll I$ since the size of the nucleus at which mass of atomic remains concentrated is very small compared to interatomic distance. Hence we may put

$$J^2 = J_y^2 + J_z^2 = \frac{j(j+1)h^2}{4\pi^2}$$

$$\therefore \quad E_r = \frac{J_y^2}{2I} + \frac{J_z^2}{2I} = \left(\frac{J_y^2 + J_z^2}{2I}\right) = \frac{j(j+1)h^2}{2I \cdot 4\pi^2}$$

$$= \frac{h^2}{8\pi^2 I} j(j+1) = \frac{\hbar^2}{2I} j(j+1), \qquad \text{where } \hbar = \frac{h}{2\pi}$$

$$= Bhcj(j+1), \qquad \ldots(1)$$

where $B = \frac{h}{8\pi^2 Ic}$ cm$^{-1}$ is called the *rotational constant* and is characteristic of molecule.

Thus, an assembly of diatomic molecules can be partitioned regarding their rotational motion into a a number of quantized states possessing the discrete energy values $Bhc\, j(j+1)$. The possible rotational energies of the molecules are given by successive integral values of $j$ from one onwards. Thus the smallest value apart from zero that $E_r$ can assume is

$$(E_r)_{\min} = Bhc . 1 (1+1) = 2Bhc = \frac{h^2}{4\pi^2 I}$$

which is inversely proportional to the moment of inertia of the molecule. For a monoatomic gas atom, it is extremely small and hence the minimum rotational energy is very high. As a result the *monoatomic gases can not be set into rotation.*

Let us consider the case of hydrogen molecule. For it, moment of inertia $I = 4{\cdot}67 \times 10^{-36}$ kg-m$^2$ and hence

$$(E_r)_{\min} = \frac{h^2}{4\pi^2 I} \approx 2 \times 10^{-21} \text{ joule}$$

The energy of translation of a gas molecule at temperature $T$ is given by

$$E_t = \frac{3}{2} kT \approx 2 \times 10^{-23} \text{ joule}$$

If may clearly thue seen that below 60K, the mean energy of translation of a hydrogen molecule is small compared with the minimum rotational energy value above zero that the molecule can possess. Consequently below 60K only a very small fraction of the molecules will possess any rotational energy and hence the *gas will behave as if it were monoatomic.*

Now the number $N_j$ of molecules in the $j^{th}$ rotational state can be found from a generalization of Maxwell's distribution law.

Thus $$N_j = N_0 (2j+1) \exp\{-j(j+1) Bhc/kT\}, \qquad \ldots(2)$$

where $(2j+1)$ the number of states (called the *eigen states*) corresponding to the same energy.

Hence $(2j+1)$ is the degeneracy factor to the *weight factor* of the $j^{th}$ state.

It follows from eqn. (2) that excitation of rotational states entirely depends upon the values of $B$ and $T$. If $T$ is very small $N_j$ will have very small value, *i.e.*, at extremely low temperatures, practically no excitation is possible. Comparing the case of two gases $H_2$ and $N_2$, it will be seen that excitation of rotational motion in $H_2$ is much more difficult than in $N_2$ because the rotational constant $B$ (which is inversely proportional to $I$) is large in the case of $H_2$.

Substituting eqn. (1) eqn. (2), we get

$$N_j = N_0 (2j+1) \exp(-E_r/kT). \qquad \ldots(3)$$

Hence the average rotational energy of the molecule is given by

$$\overline{E} = \frac{\Sigma E_r (2j+1) \exp(-E_r/kT).}{\Sigma (2j+1) \exp(-E_r/kT)} \qquad \ldots(4)$$

At very low temperatures, the Boltzmann's factor exp. $(-E_r/kT)$ for the lowest state $(j=0)$ is equal to zero. Hence specific heat

$$C_r = N \frac{d\overline{E}_r}{dT} = N \frac{d}{dT} \frac{\Sigma E_r (2j+1) \exp(-E_r/kT)}{\Sigma (2j+1) \exp(-E_r/kT)}$$

$$= N \frac{d}{kT}(E_0) = 0 \text{ since } E_0 \text{ is independent of temperature.}$$

Now to find $\boldsymbol{E_r}$ and $C_r$ we introduce a new function $F_r$, known as the *rotational partition function* and defined by the relation

$$F_r = \Sigma (2j+1) \exp(-E_r/kT). \qquad \ldots(5)$$

Then $$\frac{dF_r}{dT} = \frac{E_r}{kT^2} \Sigma (2j+1) \exp(-E_r/kT).$$

Hence from (4), we get

$$\overline{E}_r = kT^2 \frac{d}{dT}(\log F_r).$$

Therefore specific heat due to rotational motion is

$$C_r = N \frac{d}{dT}(\overline{E}_r) = Nk \frac{d}{dT}\left[T^2 \frac{d}{dT}(\log F_r)\right]$$

$$= R \frac{d}{dT}\left[T^2 \frac{d}{dT}(\log F_r)\right\} \qquad \ldots(6)$$

If we now introduce a rotational temperature $\Theta_r = \frac{h}{4\pi^2 Ik}$ the value of $F_r$ can be eveluated. We have

$$F_r = \Sigma (2j+1) \exp(-E_r/kT)$$

$$= \sum_{j=1}^{\infty} (2j+1) \exp\{-j(j+1)\hbar^2/2IkT\}$$

where $$E_r = \frac{\hbar^2}{2I} j(j+1)$$

Introducing a quantity $\mu = \frac{\hbar^2}{2IkT}$

$$F_r = \sum_j (2j+1) \exp\{-j(j+1)\mu\}$$
$$= \sum_j 2\left(j+\frac{1}{2}\right) \exp\{[-(j+\frac{1}{2})^2 - \frac{1}{4}]\mu\}$$
$$= e^{\mu/4} \sum_j 2\left(j+\frac{1}{2}\right) \exp\{-(j+\frac{1}{2})^2 \mu\}.$$

*At high temperatures* μ is small and the summation can be replaced by integration.

$$\therefore \qquad F_r = 2e^{\mu/4} \int_0^\infty \left(j+\frac{1}{2}\right) \exp\{-(j+\frac{1}{2})^2 \mu\} dj.$$

If we substitute $(j+\frac{1}{2}) = x$ so that $dj = dx$, we get

$$F_r = 2e^{\mu/4} \int_{1/2}^\infty x e^{-x^2 \mu} dx \approx 2e^{\mu/4} \int_0^\infty x e^{-\mu x^2} dx.$$

Here we have replaced limit $\frac{1}{2}$ by zero because integral represents the area under the curve defined by the function between the two limits ; the area bounded from $\frac{1}{2}$ to ∞ is approximately equal to area bounded from 0 to ∞.

Now $\int_0^\infty x e^{-\mu x^2} dx$ is a standard integral whose value is $\frac{1}{2\mu}$

Hence

$$F_r = 2e^{\mu/4} \frac{1}{2\mu} = \frac{e^{\mu/4}}{\mu},$$

and since we are considering higher temperature of smaller μ,

$$e^{\mu/4} \approx 1$$

$$\therefore \qquad F_r \approx \frac{1}{\mu} \approx \frac{2IkT}{\hbar^2} = \frac{kT}{h} \cdot \frac{8\pi^2 I}{h} = \frac{kT}{Bh}$$

and then substitution of $F = \frac{kT}{Bh}$ in eqn. (6) gives

$$C_r = R \frac{d}{dT}\left[T^2 \frac{d}{dT}\left\{\log\left(\frac{kT}{Bh}\right)\right\}\right]$$
$$= R \frac{d}{dT}\left[T^2 \times \frac{Bh}{kT} \times \frac{k}{Bh}\right] = R \frac{d}{dT}(T)$$
$$\Rightarrow \qquad C_r = R.$$

Thus that high temperatures, $C_r$ is approximately equal to the classical value. It can be calculated from (6) that at intermediate temperatures the specific heat due to rotational motion lies between 0 and *R*.

## 9.10. Quantization of Vibrational Motion and its Contribution to Specific Heats :

At higher temperatures, the vibrational motion is also excited in addition to the rotational motion. The actual motion is rather complicated but it may be imagined that the motion is simple harmonic.

As the two constituent atoms tend to move away from each other, restoring forces come into operation. These forces can be supposed to be proportional to the small increase '*x*' in the distance between the atoms over the equilibrium distance $r_0$. Then the equation of motion of the atom of mass $m_1$ distant $r_1$ from the centre of gravity is

$$m_1 \frac{d^2 r_1}{dt^2} = -Kx.$$

Similarly for the other atom of mass $m_2$, distant *r* from the centre of gravity, the equation of motion is

$$m_2 \frac{d^2 r_2}{dt^2} = -Kx.$$

Now if $r = r_1 + r_2$, we get

$$\frac{d^2 r}{dt^2} = \frac{d^2 r_1}{dt^2} + \frac{d^2 r_2}{dt^2}$$
$$= -\frac{Kx}{m_1} - \frac{Kx}{m_2} = -Kx\left(\frac{1}{m_1} + \frac{1}{m_2}\right) = -\frac{K}{m} x,$$

where *m* is the reduced mass. Thus we get for simple harmonie motion

$$m \frac{d^2 r}{dt^2} + Kx = 0$$

The solution of this equation is

$$x = A \cos 2\pi\nu t \qquad \ldots(1)$$

where *A* is the amplitude and ν the frequency of the simple harmonic motion given by the relation

$$\nu = \frac{1}{2\pi}\sqrt{\left(\frac{K}{m}\right)} \text{ or } 4\pi^2\nu^2 = \frac{K}{m}$$

Now in a simple harmonic motion, the energy is represented by two squared terms, *viz.*

$$\varepsilon_\nu = \frac{1}{2} m \left(\frac{dx}{dt}\right)^2 + \frac{1}{2} Kx^2$$

where first term represents the kinetic energy and the second term the potential energy. Substituting the value of *x* and *dx/dt* from eqn. (1) and $K = 4\pi\nu^2 m$, we get

$$\varepsilon_v = \frac{1}{2} m (4\pi^2\nu^2 A^2 \sin^2 2\pi\nu t) + \frac{1}{2} \cdot 4\pi\nu^2 m.\ A^2 \cos^2 2\pi\nu t$$

or

$$\varepsilon_v = 2\pi^2\nu^2 m A^2. \qquad \ldots(2)$$

According to quantum mechanics, this energy due to vibrational motion is also limited to a series of discrete values, like the rotational energy. The values of unknown amplitude *A* of equation (2) can be obtained from the Sommerfeld quantum-condition

$$\oint p_x \, dx = vh \qquad \ldots(3)$$

where *v* is an integer known as vibrational quantum number and the integration extends over a period. Now

$$\oint p_x\,dx = \oint m\frac{dx}{dt}.\,dt$$

$$= \oint m\,(-2\pi\nu A \sin 2\pi\nu t)\,(-2\pi\nu A) \times \sin 2\pi\nu t\,dt) \quad \text{using (1)}$$

$$= \oint m.\,4\pi^2\nu^2 A^2.\,\sin^2 2\pi\nu t\,dt$$

$$= 2\pi^2\nu^2 A^2 m \int_0^T [1-\cos 4\pi\nu t]\,dt$$

$$= 2\pi^2\nu^2 A^2 m\,[T-0] = 2\pi^2\nu^2 A^2 m.\,(1/\nu)$$

$$\Rightarrow \qquad \oint p_x\,dx = 2\pi^2\nu\,mA^2$$

Hence from equation (3), we get

$$2\pi^2\nu\,mA^2 = vh$$

$$A^2 = \frac{vh}{2\pi^2\nu\,m},$$

Therefore the energy due to vibrational motion is obtained from (2) as

$$\varepsilon_v = 2\pi^2\nu\,m.\frac{vh}{2\pi^2\nu\,m} = vh\nu. \qquad \ldots(4)$$

According to it, $\varepsilon_v$ can have any value continuously from zero to infinity. But this expression was found to be in error. Quantum mechanical analysis showed that

$$\varepsilon_v = (v+\tfrac{1}{2})\,h\nu \qquad \ldots(5)$$

where $v$ has any integral value 0, 1, 2,...etc.

The oscillators can therefore possess the quantized energies

$$\tfrac{1}{2}h\nu,\ (1+\tfrac{1}{2})\,h\nu,\ (2+\tfrac{1}{2})\,h\nu, \ldots\ldots (v+\tfrac{1}{2})\,h\nu$$

*i.e.,* $$\tfrac{1}{2}h\nu,\ \tfrac{3}{2}h\nu,\ \tfrac{5}{2}h\nu, \ldots\ldots (v+\tfrac{1}{2})\,h\nu.$$

Then according to quantum theory the vibrational energies levels of an oscillator are separated by equal steps $h\nu$. The important feature of quantum theory is that the minimum vibrational energy of an oscillator is not zero but $\frac{1}{2}h\nu$.

Let us now calculate the total energy due to oscillations (or vibrations). Let $N_v$ be the number of oscillators with energies $\frac{1}{2}h\nu$ (zero point energy), $N_v$ the number with the energy $(v+\frac{1}{2})\,h\nu$. Then from Maxwell-Boltzmann Law.

$$N_v = N_0 \exp\,(-vh\nu/kT). \qquad \ldots(6)$$

The weight factor or degeneracy factor is unity as each corresponds to a distinct energy depending upon the value of $r$ itself.

The total energy due to vibrational motion is given by

$$E_v = \sum_v N_v \varepsilon_v$$

$$= \sum_v N_v\,(v+\tfrac{1}{2})h\nu$$

$$= \frac{1}{2}N\,h\nu + N_0 \sum_{\nu}^{\infty} vh\nu \exp\{-vh\nu/kT\} \qquad \ldots(7)$$

where $\sum_v N_v = N$ is the total number of oscillators.

Let us now introduce the function $F_v$ called the *partition function for harmonic oscillators*, such that

$$F_v = \sum_{v=0}^{\infty} e^{-vh\nu/kT} = 1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \ldots$$

$$= \frac{1}{1-e^{-h\nu/kT}}. \qquad \ldots(8)$$

Hence $N = \Sigma N_v = \Sigma N_0\,e^{-vh\nu/kT}$ using (6)

$$\Rightarrow \qquad N = N_0 F_v. \qquad \ldots(9)$$

Now putting $\frac{h\nu}{kT} = x$, we have

$$F_v = \Sigma e^{-vx},\ \frac{\partial F_v}{\partial x} = -\Sigma v\,e^{-vx}$$

Hence from (7), we get for the energy due to oscillations

$$E_v = \frac{1}{2}Nh\nu - N_0 h\nu\frac{\partial F_v}{\partial x}$$

$$= \frac{1}{2}Nh\nu - \frac{N_0 h\nu F_v}{F_v}\frac{\partial F_v}{\partial x}$$

or $$E_v = \frac{1}{2}Nh\nu - h\nu N\frac{\partial}{\partial x}(\log F_v). \qquad \text{using (9)}$$

Therefore the contribution of vibrational motion to specific heat is given by

$$C_v = \frac{dE_v}{dT} = -Nh\nu\frac{\partial}{\partial T}\left\{\frac{\partial}{\partial x}(\log F_v)\right\}$$

$$= -Nh\nu\frac{\partial}{\partial x}\left\{\frac{\partial}{\partial x}(\log F_v)\right\}\frac{dx}{dT}$$

$$\Rightarrow \qquad C_V = -Nh\nu\frac{\partial^2}{\partial x^2}(\log F_v)\frac{dx}{dT}. \qquad \ldots(10)$$

But since $x = \frac{h\nu}{kT}$

$$\frac{dx}{dT} = -\frac{h\nu}{kT^2} = -\frac{h\nu}{k}\left(\frac{kx}{h\nu}\right)^2 = -\frac{kx^2}{h\nu}$$

With this substitution equation (10) becomes

$$C_v = Nkx^2\frac{\partial^2}{\partial x^2}(\log F_v)$$

$$= Rx^2 \frac{\partial^2}{\partial x^2}(\log F_v)$$

$$= Rx^3 \frac{\partial}{\partial x}\left(\frac{1}{F_v}\frac{\partial F_v}{\partial x}\right)$$

$$= \frac{Rx^2 e^x}{(e^x-1)^2} \qquad \text{using (8)}$$

$$= R \cdot \frac{\left(\frac{h\nu}{kT}\right)^2 e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2} \qquad \ldots(11)$$

*At very high temperatures* $\frac{h\nu}{kT}$ approaches zero and $e^{h\nu/kT}$ one.

Hence

$$C_v = R \frac{\left(\frac{h\nu}{kT}\right)^2 e^0}{\left[1+\frac{h\nu}{kT}+\frac{1}{2!}\left(\frac{h\nu}{kT}\right)^2+\ldots-1\right]^2}$$

$$= R \frac{\left(\frac{h\nu}{kT}\right)^2}{\left(\frac{h\nu}{kT}\right)^2\left[1+\frac{1}{2!}\frac{h\nu}{kT}+\ldots\right]}$$

$= R$. Neglecting higher terms in the denominator.

This at very large values of $T$, $C_v$ is approximately equal to the classical value.

## 9.11 Calculation of Specific Heat of Diatomic Gases :

As already pointed out, the specific heat of diatomic gases is composed of a rotational part plus a vibrational part. In all the diatomic gases which do not contain hydrogen, the rotational degrees of freedom are completely excited even at very low temperatures *i.e.*, $C_r = R$. It is therefore sufficient only to consider the contribution of vibrational motion. The value of $C_V$ can be calculated from formula (11) of the last section. Thus the specific heat of a diatomic gas is given by

$$C_V = C_t + C_r + C_v$$

$$= \frac{3}{2}R + R + R\frac{x^2 e^x}{(e^x-1)^2}$$

$$= \frac{5}{2}R + R\frac{x^2 e^x}{(e^x-1)^2} \qquad \text{where } x = \frac{h\nu}{kT}$$

The values of specific heat of diatomic gases like $Cl_2$, $Br_2$, $I_2$, HCl etc. as calculated from above formula are in good agreement with experimental facts. At ordinary temperatures, the molecules of hydrogen, oxygen, nitric oxide, hydrogen chloride etc., in which the atoms are firmly bound, are almost in the lowest vibrational level. As a result they have no vibrational energy relative to the zero point value and hence behave as if they were rigid. As the temperature is increased, these molecules commence to occupy higher vibrational levels and contribute to the specific heat. In $Cl_2$, $Br_2$ and $I_2$, on the other hand, the vibratory motion is excited even at room temperature. Thus for these, a large number of molecules have appreciable vibrational energy in excess of the zero point energy value even at normal temperatures and hence their $C_V$ is found to be larger than $\frac{5}{2}R$ even at room temperature.

In order to illustrate the use quantum theory, let us consider the case of chlorine. For chlorine the second vibrational state ($v = 1$) lies; $5{\cdot}65 \times 10^4$ m$^{-1}$ above the first ($v = 0$). The difference in energy between these two states is thus

$$\varepsilon_1 - \varepsilon_2 = h\nu = h\frac{c}{\lambda}$$

$$= 6{\cdot}6 \times 10^{-34} \times 5{\cdot}65 \times 10^4 \times 3 \times 10^8 = 1{\cdot}11 \times 10^{-20} \text{ joule.}$$

Now since $k = 1{\cdot}38 \times 10^{-23}$ J/K; at 15°C (288K), the ratio of the Boltzmann factor for the two states is

$$e^{-(\varepsilon_1-\varepsilon_2)/kT} = e^{-1{\cdot}11\times10^{-20}/1{\cdot}38\times10^{-23}\times288}$$

$$= e^{-2{\cdot}30} = 0{\cdot}061.$$

Thus the number of molecules in the second vibrational state is 0·061 times that in the first. If we assume that the fraction $e^{-(\varepsilon_1-\varepsilon_0)/kT}$ of all the the molecules are in the second state, the excess vibrational energy due to this cause in a gram molecule of gas containing $N$ molecules is equal to

$$N(\varepsilon_1-\varepsilon_0)\,e^{-(\varepsilon_1-\varepsilon_0)/kT}$$

and hence the contribution of the excess energy of the molecular heat is

$$\frac{d}{dT}\left[N(\varepsilon_1-\varepsilon_0)\,e^{-(\varepsilon_1-\varepsilon_0)/kT}\right]$$

$$= N\frac{(\varepsilon_1-\varepsilon_0)^2}{kT^2}e^{-(\varepsilon_1-\varepsilon_0)/kT} = Nk\left(\frac{\varepsilon_1-\varepsilon_0}{kT}\right)^2 e^{-(\varepsilon_1-\varepsilon_0)/kT}$$

$$= 0{\cdot}47\,R \qquad (\because Nk = R).$$

Adding the usual $\frac{3}{2}R$ for a diatomic molecule, we have

$$C_V = \frac{3}{2}R + 0{\cdot}47\,R = 2{\cdot}97\,R$$

$$= 5{\cdot}88 \text{ calories/mole degree.}$$

This is in fair agreement with the observed value of 6·02.

Thus quantum theory succeeds where clasical theory fails

When a similar calculation is made for HCl for which the wave number, $\bar{\nu} = 2886$ cm$^{-1}$, we get

$$\varepsilon_1 - \varepsilon_0 = h\nu = h\frac{c}{\lambda} = 6{\cdot}6 \times 10^{-34} \times 2886 \times 10^2 \times 3 \times 10^8.$$

$$= 5{\cdot}72 \times 10^{-23} \text{ joule}$$

The ratio of Boltzmann factor in this case

$$e^{-(\varepsilon_1-\varepsilon_0)/kT} = 5 \times 10^{-2}.$$

Thus molecular vibration can contribute nothing appreciable to the specific heat of HCl is agreement with the observed fact that for it $C_V = \frac{5}{2} R$ very nearly. For $O_2$, the wave number is 1565 cm$^{-1}$ and vibration may contribute about 3·026 $R$ to $C_r$. For gases such as $N_2\, (\bar{\nu} = 2345 \text{cm}^{-1})$ and $H_2\, (\bar{\nu} = 4433 \text{ cm}^{-1})$ the second vibrational state is far above the first and hence molecular vibrations can make no contribution to the specific heat.

## SOLVED EXAMPLES

**Ex 6.** *Supoose that the molecules of an ideal diatomic gas are rigid, but free to rotate about either of two mutually perpendicular axes, these axes being at right angles to the line joining the two atoms of the molecule. Find $c_v$, $c_p$ and $\gamma$ for such a gas and compare with the experimental value of $\gamma$ for diatomic gases.*

**Solution :** If the molecules of a diatomic gas are rigid, there exist only five degrees of freedom, three of translation and two of rotation. The kinetic energy per degree of freedom according to equipartitional principle of energy, is equal to $\frac{1}{2} k\, T$.

Therefore the kinetic energy associated with five degrees of freedom $= \frac{5}{2} k\, T$.

Thus kinetic energy per molecule $= \frac{5}{2} k\, T$

and kinetic energy per gram mole $= \frac{5}{2} N k\, T$ or $E = \frac{5}{2} RT$.

Hence the specific heat is given by

$$C_V = \frac{dE}{dT} = \frac{5}{2} R$$

and

$$C_P = C_V + R = \frac{7}{2} R$$

$\therefore$

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{7}{2} R}{\frac{5}{2} R} = \frac{7}{5} = \mathbf{1{\cdot}40}.$$

The experimentally observed value of $\gamma$ at 15°C are given in the following table :

| Gas | Value of $\gamma$ |
|---|---|
| Hydrogen ($H_2$) | 1·41 |
| Nitrogen ($N_2$) | 1·404 |
| Oxygen ($O_2$) | 1·401 |
| Carbon-mono-oxide (CO) | 1·404 |
| Hydrogen Chloride (HCl) | 1·41 |

The above values of $\gamma$ are in excellent agreement with the theoretical values.

**Ex 7.** *Calculate in terms of kT the vibrational contribution of energy of 1 gram mole. of hydrogen at a temperature at which $\frac{h\nu}{kT} = 2$. Given vibrational constant $\bar{\nu} = 4400$ cm$^{-1}$. Calculate this temperature. Given Auogadro number $N = 6{\cdot}0 \times 10^{23}$ per g-mole and $e = 2{\cdot}7183$, $h = 6{\cdot}6 \times 10^{-34}$ joule-sec., $k = 1{\cdot}38 \times 10^{-23}$ joule/K.*

**Solution :** The vibrational contribution to energy of 1 molecule of hydrogen is given by

$$\bar{\varepsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} = \frac{h\nu/kT}{e^{h\nu/kT} - 1} .\, kT$$

$\therefore$ The vibrational contribution to energy of 1 gram mole of hydrogen is

$$E_v = N . \frac{h\nu/kT}{e^{h\nu/kT} - 1} .\, kT \text{ where } N \text{ is Avogadro number.}$$

Given

$$\frac{h\nu}{kT} = 2,\ N = 6 \times 10^{23}$$

$\therefore$

$$E = 6 \times 10^{23} \times \frac{2}{e^2 - 1} kT$$

$$= \frac{6 \times 10^{23} \times 2}{(2{\cdot}7183)^2 - 1} kT$$

$$= \frac{6 \times 10^{23} \times 2}{(7{\cdot}406) - 1} kT = \frac{6 \times 10^{23} \times 2}{(6{\cdot}406)} kT$$

$$= \mathbf{1{\cdot}874\ kT.}$$

As $\frac{h\nu}{kT} = 2$.

$$\Rightarrow \quad T = \frac{h\nu}{2k} = \frac{hc\bar{\nu}}{2k}$$

$$= \frac{6{\cdot}6 \times 10^{-34} \times 3 \times 10^8 \times 4400 \times 10^2}{2 \times 1{\cdot}38 \times 10^{-23}}$$

$$= \mathbf{3179\ K.}$$

**Ex. 8.** *A diatomic gas is in thermal equilibrium at temperature 5000 K. Its rotational constant is*

$$B = 2{\cdot}000 \ cm^{-1}.$$

*Compute the relative populations in the rotational states* $j = 3$, $j = 10$ and $j = 20$.

**Solution.** The rotational energy of diatomic molecule is given by

$$\varepsilon_j = Bhc\, j\, (j+1) \text{ where } j = 0, 1, 2 \ldots$$

For the particular diatomic gas for which $B = 2{\cdot}000$ cm$^{-1}$

$$Bhc = (2 \times 10^2\ m^{-1}) \times (6{\cdot}6 \times 10^{-34} \text{ J-s} \times (3 \times 10^8 \text{ m/s}) = 3{\cdot}96 \times 10^{-23} \text{ joule}$$

Hence energy values for the states $j = 0$, 10 and 20 are

$$\varepsilon_0 = Bhc .\ 0\ (0 + 0) = 0$$

$$\varepsilon_{10} = Bhc\ 10\ (10 + 10) = 110 \times 3{\cdot}96 \times 10^{-23}$$

$$= 1{\cdot}356 \times 10^{-21} \text{ joule}$$

and

$$\varepsilon_{20} = Bhc .\ 20 .\ (20 + 1) = 420 \times 3{\cdot}96 \times 10^{-23}$$

$$= 16{\cdot}63 \times 10^{-21} \text{ joule}$$

Now the population factor for *jth* energy level is

$$\frac{N_j}{N_0} = (2j + 1) \exp\, (-\varepsilon_j/kT).$$

We have $T = 500\text{K}$.

$$\therefore \quad kT = 1{\cdot}38 \times 10^{-23} \times 500$$

$$= 6{\cdot}9 \times 10^{-21} \text{ joule}$$

Therefore, the population ratio for $j = 0$,

$$\frac{N_0}{N_0} = (0+1)\, e^{0/kT} = 1,$$

*i.e.*, all the molecules of the diatomic gas are in their zero rotational energy state (also called the ground state) correspouding to $j = 0$.

For $j = 10$, the population ratio is

$$\frac{N_{10}}{N_0} = (20+1) \exp\,(-\varepsilon_{10}/kT) = 21 \exp\left(-\frac{4{\cdot}356 \times 10^{-21}}{6{\cdot}9 \times 10^{-21}}\right)$$

$$= 21 \exp\,(-4{\cdot}356/6{\cdot}9) = 21 \exp\,(-0{\cdot}63)$$

or
$$\log_e \frac{N_{10}}{N_0} = 2{\cdot}3 \log_e 21 - 0{\cdot}63$$

or
$$2{\cdot}3 \log_{10} \frac{N_{10}}{N_0} = 2{\cdot}3 \log_{10} 21 - 0{\cdot}63$$

or
$$\log_{10} \frac{N_{10}}{N_0} = \log_{10} 21 - \frac{0{\cdot}63}{2{\cdot}3} = \log 21 - 0{\cdot}27$$

$$= 1{\cdot}3222 - 0{\cdot}27 = 1{\cdot}0522$$

or
$$\frac{N_{10}}{N_0} = 11{\cdot}28.$$

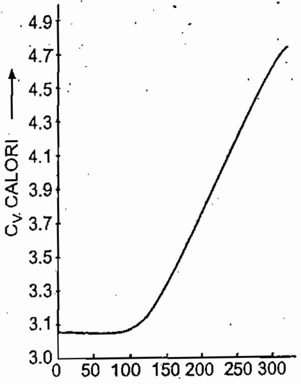
For $j = 20$, the population ratio is

$$\frac{N_{20}}{N_0} = (40+1)\ (-\varepsilon_{20}/kT) = 41 \exp\left(\frac{16{\cdot}63 \times 10^{-21}}{6{\cdot}9 \times 10^{-21}}\right)$$

$$= 41\, e^{-3{\cdot}4} = 3{\cdot}710.$$

## 9.12. Variation of Specific Heat of Hydrogen

Eucken has determined the specific heat at constant volume of hydrogen at low temperatures. He arrived at the result that from 200 K to 500 K, $C_V = \frac{5}{2} R$ very closely but sinks down to $\frac{3}{2} R$ *at about 60 K, i.e., at temperature below about 60K, hydrogen behves as a monoatomic gas.* Since then the investigation has been repeated by many workers and the results are independently confirmed by the work of Scheel and Heuse and by that of Brinkworth. The variation of specific heat curve of hydrogen with temperature has been shown in fig. 9.7 and the values obtained by Eucken at various absolute temperatures in table given below



(Fig. 7.7)

| *Absolute temp. (K)* | $C_V$ *Calories per mole per K* | Absolute temp. (*K*) | $C_V$ *Calories per mole. per K* |
|---|---|---|---|
| 35 | 2·98 | 80 | 3·14 |
| 45 | 3·00 | 100 | 3·42 |
| 60 | 2·99 | 196·5 | 4·39 |

These experimental data of Eucken suggest the possibility that below 20K, the specific heat of hydrogen may fall below $\frac{3}{2} R$ a result generally known as the ***degeneration of gases.***

The general explanation of this variation was originated by Ehrenfest who showed that on account of quantization, the rotational and vibrational specific heats $C_r$ and $C_v$ tend to disappear at low temperatures. Several other attempts were made to explain the observed specific heat values given by Eucken but with no success. In 1927, Hori worked out a rotational analysis of Lyman bands of hydrogen and calculated the value of ratational constant $B \left(= \frac{h}{8\pi^2 Ic}\right)$ to be $59{\cdot}534 \text{ cm}^{-1}$ for the fundamental state of hydrogen from which $I$ and $r$ (interatomic distance) were calculated to be $0{\cdot}47 \times 10^{-47} \text{ kg-m}^2$ and $7{\cdot}6 \times 10^{-11}$ m respectively. Then substituting the value of $B$, the characteristic energy value

$$E = B\, ch\, J\,(J+1),$$

was calculated but it also failed completely to explain the observed $C_r$ (specific heat due to rotation) values.

The explanation came from the analysis of band spectrum of diatomic gas consisting of two identical atoms like $H_2$ and $N_2$. Molecules containing at least two similar nuclei have certain peculiar and sometimes astonishing properties. Thus peculiarity appears in the absence or faintness of alternate lines, *i.e.*, in certain bands from such molecules alternate lines are weaker or perhaps missing entirely. When the two atoms are different as in HCl or unequal in mass, the phenomenon is no longer observed. After the advent of wave mechanics, it was pointed out by Hund that this phenomenon could be explained as an effect of nuclear spin*. As every atom and consequently a diatomic molecule has in general a spin value of $i$ units, there will be a spin degeneracy equal to $(2i+1)$ for every value of $i$. If the two atoms of a diatomic molecule have spin $i$ and $i'$, the spin degeneracy factor or weight factor of the molecule is $(2i+1)\,(2i'+1)$. But if the molecule is homonuclear with two identical nuclei it may have different statistical weight factors. For example, the hydrogen mucleus has been shown experimentally to have a spin of $\frac{1}{2}$, *i.e.*, $i = \frac{1}{2}$. When two atoms of hydrogen combine to form a molecule, two possible combinations of nucleur spin can arise. In one of these, the two spins can be parallel (↑↑); in which case the resultant spin quantum number $I = \frac{1}{2} + \frac{1}{2} = 1$; but in another case, the two spins can be anti-parallel (↓↑) and then $I = \frac{1}{2} - \frac{1}{2} = 0$. Also for each value of the resultant spin $I$, there are $(2I+1)$ orientations possible in a magnetic field, *i.e.*, there is $(2I+1)$ fold degeneracy corresponding to each value of $I$.

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*Nuclei of atoms are composed of protons and neutrons. These particles spins on their own axes and they thus possess angular momentum. The resultant angular momentum for all the protons and neutrons present in a nucleus is called the nuclear spin.

Hence when spins are parallel ($I = 1$), the degeneracy factor is 3 and when the two spins are anti-parallel ($I = 0$) this factor is equal to unity. Thus, the statistical weight of the molecular state of $H_2$ with spin in the same directions is three times as large as that for state in which the axes are parallel but spins in opposite direction. Moreover, the rotational levels with even value of the rotational quantum number $J$ are considered *symmetric* while those with odd values of $J$ as *anti-symmetric*. In hydrogen spectrum, the fairly intense rotational lines correspond to odd values of rotational quantum number $J$, while the fainter lines correspond to even values of $J$.

The levels with even values of $J$ are smaller in number and are the so-called symmetric levels states for a pair of similar nuclei that are symmetric in the nuclear spins have been called *ortho states* while those anti-symmetric in the spins *para state* ('Ortho' means straight or proper *i.e.*, ordinary, para' side by sine, *i.e.*, a variant, the less common variety). Thus ordinary $H_2$ gas consists of two varieties :

**(1) Ortho hydrogen** in which the nuclear spins are parallel and the resultant spin $I$ is equal to unity. The ortho molecules can possess only odd valued rotational quantum number ($J = 1, 3, 5 \ldots$).

**(2) Para hydrogen** in which the nuclear spins are anti-parallel and the resultant spin of the molecules is zero. The para molecules can possess only even valued rotational states including the state of no rotation with $J = 0$, *i.e.*, $j = 0, 2, 4, \ldots$ etc.

These forms of hydrogen exist side by side and possess a similar physical and chemical properties but they differ from each other in their low temperature heat capacities and also in their electronic band spectra. Dennison, therefore, pointed out that *hydrogen must be treated as a mixture of two distinct gases*–para and ortho. At ordinary temperatures the ortho hydrogen molecules are three times as numerous as para hydrogen molecule and their proportion remains the same in the gas *i.e.*, do not change during the experiments on measurement of specific heat.

As already discussed, if the spin value of each nucleus is $\frac{1}{2}$, the resultant spin of diatomic molecule is $2i$ for parallel arrangement and zero for anti-parallel arrangement. Therefore, the set of resultant spin values can be given as

$$2i, 2i-1, 2i-2, \ldots, 2, 1, 0, \text{ i.e., } I = (2i - n),$$

which in general may be expressed as $(2i - n)$; where $n$ is an integer $\hbar = 0, 2, 4, \ldots$ give the first, third and fifth terms etc. corresponding to the *anti-symmetric levels or para states*.

Since the degeneracy factor is $(2i + 1)$, it may now be written as $[2(2i - n) + 1]$ and we can write

$$= \frac{\text{Statistical weight of ortho state}}{\text{Statistical weigth of para state}}$$

$$= \frac{\sum\limits_{n=0,2,4,\ldots} 2(2i-n)+1}{\sum\limits_{n=1,3,5,\ldots} 2(2i-n)+1}$$

$$= \frac{(4i+1)+(4i-3)+(4i-7)+\ldots}{(4i+1)+(4i-5)+(4i-9)+\ldots}$$

$$= \frac{(i+1)(2i+1)}{i(2i+1)} \qquad \ldots(i)$$

$$= \frac{3}{1} \text{ for hydrogen for which } i = \frac{1}{2}.$$

Thus the statistical weight of ortho hydrogen is 3 while that of para is one. Dennison pointed out that the specific heat of hydrogen should be calculated by considering the ortho and para states as separates gases. Hence we should introduce two different partition functions for the para and ortho molecules respectively which are

$$F_{\text{para}} = \sum_{j=0,2,4,\ldots} (2j+1)\exp\{-E_j/kT\}$$

$$= \sum_{j=0,2,4,\ldots} (2j+1)\exp\{-j(j+1)Bch/kT\}$$

$$= 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + 13e^{-42\sigma} + \qquad \ldots(ii)$$

and

$$F_{\text{ortho}} = \sum_{j=1,3,5,\ldots} (2j+1)\exp\{-E_j/kT\}$$

$$= \sum_{j=1,3,5,\ldots} (2j+1)\exp\{-j(j+1)Bch/kT\}$$

$$= 3e^{-2\sigma} + 7e^{-12\sigma} + 11e^{-30\sigma} + \qquad \ldots(iii)$$

where

$$\sigma = \frac{h^2}{8\pi^2 IkT} = \frac{\Theta}{T} = \frac{84 \cdot 8}{T}. \qquad \ldots(iv)$$

The equilibrium proportion of the para and ortho hydrogen can now be obtained remembering that the statistical weight of ortho hydrogen is three while that of para is one and that the number $N_j$ of molecules in the $j^{th}$ rotational state is by Boltzmann's law given by (vide equation (ii) of § 9·2).

$$N_j = N_0(2j+1)\exp\{-j(j+1)Bch/kT\} = N_0F_r.$$

$$\therefore \qquad N_{pr} = N_0F_{pr} \text{ and } N_{0r} = 3N_0F_{0r}.$$

Thus, the ratio of hydrogen molecules in the ortho form to that in para form is

$$\frac{N_{or}}{N_{pr}} = \frac{\text{Ortho } H_p}{\text{Para} - H_2} = \frac{3N_0F_{0r}}{N_0F_{pr}} = \frac{3E_{0r}}{F_{pr}}$$

$$= \frac{\sum\limits_{j=1,3,5,\ldots} 3(2j+1)\exp\{-E_j/kT\}}{\sum\limits_{j=2,4,6,\ldots} (2j+1)\exp\{-E_j/kT\}}$$

$$= \frac{3[3\exp\{-E_1/kT\} + 7\exp\{-E_2/kT\} + 11\exp\{E_5/kT\} + \ldots]}{[1 + 5\exp\{-E_2/kT\} + 9\exp\{-E_4/kT\} + 13\exp\{-E_6/kT\} + \ldots]} \qquad \ldots(v)$$

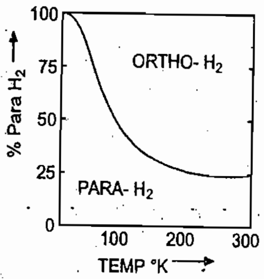
Thus the ratio of the nmber of molecules in the para state to those in the ortho state can be evaluated by inserting the rotational energies in the various levels as determined from the spectrum of molecular hydrogen; the terms in both numerator and denominator being summed up as long as they contribute effectively to the total at different temperatures. As a matter of fact $\exp\{E_j/kT\}$ falls off rapidly as $j$ increases and hence only the first five rotational levels of hydrogen need be taken into account. The calculated percentage of ortho and para forms at different temperatures are shown in table below. Fig. 9.8 depicts graphically the ortho and para forms proportions as a function of temperature.

**Table : Ortho-Para Composition of Equilibrium Hydrogen**

| Temp. $K$ | Ortho-$H_2$% | Para-$H_2$% |
|---|---|---|
| 20 | 0·18 | 99·82 |
| 40 | 11·39 | 88·61 |
| 50 | 23·11 | 76·89 |
| 60 | 34·61 | 65·39 |
| 70 | 44·17 | 55·83 |
| 80 | 51·61 | 48·39 |

| | | |
|---|---|---|
| 100 | 61·49 | 38·51 |
| 120 | 67·13 | 32·87 |
| 170 | 72·01 | 27·99 |
| 273 | 74·87 | 25·13 |
| Very large | 75·00 | 25·00 |

It may be noted both from table and graph that at low tempratures the equilibrium mixture should approach more and more nearly to pure para hydrogen. It is due to almost all the molecules being in the lowest ($J = 0$) state at these temperatures and $J = 0$ corresponds to the para form. As the temperature is increased, the proportion of para form in equilibrium hydrogen decreases from 100% to a limiting value of 25%. Hence at ordinary temperatures the ortho and para forms are in the proportion of 3 : 1 in agreement with the intensities of alternate lines in the band spectrum of ordinary hydrogen.



(Fig. 9.9)

It was on this basis that Dennison explained the results obtained by Eucken. from § 9·9, the rotational energy of a mole of equilibrium hydrogen containing $N$ molecules may be written as

$$E_j = kNT^2 \frac{d}{dT} \log F_r = RT^2 \frac{d}{dT} (\log F_r)$$

$$= -\frac{Nh^2}{8\pi^2 I} \cdot \frac{d}{d\sigma} \log F_r$$

where σ is given by equation (iv).

If the temperature is now changed so slowly that the hydrogen remains continuously in equilibrium, its rotational specific heat at constant volume will be

$$C_{Vr} = \frac{dE_{Vr}}{dT} = R\sigma^2 \frac{d^2}{d\sigma^2} \log F_r$$

Corresponding expressions for para and ortho hydrogen are obtained by including the terms for even or odd values of $j$ respectively. Thus,

$$C_{vr} = R\sigma^2 \frac{d^2}{d\sigma^2} \log F_{pr}, F_{pr} = 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \ldots$$

and

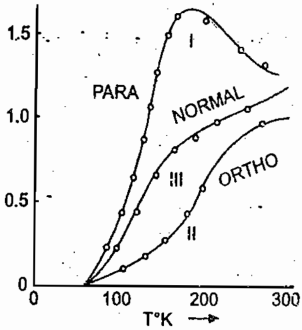
$$C_{0r} = R\sigma^2 \frac{d^2}{d\sigma^2} \log F_{0r}, F_{0r} = 3e^{-2\sigma} + 7e^{-12\sigma} + \ldots$$

Knowing that the ordinary $H_2$ is a mixture of one part of para and 3 parts of ortho hydrogen, we have rotational specific heat of $H_2$ given by

$$C_r = \frac{1}{4} C_{pr} + \frac{3}{4} C_{0r}. \qquad \ldots(vi)$$

The above formula gives the correct values of $C_r$ for hydrogen and it has been experimentally verified. The calculated values of $C_{pr}$ and $C_{0r}$ are plotted by curves $I$ and $II$ respectively of fig. 9.9, while curve No. $III$ represents $C_r$ given according to equation (vi). The signs on them denote the values experimentally obtained by Eucken and Hiller. The uppermost curve which is for para hydrogen shows an interesting

maximum well above the classical value, at about 16 K The figure shows clearly that the experimental values follow the theoretical curves very closely thus verifying the prediction that ordinary hydrogen gas is a mixture of two forms of molecules in the proportion of 1 : 3. From these curves it thus appears that the modern theory is fairly successful in according for the specific heat of hydrogen at various temperatures.



(Fig. 9.10)

Later works have completely established the truth of Dennison's predictions. At low temperatures, there is found to be a slight tendency for ortho hydrogen to change over to para form, since this form has the lower energy. It is found possible to accelerate the rate of two inter conversion by the presence of charcoal (which acts like a chemical catalyst). In this way, at 20 K it becomes nearly pure para hydrogen within a few hours. By this means para hydrogen has been prepared and its properties such as vapour pressure, boiling point, triple point electrical conductivity and its specific heat as a function of temperature studied. These are found to be different from those of ordinary hydrogen. The properties of pure ortho hydrogen are inferred indirectly by comparison with those of the normal hydrogen. In has, infact, been established that the above properties of ordinary hydrogen are the averages of the properties of the ortho and para hydrogen composing the mixture.

## EXERCISES

### Short Answer Questions

1. State Dulong and Petit's law for specific heat of solids.
2. What are important experimental observations about the variation of specific heat of solids with temperature. ***(Rohilkhand 2004, 2005)***
3. Give Einstein's assumptions to explain the variation of the specific heat of solids with temperature. ***(Rohilkhand 2005, 2003)***
4. What do you mean by Einstein's frequency and Einstein's temperature of a solid ?
5. State Dulong and Petit's law. Show that the departure from the law at low temperature has been explained by Einstein's theory. ***(Mumbai Univ. 2004)***
6. Write Einstein's expression for the atomic heat of a solid. What are limitations of Einstein's theory.
7. State the assumptions of Deby's theory of specific heat of solids.
8. What improvements did Debye make in Einstein's theory and why ?
9. What do you mean by Debye's temperature and Debye's maximum frequency ? Express maximum frequency $\nu_m$ in terms of Debye's temperature.
10. What is Debye's $T^3$ law.
11. State limitations of Debye's theory. What are Born Karnman modifications to Debye's theory.
12. Apply law of equipartition of energy to obtain expression for specific heat of monoatomic and diatomic gases.

13. Discuss the variation of molar specific heat of diatomic gases with temperature. *(Agra 2006, 2002)*

14. Explain qualitatively why maximum molar heat of a solid is $3R$ and of a diatomic gas it is $\frac{9}{2}R$.

## Long Answer Questions

1. State Dulong and Petit's law. Explain how this law fails to account for the experimental results. Show that for high temperatures, both Einstein formula and Debye's formula for the specific heats of solid reduce to Dulong and Petit's law. ***(Mumbai Univ. 2004)***
2. State the assumptions of Einstein's theory to explain the variation of specific heat of a solid with temperature. Show that at relatively high temperatures, the molar specific heat of an Einstein solid reaches a constant value which is not only independent of temperature but also of ν. ***(Rohilkhand 2006, Kanpur 2005)***
3. Discuss Einstein's model of specific heat of solids. ***(Rohilkhand 2006 Imp.)***
4. Derive Debys's formula for the specific heat of solids. Comment on the assumptions and achievements of the theory and compare it with Einstein's theory of specific heats.
5. Give a critical account of the development in the theory of specific heats of solids. What is Raman's contribution to this subject?
6. What is the fundamental difference between assumptions of Einstein and Debys's theory of specific heats of solids. Derive Debys's $T^3$ law. Illustrate diagrammatically the nature of frequency spectrum of solid on the models of Einstein's and more modern ideas.
7. Prove with the help of necessary mathematical theory that the specific heat of a solid at low temperature varies as the cube of the temperature. Discuss critically how far you agree with the theoretical foundations of this derivation. Also discuss the modern improvements in the theory. ***(Agra 2004)***
8. Where did Einstein go wrong in deriving specific heat formula for solids? What was Debye's approach in this matter? Derive Debye's formula for specific heat of solids. ***(Mumbai 2002)***
9. Deduce Einstein's expression for specific heat of a solid. Show that at relatively high temperatures, $C_v$ approaches a constant value which is not only independent of temperature but also of ν. ***(Mumbai 2003)***
10. (a) Show that in an isotropic continuous medium of volume $V$, the number of standing wave modes of vibrations in the frequency range ν and ν + $d\nu$ is given by

$$4\pi V\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\nu^2\, d\nu$$

where $c_l$ and $c_t$ are the velocities of longitudinal and transverse waves respectively in the medium. ***(Mumbari 2003)***

(b) Using Debye's procedure, deduce an expression for the specific heat of monoatomic solid at very low temperatures. Interpret the result.

(c) Write a critical note on Debye's assumptions. ***(Agra 1998)***

11. With the help of partition function or otherwise, describe Debys's theory of specific heats of solids. Discuss its agreement with the experimental results. ***(Rohilkhand 1999)***
12. What do you mean by internal degrees of freedom of a gas molecule? How specific heat of a gas depends upon the degrees of freedom? ***(Meerut 2001)***
13. Discuss the relative contributions of translational, vibrational and rotational degrees of freedom to the specific heat of a diatomic molecule. ***(Meerut 2006)***
14. Give a general description of the variation of specific heat of a diatomic gas with temperature, and outline the theoretical attempts to explain this quantitatively. Why is the case of hydrogen of special significance in this respect?
15. Establish the law of equipartition of energy in classical statistical mechnics. How does this law agree with the observations for diatomic gases? Give a detailed description of the expected and observed behaviour for a particular gas at various temperatures. ***(Meerut 1997)***
16. Discuss and prove the law of equipartition of energy. Obtain the specific heat of a gas of diatomic molecules with unlike atoms. ***(Meerut 1999; Agra 2002)***
17. Discuss clearly the temperature variation of the specific heat of a gas of non-interacting hydrogen molecules stating what approximations are made.
18. Compare and construct the manner in which heat energy is taken up by a solid and a diatomic gas. Explain the variation of specific heat of $H_2$ gas with temperature.
19. Describe how the specific heat of hydrogen varies with temperature and explain how this variation is accounted for theoretically. ***(Rohilkhand 1996; Agra 1995)***
20. Discuss the theory of specific heat of diatomic gases. Derive expressions for the rotational partition function and the contribution of rotational energy to the specific heat. Explain the experimental results for the specific heat of hydrogen gas on the basis of ortho and para forms. ***(Rohilkhand 2002)***
21. Discuss the variation of molar rotational and vibrational specific heats for a diatomic molecules (i) at low temperatures (ii) at high temperatures, The diatomic molecule possess rotational energy levels given by

$$\varepsilon_r = \frac{h^2 J}{8\pi^2 I}(J+1), \text{ where } J = 0, 1, 2, \ldots$$

and vibrational energy levels are given by $\varepsilon_v = (v+\frac{1}{2})h\nu$ where $v = 0, 1, 2, \ldots$

***(Purvanchal 2005, Kanpur 2005, 1986)***

22. Give the theory of specific heat of hydrogen gas. Derive expressions for the rotational partition function and the contribution of rotational energy to the specific heat. Discuss in detail, how the experimental results for the specific heat of hydrogen, are explained on the basis of ortho and para forms of hydrogen. ***(Kanpur 2003, Rohilkhand 1991)***
23. Write short explanatory notes on:
    (a) Temperature variation of specific heat of solids
    (b) The Debye's $T^3$ law.
    (c) Degrees of freedom and specific heat of gases.

(d) Ortho and para hydrogen.

(d) Variation of specific heat of hydrogen.

## Numericals

1. For copper $\nu_E = 4{\cdot}8 \times 10^{12}$ vib/sec. Calculate $\theta_E$ for it. [**Ans.** 229·6 K]
2. If Einstein temperature $\theta_E = 100$ K, calculate Einstein frequency. [**Ans.** $2{\cdot}08 \times 10^{12}$ sec$^{-1}$]
3. Employing Einstein's theory to calculate the atomic heat of that solid at 100 K for which Einstein's temperature $\theta_E = 200$ K. [**Ans.** 2·17 R]
4. Einstein temperatures for two solids are respectively 100 K and 200 K. Calculate their atomic heat at 1000 K. [**Ans.** 3·3 *R*, 3·6 *R*]
5. If the frequency of all the atoms of solid are equal and Einstein temperature $\theta_E = 100$K, then calculate the specific heat of the solid at temperature (i) 25 K, (ii) 500 K. [**Ans.** (i) 1·75 (ii) 7·5 cal/g-mol K]
6. Debye temperature for diamond is 2230 K. Calculate for it
   (i) Maximum lattice frequency $\nu_m$
   (ii) Molar specific heat at temperature 20 K.
   [**Ans.** (i) $4{\cdot}7 \times 10^{13}$ s$^{-1}$ (ii) 1·4 joule/kilomole]
7. Assuming the classical theory of specific heat to bhe correct, calculate the thermal energy7 of 1 mole of copper at temperature $T = \theta_D$. For copper Debye temperature $\theta_D = 340$ K.
   [**Hint :** $E = 3NkT$]
   [**Ans.** 8474 joule/mole]
8. If in a solid, frequency of all Planck's oscillators is the same, then calculate the total energy of 1 g-mole of the solid at temperature (i) 40 K, (ii) 400 K. [Given $\frac{h\nu}{K} = 80$ K]
   [**Ans.** (i) 37·5 R, (ii) 1091 *R*]
9. The characteristic Debye's temperature for diamond is 1860 K and the characteristic Einstein temperature $\frac{h\,\nu_E}{k}$ is 1450 K. Calculate $C_v$ at 207 K from the Einstein and Debye equation. $R = 8{\cdot}31$ J/mole K. *(Mumbai 2001)*
   [**Ans.** (i) 0·14 J/g-atom K (iii) 2·67 J/g-atom K]
10. Calculate the vibrational contribution to energy in terms of $kT$ for a diatomic gas at a temperature for which $\frac{h\nu}{kT} = 0{\cdot}2$ for
    (i) 1 atom (ii) 1 gram-atom
    If vibrational frequency $\nu = 1{\cdot}3 \times 10^{14}$ s$^{-1}$, calculate the temperature also. Given $e^{0{\cdot}2} = 1{\cdot}222$.
    [**Ans.** (i) 0·9 $kT$ (ii) $5{\cdot}4 \times 10^{23}$ $kT$, 3108 K]
11. Vibrational constant for chlorine is 560 cm$^{-1}$. Calculate $\frac{h\nu}{kT}$ at 200 K. [**Ans.** 3·96]
12. Force constant for HCl is 540 N/m. Calculate
    (i) Fundamental frequency of vibration
    (ii) Gap between vibrational energy levels

(iii) Will these levels be excited at 400 K temperature also ?
[**Ans.** (i) $9{\cdot}2 \times 10^{14}$ s$^{-1}$ (ii) $6{\cdot}06 \times 10^{-19}$ J (iii) No]

13. For HCl, $B = 10{\cdot}1$ cm$^{-1}$ and $\nu = 9{\cdot}2 \times 10^{14}$ s$^{-1}$. Calculate the temperature at which value of $C_V$ rises from $\frac{3}{2}R$ to $\frac{5}{2}R$ and then from $\frac{5}{2}R$ to $\frac{7}{2}R$. [**Ans.** 29 K, $4{\cdot}4 \times 10^4$ K]
14. Rotational energy level for HF is given by
    $$\in j\,(j+1)\,Bch$$
    where $j = 0, 1, 2, \ldots$ and $B = 2$ cm$^{-1}$.
    The degeneracy of $j$th energy state is $(2j+1)$. Calculate the relative number for $j = 1, 2, 3$ at temperature 300 K. *(Kumaun 1987, 89)*
    [**Ans.** 2·94, 4·72, 6·24]
15. The first excited state of atomic hydrogen is 10 eV above its lowest state. At what temperature will the hydrogen atom be excited to this state ?
    [**Hint :** $\frac{3}{2}kT = 10\,eV$]
    [**Ans.** $7{\cdot}7 \times 10^4$ K]
16. The rotational energy of a diatomic molecule is given by $E_J = B\,ch\,J\,(J+1)$ where $J = 0, 1, 2, \ldots$ For a gas $B = 20$ cm$^{-1}$, deduce to population ratio $\frac{N_J}{N_0}$ at a temperature of 300 K for $J = 1, 3, 6$ and 10, remembering that a weight factor $(2J+1)$ is attached with $J$th state.
    [**Ans.** $\frac{N_1}{N_0} = 0{\cdot}5618$, $\frac{N_3}{N_0} = 0{\cdot}3300$, $\frac{N}{N_0} = 1{\cdot}688 \times 10^{-23}$ and $\frac{N_{10}}{N_0} = 1{\cdot}698 \times 10^{-97}$
    Obviously the the relative population of gas molecules decreases rapidly with increase of rotational energy.]
17. Calculate in terms of $kT$ the vibrational contribution of energy of 1 gm. mole of hydrogen at a temperature at which $h\nu/kT = 2$. Given vibrational constant $\bar{\nu} = 400$ cm$^{-1}$. Calculate this temperature. [**Ans.** 1·874 $kT$; 3179K]
18. Find the relative numbers of $Cl_2$ molecules in the zeroth and the first vibrational levels at a temperature of 1000k if $\omega_e$ 565 cm$^{-1}$ and $\omega_e x_e = 4$ cm$^{-1}$ for the ground state of $Cl_2$.
    [**Ans.** 0·01142]
19. The first vibrational level of a diatomic molecules is 600 cm$^{-1}$ above the zeroth. Deduce the relative population of molecules in these two levels at a temperature of 127°C. [**Ans.** 0·1]
    [**Hint.** $N_1/N_0 = \exp(-\varepsilon/kT)\ \exp(-hc\bar{\nu}/kT)$]

## MULTIPLE CHOICE QUESTIONS : SELECT THE RIGHT CHOICE :

1. According to Dulong and Petit's law the atomic heat of a solid is :
   (a) $R$ (b) $\frac{3}{2}R$ (c) $3R$ (d) $\frac{5}{2}R$
2. In Einstein's theory of specific heat of solids, all the atoms of a solid vibrate with : *(Rohilkhand 2004)*
   (a) zero frequency (b) one and the same frequency
   (c) unknown frequency (d) different frequencies.

3. In Debye's theory of specific heat of solids the atoms of a solids vibrate :
   (a) with zero frequency
   (b) one and the same frequency
   (c) different longitudinal frequencies only
   (d) different longitudinal and transverse frequencies.
4. In an isotropic continuous medium of volume $V$, the number of standing wave modes in the frequency range $\nu$ and $\nu + d\nu$ is given by :
   (a) $\frac{4\pi V \nu^2 d\nu}{c_l}$ (b) $4\pi V\left(\frac{1}{c_l^3}+\frac{1}{c_t^3}\right)\nu^2 d\nu$
   (c) $4\pi V\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\nu^2 d\nu$ (d) $\frac{4\pi V}{h^3}\left(\frac{1}{c_l^2}+\frac{1}{c_t^2}\right)\nu^2 d\nu$.
   where $c_l$ and $c_t$ are velocities of longitudinal and transverse waves respectively.
5. In specific heat of solids at low temperatures $C_v \propto T^3$ law is followed. It is explained by :
   (a) Dulong and Petit's theory
   (b) Einsteins' theory
   (c) Debye's theory
   (d) Both Einstein's theory and Debye's theory
6. The specific heat of gases have :
   (a) only one value $C_v$ (b) only two values $C_p$ and $C_v$
   (c) infinite values between 0 and $\infty$ (d) four values $C_p$, $C_v$, 0 and $\infty$.
7. Debye's temperature is :
   (a) 273 K (b) 273·15 K (c) $\frac{h\nu_m}{k}$ (d) $\left(\frac{h}{k}\right)^2 \nu_m$.
8. Einstein's temperature ($\Theta_E$) is equal to :
   (a) 273·15 K (b) $\frac{h}{k}\Theta_E$ (c) $\frac{h}{v}\Theta_E$ (d) $\frac{h\nu_m}{k}$
9. According to Debye's theory the atomic heat of a solid at low temperature is :
   (a) proportional to absolute temperature ($T$)
   (b) proportional to square of absolute temperature ($T^2$)
   (c) proportion to cube of absolute temperature ($T^3$)
   (d) zero.
10. The molar heat of a diatomic gas due to translational motion is :
   (a) zero (b) $\frac{3}{2}R$ (c) $3R$ (d) $\frac{7}{2}R$.
11. The minimum vibrational energy of an oscillator is :
   (a) $\frac{1}{2}h\nu$ (b) $h\nu$ (c) $\frac{3}{2}h\nu$ (d) zero.
12. Vibrational energy levels of an oscillator are :
   (a) not equidistant (b) equidistant with a separation $\frac{1}{2}h\nu$
   (c) equidistant with a gap $h\nu$ (d) continuous

13. The minimum rotational energy of a diatomic molecule is :
   (a) $\frac{1}{2}h\nu$ (b) $h\nu$ (c) $\frac{3}{2}h\nu$ (d) zero.
14. The minimum distance between two rotational energy levels of a diatomic molecule is :
   (a) $B'$ (b) $2B'$ (c) $3B'$ (d) $4B'$
   $\left(\text{where } B' = \frac{\hbar^2}{8\pi^2 I}.\right)$
15. The molar specific heat at constant volume of a diatomic gas is $\left(\text{with } x = \frac{h\nu}{kT}\right)$:
   (a) $\frac{3}{2}R$ (b) $\frac{5}{2}R$
   (c) $R\left(\frac{5}{2}+\frac{x^2 e^x}{e^x-1}\right)$ (d) $R\left(\frac{3}{2}+\frac{x^2 e^x}{e^x-1}\right)$

### ANSWERS

1. (c) 2. (b) 3. (d) 4. (c) 5. (c) 6. (c) 7. (c) 8. (b)
9. (c) 10. (b) 11. (a) 12. (c) 13. (d) 14. (b) 15. (c).

# 10

# LOW TEMPERATURE PHYSICS

## 10.1. Introduction :

For a long time it was considered that nothing could be colder than ice and hence the temperature of ice was chosen as the zero (starting point) of the scale in all earlier systems of temperature measurement. About 150 years ago scientists began to realize that the temperatures well below the ice point were possible and that temperature scale had a lower limit. With the knowledge of gas laws the lowest temperature attainable, at least theoretically, came to be regarded 273°C below the melting point of ice, which is used as the zero of the absolute scale of thermometry and hence called the *absolute zero temperature*. Since then scientists all over the world have been attempting to find out ways and means to achieve this limit of low temperature. This march towards absolute zero makes a fascinating study and has given rise to a new branch of physics known as the *low temperature physics.*

We shall deal in this chapter with the various nethods which have been employed to produce these low temperatures and then with the methods of measuring them. We shall, however, make brief references to the earlier methods and describe in detail the modern ones.

## 10.2. Production of Low Temperatures

The present day scientific works leading to the discovery of some new phenomena like superconductivity and superfluidity, call for the production of extremely low temperatures. These temperatures are specially essential for the study of the effect of low temperature on many properties of substances, like their atomic heat, susceptibility, thermal and electrical conductivities etc. and in the exploration of upper atmosphere.

Hence the techniques of producing low temperatures have extremely been developed and now the methods are at hand to go down even upto $10^{-6}$K. The general principle involved in the production of low temperature is to devise ways and means for removing heat content from a body. The methods generally employed for the purpose are the following :

**(1) Freezing Mixtures.** Temperature lower than 0°C can be produced by mixing certain salts with ice, When salt is mixed with ice, it gives, some heat to the ice causing a little of it to melt. Now salt gets dissolved in the water produced by the melting of ice. The necessary heat for this process *viz.*, the heat which salt absorbs while dissolving (heat of solution) and the heat of fusion which ice absorbs while melting (latent heat) is extracted from the mixture itself and consequently the temperature of mixture falls below zero. This process can not, however, go indefinitely. The lowest temperature that can be attained by this method is fixed depending upon the salt and is called the *eutectic temperature.* When this temperature is reached, more salt refuses to go in solution and hence there is no further fall of temperature. Thus no purpose will be served by adding more salt. The lowest temperatures reached by mixing different salts with ice are given in table below :

| Salt | Amount of salt in 100 gram of mixture | Lowest (eutectic) Temperature in °C |
|---|---|---|
| $MgSO_4$ | 19·00 | – 3·9 |
| KCI | 19·7 | – 11·1 |
| $NH_4Cl$ | 18·6 | – 15·8 |
| NaCl | 22·4 | – 21·2 |
| $CaCl_2$ | 29·8 | – 55 |
| KOH | 31·5 | – 65 |

It may be observed that the temperature thus reached are not low enough.

**(2) Evaporation of liquids under reduced pressure.** When a liquid evaporates, it requires heat for conversion from liquid to gaseous state (*i.e.*, latent heat of vaporization). If the liquid is thermally isolated and allowed to evaporate, the necessary latent heat will be supplied by the liquid itself, and consequently a cooling will take place. The amount of cooling depends upon the nature of the liquid and rate of evaporation. If the evaporation is promoted by reducing the pressure on the liquid surface and a volatile liquid with large latent heat of vaporization be chosen; the cooling produced can really be intensified. A familiar example of this method is the rapid evaporation of liquid ammonia or sulphur dioxide in ice plants and refrigerators.

Very low temperatures can be produced by the evaporation of liquid hydrogen and liquid helium. Liquid hydrogen boiling under normal pressure gives – 255·78°C while with helium – 268·9°C is reached. Keesom in 1932 was successful in producing a temperature as low 0·726K by reducing the pressure on the surface of liquid helium down to 0·036 mm of Hg. With liquid helium isotope $He^3$ boiling under reduced pressure a temperature of 0·4K can be reached.

**(3) Adiabatic expansion of compressed gases.** If a highly compresed gas is suddenly allowed to expand adiabatically against some external pressure, it has to do a large amount of external work against the pressure (and also some internal work against intermolecular attractions) at the expense of its own internal energy. As the internal energy of a gas is a function of its temperature, a large cooling is, therefore, produced in this process.

If $T_1$ and $P_1$ are the initial temperature and pressure of a given mass of the gas while $T_2$ and $P_2$ the final temperature and pressure respectively, then since the process is adiabatic, we have

$$T_1 P_1^{(1-\gamma)/\gamma} = T_2 P_2^{(1-\gamma)/\gamma}$$

or, the final temperature of the gas

$$T_2 = T_1 \left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}} = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{(\gamma-1)}{\gamma}}$$

It may be seen that at ordinary initial temperature $T_1$ and for high pressure dufference, the expanding mass of the gas may be liquefied or even solidified. For example if $CO_2$ gas at room temperature (27°C) compressed to a pressure of 150 atmospheres is suddenly released to atmospheric pressure, the final temperature is

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{(\gamma-1)}{\gamma}} = 300 \left(\frac{1}{150}\right)^{\frac{1\cdot3-1}{1\cdot3}} = 96 \text{ K.}$$

This temperature is so low that the expanding mass of $CO_2$ gets solidified, which is known as *dry ice*.

This fact has been made the basis of various methods for liquefying gases which has opened up a new line in the attainment of low temperature. Thus Cailletet (1877) was able to liquefy oxygen using this method. It was followed by Pictet, Wroblewski and Olszewski who employed almost identical methods. *Kapitza*, in the year 1934 utilized this process for the liquefaction of both hydrogen and helium. *Simon* (1948) could liquefy helium by its adiabatic expansion very easily.

**(4) Joule-Thomson expansion coupled with Regenerative Cooling.**

When a gas at sufficiently low temperature, is allowed to escape adiabatically through a fine orifice from the region of constant high pressure to the region at constant low pressure, it suffers a fall of temperature. Any gas below its inversion temperature gets cooled on suffering this Joule-Thomson expansion. *The cooling so produced, however, is proportional to the differences of pressure on the two sides of the orifice and increases as the initial temperature of the gas is decreased.* Thus, for air the fall in temperature for a pressure difference of one atmosphere, at an initial temperature of – 90°C is 150°C while it is 0·275°C, if the initial temperature is 0°C. Moreover, at initial temperature of – 20°C, the air cools by 11·7°C when the pressure on the two sides are 50 atmosphere and 1 atmosphere respectively and this cooling increases to 42°C, if the pressure on the two sides are kept 210 and 1 atmosphere respectively. The Joule-Thomson *cooling can be intensified by employing the process called the 'regenerative cooling'.* In this process a portion of the gas which suffers Joule-Thomson expansion and becomes cooled is employed to cool other portions of the incoming gas before the latter reaches the nozzle to suffer Joule-Thomson expansion. After suffering the Joule-Thomson expansion at the nozzle, the incoming gas becomes still more cooled. By a continuous application of this process, the temperatures of the gas coming out of the nozzle falls progressively and ultimately a temperature may be reached at which the gas starts liquefying on the low pressure side.

This process has been used in the liquefaction of a number of gases. Linde in Gemany and Hampson in England combined regenerative cooling with Joule-Thomson effect, for the first time in 1895, to produce liquefied air. Dewar, in 1898, could liquefy hydrogen at a temperature of – 205°C by this process while Kamerlingh Onnes was able to liquefy helium using this method at – 269°C under one atmospheric pressure.

**(6) Adiabatic desorption.** The process of *desorption* of gas by a solid is analogous to the vaporisation of liquid. Just as when a liquid vapourises, heat is absorbed; in a similar way when a gas is desorbed, (*i.e.*, removed from) by a solid, there is absorption of heat and the solid is cooled. There is another process of *adsorption* which is analogous to the condensation of vapour and in which heat is liberated. Charcoal is a good adsorbing solid and when cooled to a low temperature can adsorb a number of gases with the liberation of heat. If the heat liberated is conducted away and the adsorbed gas is removed with the help of an exhaust pump under adiabatic condition, the charcoal draws its own internal energy and gets further cooled. Simon has used this process to good advantage in liquefying helium.

**(7) Adiabatic demagnetisation.** Temperatures considerably below 1K can be reached by 'adiabatic demagnetisation methods' due to Debye (1926) and Giauque (1927). When a paramagnetic substance is magnesized, external work is done on it in aligning the elementary magnets in the direction of the external field. This work is stored in the substance in the form of magnetic energy and consequently its temperature rises. Conversely, if the magnetized substance is demagnetized adiabatically, it has to do work and the required energy for it is drawn from within itself. As a result the substance cools. Considerable cooling can be produced by employing strong magnetic field and low initial temperature.

Debye, Giauque and Maedougall, in 1938 were able to produce the temperature 0·25 K with the help of paramagnetic salt gadolinium sulphate. De-Hass and Wiersma at Leiden, in 1946, have reached 0·003 K using a mixture of chrome-potassium alum and aluninium-potassium alum. Later in 1956, Gorten and Klerk used powdered mixed crystals of chromium alum and aluminium alum and were able to reach a temperature of 0·3 K. Still lower temperatures upto $10^{-5}$ K can be reached by the use of *nuclear paramagnetism* as suggested by Simon and Kurti. It may be mentioned that the attainment of absolute zero is an impossibility.

Hass, in 1941, was able to produce temperature upto 0.002 K using a double sulphate of potassium and aluminium. Klerk, Stenland and Gorter used powdered mixed crystals of chromium alum and aluminium alum and went down to a temperature of 0.0014 K.

### 10.3. Approach to Absolute zero by Adiabatic Demagnetization

The process of adiabatic demagnetization marks a remarkable step forward in the attainment of the absolute zero. Before its advent, the lowest temperature which could be reached by boiling helium (He$^4$) under reduced pressure was only slightly less than 1 K. Even the boiling of rate isotope 'helium three' (He$^3$) under reduced pressure could not attain a temperature less than 0·40 K, a limit which could be reached by use of gases. Debye, in 1929, and Giauque, in 1927, independently proposed a method of *'magnetic cooling'* or of *'adiabatic demgnetization'* to go still lower in the scale of temperature towards our goal of absolute zero.

**Principle.** A paramgnetic substance contains atoms which behave like small magnets, or the dipoles all lying in a disorderly manner in neutralizing groups. When such a substance is magnetized, these groups of dipoles get broken up and the axes of the magnetic atoms set themselves parallel to the lines of force. Obviously, an external work is done on the specimen which appears in it in the form of heat and results in a rise of temperature. If this already magnetized substance is suddenly demagnetized, the axes of the atomic magnets will tend, under the influence of thermal agitation, to resume their natural neutralizing disorderly state. Now work will be done by the substance and required energy for it will be drawn from the substance itself and consequently its temperature will be lowered. This result is known as *magnetocaloric effect.*

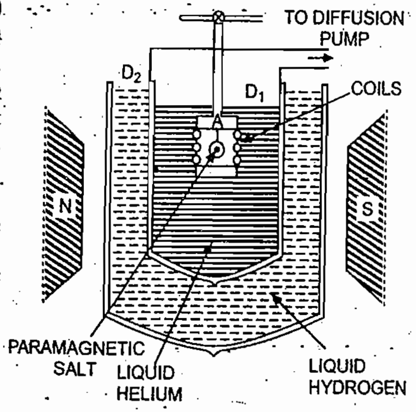
Now all paramagnetic substances are not equally magnetized by a given magnetic field. Those which are strongly magnetized by a field than others are said to have a higher *magnetic susceptibility* ($\chi$). The ratio $\frac{\text{Intensity of magnetization of specimen}}{\text{Intensity of magnetizing field}}$ For any material is called the *susceptibility of the material.* The susceptibility of paramagnetic substance does not depend upon the field strength but does certainly depend upon temperature. According to *Curie's law*, the paramagnetic susceptibility $\chi$ of a substance is inversely proportional to the absolute temperature $T$;

*i.e.*,

$$\chi \;\alpha\; \frac{1}{T} \text{ or } \chi = \frac{C}{T},$$

where C is a constant. Thus, the susceptibility of a paramagnetic substance is higher at the lower temperature. The size of the magnetocaloric effect also increases as the initial temperature of the substance is lowered. Hence if Curie's law be resumed to hold good at the temperature of liquid helium, a paramagnetic substance should be powerfully magnetized at that very low temperature and hence when this substance is adiabatically demagnetized, a large cooling should be produced providing a temperature lower than that of liquid helium.

**Method.** Fig. 10.1. gives a general outline of the apparatus used in these experiments. The sample (paramagnetic salt, gadolinium sulphate, say) is suspended in vessel surrounded by liquid helium cooled to nearly 1K contained in a Dewar flask $D_1$ which in turn is surrounded by a Dewar flask $D_2$ containing liquid hydrogen. The whole arrangement is placed between the poles of a strong electromagnet, providing a magnetic field of the order of 1 tesla.



(Fig. 10.1)

Now the following procedure is adopted :

(a) The magnetic field is switched on so that the specimen is magnetized.

(b) The heat produced during the proeess of magnetization is conducted away by the gaseous helium in $A$ to the liquid in $D_1$. Thus the specimen in $A$ is left both cold and highly magnetized. It corresponds to *isothermal magnetization.*

(c) The helium gas from the cylinder $A$ is now pumped off with a high vacuum pump. Thus the specimen is now thermally isolated from $D_1$ and $D_2$.

(d) The magnetic field is now switched off. Instantaneous adiabatic demagnetization of the salt takes place and its temperature falls.

The temperature of the specimen is determined by fitting a coaxial solenoid coil round the tube $A$ and measuring the self-inductance and hence susceptibility ~~of the substance with the help~~ of an alternating current bridge at the beginning and at the end of the experiment. If $\chi_1$ is the susceptibility at temperature $T_1$ of the helium bath and $\chi_2$ the susceptibility after adiabatic demagnetization at temperature $T_2$, then according to Curie's law

$$\frac{\chi_1}{\chi_2}=\frac{T_2}{T_1}$$

or

$$T_2=\frac{\chi_1}{\chi_2}T_1.$$

whence $T_2$ can be easily evaluated, which is called the *Curie's temperature or magnetic temperature.* From it, the Kelvin temperature can be determined.

## Theory

When a paramagnetic solid is placed in a magnetising field $H$, its elementary magnetic dipoles get aligned in the direction of the field. The *magetic moment per unit volume* thus produced is called the *intensity of magnetisation* and is denoted by $I$. According to Curie's Law, this intensity of magnetisation is directly proportional to magnetising field $H$ and inversely proportional to temperature $T$ of the paramagnetic solid, *i.e.,*

$$I\propto\frac{H}{T}$$

or

$$I=C\left(\frac{H}{T}\right)$$

where C is a constant, called Curie constant.

If $V$ is the volume of 1 mole (molar volume), then intensity of magnetisation for 1 mole of paramagnetic substance

$$M=IV=CV\left(\frac{H}{T}\right)=\frac{KH}{T} \qquad \ldots(1)$$

Let us now suppose that 1 mole of paramagnetic solid is placed in magnetising field $H$. Then its thermodynamic behaviour can be expressed in terms of thermodynamical variables $P$, $V$, $T$ and $S$. The work by the magnetic field on the substance

$$=H\,dM$$

therefore work done by the substance $\qquad = -HdM \qquad \ldots(2)$

Also work due by the system, $\qquad dW = P\,dV \qquad \ldots(3)$

Comparing (1) and (2), we see that here $(-H)$ plays the role of $P$ and $M$ plays the role of $V$.

Therefore, replacing $P$ by $-H$ and $V$ by $M$ in Maxwell's third thermodynamic relation

$$\left(\frac{\partial T}{\partial P}\right)_S=\left(\frac{\partial V}{\partial S}\right)_P$$

We get

$$\left(\frac{\partial T}{\partial H}\right)_S=-\left(\frac{\partial M}{\partial S}\right)_H$$

or

$$\left(\frac{\partial T}{\partial H}\right)_S=\frac{-(\partial M/\partial T)_H}{(\partial S/\partial T)_H}=\frac{-T\left(\frac{\partial M}{\partial T}\right)_H}{T\left(\frac{\partial S}{\partial T}\right)_H}$$

$$=-T\left(\frac{\partial M}{\partial T}\right)_H\Big/\left(\frac{\partial Q}{\partial T}\right)_T=-\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H$$

where $C_H=\left(\frac{\partial Q}{\partial T}\right)_H$ joule/mole K is the specific heat of the substance under constant field.

For an adiabatic change in the field (entropy $S$ constant), we may write

$$dT=-\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H\cdot dH \qquad \ldots(4)$$

Differentiating equation (3) with respect to $T$ at constant $H$, we get

$$\left(\frac{\partial M}{\partial T}\right)_H=-\frac{KH}{T^2}$$

Substituting the value in (4), we get

$$dT=-\frac{T}{C_H}\times\left(-\frac{KH}{T^2}\right)dH$$

$$T\,dT=\frac{K}{C_H}H\,dH \qquad \ldots(5)$$

If $T_i$ and $T_f$ are initial and final temperature and $H_i$ and $H_f$ are initial and final magnetic fields then integrating above expression, we get

$$\int_{T_i}^{T_f}T\,dT=\int_{H_i}^{H_f}\left(\frac{K}{C_H}\right)H\,dH$$

$$\left[\frac{T^2}{2}\right]_{T_i}^{T_f}=\frac{K}{\overline{C}_H}\left[\frac{H^2}{2}\right]_{H_i}^{H_f}$$

where we have replaced $C_H$ within the integral by its average value $\overline{C}_H$. Thus

$$T_f^2 - T_i^2 = -\frac{K}{\bar{C}_H}(H_f^2 - H_i^2) \quad \ldots(6)$$

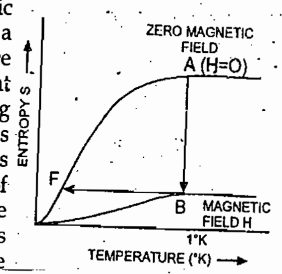
If the magnetic field is reduced from $H$ to 0, then $H_i = H$ and $H_f = 0$, so we get

or
$$T_f^2 = T_i^2 - \frac{K}{\bar{C}_H}H^2$$

or
$$T_f = T_i\left[1 - \frac{K}{\bar{C}_H}\left(\frac{H}{T_i}\right)^2\right]^{1/2} \quad \ldots(7)$$

It may be noted that $T_f < T_i$ *i.e.*, the temperature of the salt falls during the process of adiabatic demagnetization. *The fall in temperature is greater for lager values of the magnetizing field H and low values of initial temperature* $T_i$.

**T. S. diagram.** The cooling produced by adiabatic demagnetisation has been illustrated in Fig. 10.2 by means of a temperature entropy diagram. In figure, the entropy of the substance is represented schematically as a function of temperature for different external fields $H=0$ and $H=H$. The change in entropy during isothermal magnetisation is represented by the arrow $AB$. This shows that during magnetisation the entropy of the substance decreases according to the definition that entropy of a substance is a measure of its state of disorder. Now if the field is switched off the substance demagnetises adiabatically so that the temperature of the system falls from $B$ to $F$ while entropy remains constant as represented by the arrow $BF$.



(Fig. 10.2)

Using this method with the salt gadolinium sulphate, Giauque and Macdougall could only reach a temperature 0·25 K in the year 1938. A low temperature can be reached by using a mixed salt because the magnetic interactions between the paramagnetic ions are weakened when a paramagnetic salt is mixed with a non-paramagnetic salt. A mixed crystal can also give much lower temperatures. Thus de Hass, Wiersma and Kramres, succeeded in 1945, in reaching a temperature as low as 0·0034 K, using mixed crystal of chromium potassium alum and aluminium potassium alum and a field of 2·4 tesla. More recently, de Klerk, Steerland and Gortei, working with powdered mixed crystals of chromium alum and aluminium alum reached a temperature 0·001 K.

Temperatures much lower than it can be produced by the help of *nuclear demagnetization* as suggested by Kurti and Simon. In this case, the magnetic interactions are much smaller and also the magnetic moment of the nuclei is $10^3$ times that produced by the motion of the electrons. Hence one should use very much stronger magnetic field and begin with an initial temperature of the order of $10^{-2}$ K. Temperatures of the order of $10^{-5}$ K have now been reached by this method.

The attainment of the absolute zero thus seems to be very near but actually it can never be reached in practice (Third law of thermodynamics) *"Absolute zero is as far off as the end of a recurring decimal"* says Maclay.

## SOLVED EXAMPLE

**Example. 10.** *grams of a paramagneitc substance, obeying Curie's law is placed in a magnetic field of 10,000 oersteds and a temperature of 3K. Calculate the cooling produced when the field is reduced reversibly and adiabatically to zero. The Curie constant per gram is 0·05 C.G.S. units and the specific heat at constant field to remain constant is 0·01cal.* $g^{-1}K^{-1}$.

---

**Solution.** The final temperature after adiabatic demagnetization is given by [vide eqn. (7) § 10·3].

$$T_f^2 = T_i^2 - \frac{K}{\bar{C}_H}H^2.$$

Given $T_i = 3$ K, $\bar{C}_H = 0{\cdot}10$ cal. $g^{-1}K^{-1}$

$$= 0{\cdot}10 \times 4{\cdot}2 \times 10^7 \text{ ergs gm}^{-1}K^{-1}$$

and Curie constant $K = 0{\cdot}05$.

$$\therefore \quad T_f = 9 - \frac{0{\cdot}05 \times (10000)^2}{0{\cdot}10 \times 4{\cdot}2 \times 10^7} = 7{\cdot}8 \text{ K}.$$

or
$$T_f = 2{\cdot}8 \text{ K}.$$

So that the cooling produced $= T_i - T_f = 3 - 2{\cdot}8 = 0{\cdot}2$ **K.**

## 10.4 Liquefaction of Gases

The systematic work on the liquefaction of gases first began in 1823 when Faraday liquefied chlorine, hydrogen sulphide, carbon dioxide, nitrous oxide, etc. by cooling them below the room temperature and applying pressure. He generated the gas in one end of a closed tube, the other end being bent over into a simple freezing mixture, and the gas liquefied under its own pressure. Thilorier in 1835 liquefied carbon dioxide at the room temperature under a pressure of 50 atmospheres. He also produced solid carbon dioxide. Later, in 1845, Faraday liquefied ethylene, phosphine etc., by using a freezing mixture of solid carbon dioxide and ether to pre-cool the gas before applying pressure. He, however, entirely failed to liquefy gases such as oxygen, nitrogen and hydrogen even at a temperature as low as –110°C. The efforts of later workers such as Natterer who employed very high pressures to liquefy these gases also met with failure. Hence it was concluded that these gases could not be at all liquefied and were called as "permanent gases".

The famous experiment of Andrews on $CO_2$, made in 1863, led to the discovery that a gas must first be cooled to below its critical temperature before it could be liquefied under pressure. The critical temperatures of oxygen, nitrogen, hydrogen and helium are –118°C, –147°C, – 240°C and – 268°C respectively. Hence these gases must be considerably pre-cooled before they are liquefied. Taking this clue, Cailletet and Pictet, in 1877, independently succeeded in liquefying oxygen. Cailletet cooled the oxygen to – 30°C, compressed it to 300 atmospheres and then allowed it to expand adiabatically. This dropped the gas to such a low temperature that it partly liquefied at atmospheric pressure. Pictet, however, adopted a cascade process in which the necessary cooling was obtained step by step by evaporation of suitable volatile liquids under reduced pressure. K. Onnes modified the process to obtain liquid-air in large quantity. Wroblewski and Olszewski in 1883, using different cooling agents, succeeded in liquefying nitrogen. The cascade failed to liquefy neon, hydrogen and helium as their critical temperatures are too low to be obtained by any liquid evaporating under reduced pressure. Olszewski in 1893, however, obtained traces of liquid-hydrogen by cooling it to – 210°C (by liquid-oxygen evaporating under reduced pressure), and compressing it highly followed by its adiabatic expansion.

The discovery of the Joule-Kelvin effect in 1853 opened a new field for the liquefaction of gases. It was found that when any gas compressed to a high pressure and pre-cooled to below a certain characteristic temperature (called temperature of inversion) is passed through a fine nozzle to a region of low pressure ; it is further cooled. The cooling may be progressively increased by means of regenerative process. Using this, Hampson in England in 1895 and Linde in Germany in the same year, obtained liquid-air on a commercial scale. In 1902, Claude in France developed another air-liquefier. In this liquefier the adiabatic expansion of the gas in an expansion engine joins the Joule-Kelvin expansion to cool the gas to its liquefaction.

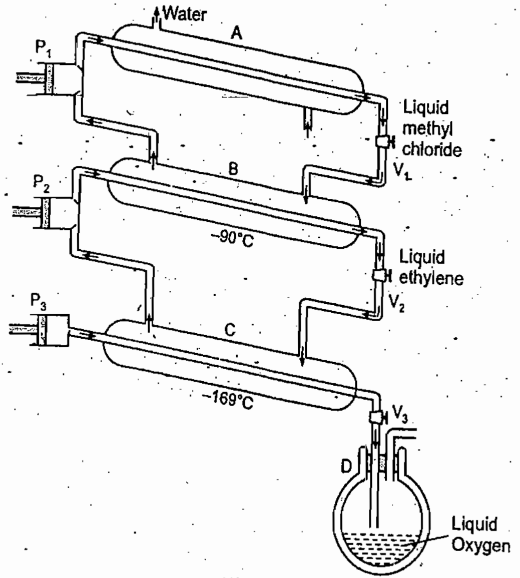
Dewar in 1898 and later Travers were able to liquefy hydrogen using the Linde-Hampson methods. They cooled hydrogen to below its temperature of inversion (which is – 80°C) by liquid-air evaporating under reduced pressure and subjected it to Joule-Kelvin expansion. This left helium as the only gas still to be liquefied whose temperature of inversion is – 240°C. At last, in 1908, Kamerlingh Onnes succeeded in extending the process to liquefy helium, using liquid-hydrogen evaporating under reduced pressure as the pre-cooling agent. Later on Kapitza (1934) modified Claude's air-liquefier to obtain liquid-helium. Thus, all the known gases have been obtained in liquid state.

Kessom, in 1926, brought to a culmination these researches by obtaining solid helium.

**Principle of Cascades**

The cascades process for producing temperatures low enough to liquefy a particular gas by compression was devised by Pictet. In this process the lowering of temperature is brought about step-by-step, employing the cooling produced by the rapid evaporation of suitable volatile liquids. First of all, a liquid at room temperature is evaporated under reduced pressure so that cooling is produced. This cooling is employed to liquefy a suitable gas which, in turn, evaporates at a lower temperature. This process is continued until a temperature is attained which is below the critical temperature of the gas to be liquefied. The gas is then liquefied under pressure.

**Kammerlingh Onne's Cascade System :** K. Onnes arranged a cascade to liquefy oxygen, employing methyl chloride and ethylene as shown in Fig. 10.3.



(Fig. 10.3)

$A$, $B$ and $C$ are three compression chambers joined in series and worked by pumps $P_1$, $P_2$ and $P_3$ respectively. The inner tube of $A$ is filled with methyl chloride gas and its outer jacket is filled with water flowing at room temperature. As the critical temperature for methyl chloride is 143°C, it liquefies at room temperature during the compression stroke of the pump $P_1$. The heat of compression is removed by the water flowing round $A$. The liquid methyl chloride formed in $A$ passes through the valve $V_1$ into the outer jacket of $B$. This jacket is connected to the suction side of the pump $P_1$ so that, as a result of the reduced pressure, the liquid methyl chloride evaporates. The temperature in $B$, therefore, falls to – 90°C. The pump sends the methyl chloride vapour back to $A$.

A similar process takes place in $B$. The inner tube of $B$ is filled with ethylene gas ; which is now maintained at – 90°C. As the critical temperature for ethylene is 10°C, it liquefies during the compression stroke of the pump $P_2$ and collects in the jacket of $C$. There it evaporates under reduced pressure. As a result, the temperature in $C$ falls to – 169°C. This is below the critical temperature of oxygen (– 118°C) which is filled in the inner tube of $C$. This oxygen, therefore, liquefies during the compression stroke of the pump $P_3$ and is collected in the Dewar flask $D$.

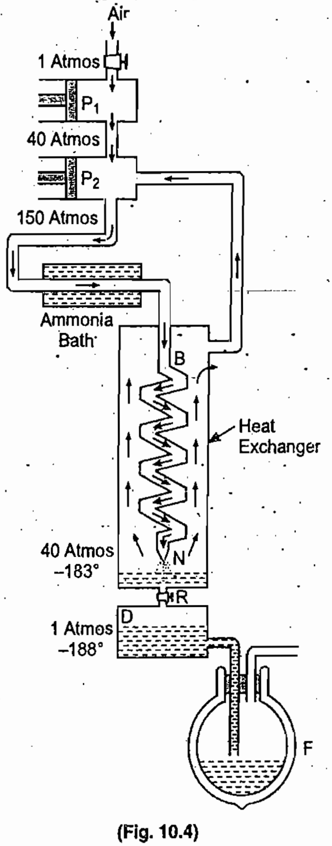
**Merits and Demerits :** The cascade method is more economical than other methods used for liquefying air (and oxygen) as it gives a larger return of liquid-air per unit of energy consumed. But it is a cumbersome method and hence not employed in the large scale preparation of liquid-air (and liquid-oxygen).

**Limitations :** The cascade process can liquefy gases upto nitrogen ($T_c = -147$°C). The gases next in serial order are neon ($T_c = -229$°C), hydrogen ($T_c = -240$°C) and helium ($T_c = -268$°C). These gases cannot be liquefied by the cascade process since there is no liquid which on evaporation will produce temperatures below the critical temperatures of these gases.

**Liquefaction of Air**

Modern methods for the liquefaction of air are based on the Joule-Kelvin effect which is made regenerative to produce progressive cooling of the gas until it liquefies. In 1895, Hampson in England and Linde in Germany used this phenomenon to construct air liquefiers.

**Linde's Air Liquefier** is illustrated in Fig. 10.4. Air, freed from carbon dioxide and water vapour*, is compressed to about 40 atmospheres by a pump $P_1$ and then to 150 atm by a second pump $P_2$. It is then passed through an ammonia-bath which removes the heat of compression. The compressed air is now sent down along a copper spiral B to a nozzle N where it is expanded to 40 atmospheres and cooled. This gas now flows upwards and cools the fresh gas coming through the spiral B and itself returns to $P_2$. The pump $P_2$ again compresses it to 150 atmospheres and sends it into the spiral B. As the process continues, the gas coming through B is cooled more and more. Ultimately, as it expands through N, its temperature falls to – 183°C at which it liquefies under the pressure of 40 atmospheres. The liquid-air is sent through a pressure-reducing valve R into the chamber D at – 188°C and 1 atmosphere pressure. From D it is collected in a Dewar flask F.



(Fig. 10.4)

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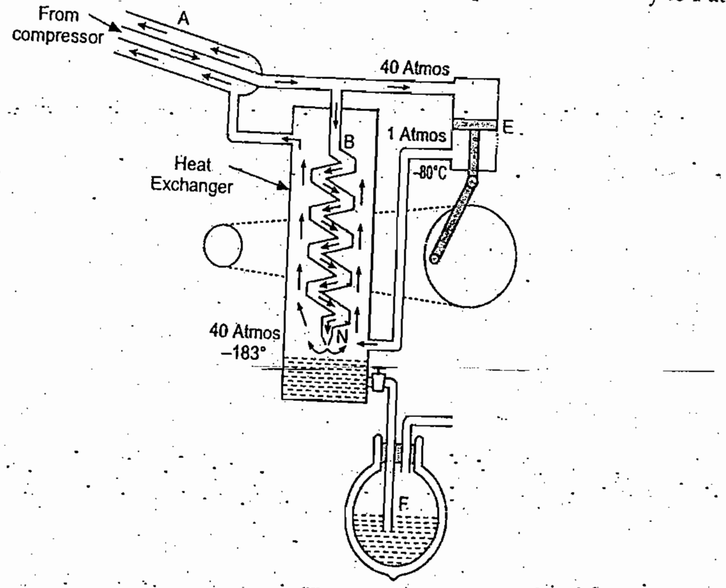
*The removal of carbon dioxide and water vapour from the air is necessary; otherwise these will soon solidify and choke the system.

**Claude**' in 1902 designed a liquefier in which a part of the compressed air is cooled by adiabatic expansion in an engine by doing external work. This cooled air cools the remaining air which then undergoes Joule-Kelvin expansion through a nozzle. The work obtained in the engine can be utilised in driving the pump which compressed the air, and hence this liquefier is thermodynamically more efficient than the Linde's liquefier.

Claude's liquefier is shown in Fig. 10.5 Air, freed from carbon dioxide and water vapour, is compressed to 40 atmospheres by a compressor (not shown) and sent along the inner tube of the condenser $A$. A part of this air (about 20%) goes down a long copper spiral $B$ to the nozzle $N$. The rest of the air goes to an expansion engine $E$ where it expands adiabatically to 1 atmosphere, doing external work. The air thus cooled to – 80°C is made to flow back through outer annular spaces between the spirals $B$ where it cools the incoming air passing down $B$. Finally, it is sent back to the compressor through the outer jacket of $A$ where it also cools the gas flowing from the compressor. The direct 20% air which is now cooled to – 80°C expands through the nozzle $N$ to 1 atmosphere and cooled to – 188°C and liquefies. The portion of air which does not liquefy rises up and returns to the compressor.



(Fig. 10.5)

A special problem with Claude's method is to find a suitable lubricant for the expansion engine since ordinary lubricants solidify at such low temperatures. Claude found petroleum-ether satisfactory which remains viscous upto – 160°.

**Use of Liquid Air :** An important laboratory use of liquid air is to cool the substances to very low temperatures at which their properties may be studied. It is also used in creating high vacuum by solidifying a gas less volatile than air. In chemical industries it is used for separation and purification of gases.

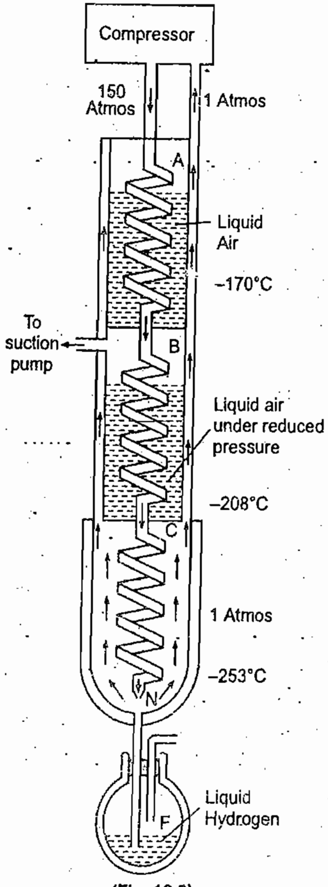
The constituents of liquid-air, such as oxygen, nitrogen, argon etc. can be easily separated. These constituents are used commercially. For example, oxygen is used in metal cutting such as breaking up old ships and other machines and fabricating new machinery. It is also employed in breathing apparatus in aeroplanes, diving suits and in mines. Similarly, nitrogen is used in the manufacture of ammonia and fertilisers. Inert gases like argon, neon, krypton separated from liquid-air have also important uses. Argon is used in gas-filled electric lamps, neon is used in discharge tubes required for illumination and advertising sign-boards.

**Liquefaction of Hydrogen**

Hydrogen could not be liquefied for a long time. Its critical temperature is – 240°C. No independent cooling agent can cool it to below this temperature. Hence the cascade process cannot be applied in this case.

The discovery of Joule-Kelvin effect opened a new field for the liquefaction of gases. Any compressed gas, *initially below its temperature of inversion*, is cooled when expanded through a fine nozzle. The cooling effect increases as the initial temperature of the gas decreases. It is remarkable that the temperature of inversion for a gas is much higher than its critical temperature. For hydrogen it is – 80°C. The gas is pre-cooled to below this temperature by liquid-air or liquid-nitrogen and then allowed to undergo Joule-Kelvin expansion. The cooling effect so produced is, however, not large enough to produce liquefaction. Consequently, the process of "regenerative cooing" is adopted.

**Hydrogen Liquefier :** Travers designed an apratus for producing large quantities of liquid-hydrogen. His arrangement is shown in Fig. 10.6. Pure hydrogen, free from dust, carbon-dioxide and water vapour is compressed to 150 atmospheres by a compressor, the heat of compression being removed by a cold water-bath (not shown). The cooled and compressed gas is sent into a spiral $A$ immersed in liquid-air where it is cooled to – 170°C. It is then passed through another spiral $B$ surrounded by liquid-air evaporating under reduced pressure. By this means the temperature of the hydrogen on leaving $B$ is reduced to – 208°C. The gas now passes through the spiral $C$ from which it expands through the nozzle $N$ to a pressure of 1 atmosphere and suffers Joule-Kelvin cooling. This expanded and cooled gas flows back over the spiral $C$ and round the outside of the liquid-air vessels, thus cools the incoming gas, and returns to the compressor. As the process continues, the hydrogen expanded through the nozzle is cooled progressively more and more, and ultimately liquefies at – 253°C at 1 atmosphere pressure. The liquid-hydrogen is collected in a Dewar flask $F$.



(Fig. 10.6)

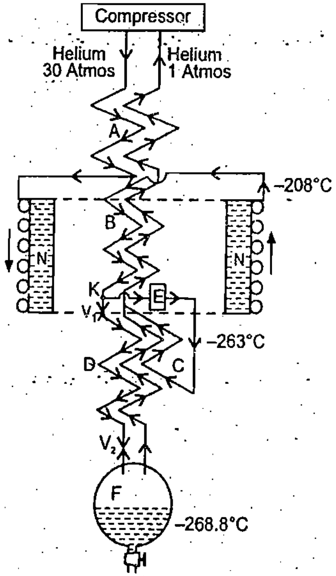
The hydrogen should be absolutely free from oxygen, nitrogen and other impurities, otherwise these will solidify before the liquefaction of hydrygen and block the plant.

**Liquefaction of Helium**

Helium was the last gas to be liquefied. All attempts made before 1908 to liquefy helium failed. The reason is obvious. The critical temperature of helium is as low as – 268°C. Hence it was necessary to cool it below – 268°C before it could be liquefied. In the system of cascade the lowest attainable temperature was – 218°C (by evaporating liquid-oxygen under reduced pressure.) Hence this method was not applicable to liquefy helium. Claude's method could also not be used to liquefy helium because there was no lubricant for the expansion engine which could resist solidification at such low temperatures.

K. Onnes, in 1908, pointed out that the temperature of inversion for helium was – 240°C and it was possible to cool it below this temperature by means of *liquid hydrogen* evaporating under reduced pressure. He actually developed a helium-liquefier in which he pre-cooled helium to – 258°C, and subjected it to Joule-Kelvin expansion and obtained liquid helium.

**Kapitza's Helium Liquefier :** Kapitza, in 1934, developed another helium liquefier using Claude's method in which both the adiabatic expansion and the Joule-Kelvin effect are utilised. He used a special expansion engine in which *no lubricant was used*. In this engine the piston was loosely fitted in the cylinder with a definite small gap between them.



(Fig. 10.7)

Kapitza's arrangement is shown in Fig. 10.7 in which the spirals carrying the helium gas are indicated by lines. The pure gas is first compressed to 30 atmospheres and then passed through the heat-exchanger $A$. It is then made to flow round a ring-shaped vessel $NN$ filled with *liquid nitrogen* under reduced pressure, where it is cooled to – 208°C, from there it passes through the heat-exchanger $B$. At a point $K$, the gas is divided into two parts : 8% of the gas passes through an expansion-valve $V_1$, and the remaining 92% to an expansion-engine $E$ which cools it to – 263°C. This cooled part flows back through the heat-exchangers $C$, $B$, $A$, and cools the incoming gas before returning to the compressor at 1 atmosphere. The gas which has passed through $V_1$ undergoes Joule-Kelvin expansion after which it flows through the heat-exchangers $C$ and $D$ and undergoes a second Joule-Kelvin expansion through the valve $V_2$ when its temperature falls to – 268·8°C. It is now partly liquefied and collected in the flask $F$. The gas which has not yet liquefied flows back through the heat-exchangers $D$, $C$, $B$, $A$ and returns to the compressor.

This liquefier is efficient and more economical than Onnes liquefier, because it uses liquid-nitrogen (as cooling agent) which is much cheaper than liquid-hydrogen used by Onnes.

## 10.5. Measurement of Low Temperatures

The techniques of accurate measurement of low temperatures are gaining importance day by day on account of the increasing use to which liquefied gases are put these days. The older methods are giving place to the new ones and a wholly new branch of physics "Low temperature thermometry" has come into being. A brief account of the various methods employed for the purpose is as follows :

**(i) Liquid Thermometers.** These thermometers can be employed for measuring moderately low temperatures. A mercury thermometer has its lower limit at – 39°C which is the freezing point of mercury. Below this mercury is replaced by alcohol with which we can reach upto – 112°C. Although alcohol is less visible than mercury, it is still superior because it expands seven times more than mercury for the same rise of temperature. The liquid thermometers can not carry us very far and are not reliable for accurate measurement. The only liquid thermometer that can be used down to – 190°C is a special type of thermometer containing distilled petroleum ether.

**(ii) Gas Thermometer :** The gas thermometers are better and can be regarded as the standard instrument for low temperature measurement. Dewar, Kemmarlingh Onnes and others have shown that these thermometers could be relied upon down to the liquefaction point of the gas used. The standard thermometers for the purpose are :

(a) *The constant volume hydrogen thermometer* which can be used to measure temperatures down to about – 253°C.

(b) *The constant volume helium thermometer* which can be safely used upto – 268·7°C (4·3K). Below this temperature the gas liquefies. A helium thermometer can, however, be used down to 1K when the pressure at which it is operated is below the vapour pressure of the liquid helium.

These thermometers are quite accurate but in practice are inconvenient to work with on account of being quite bulky and their slowness in adjusting themselves to the temperature of the bath :

**(iii) Resistance Thermometers :** These are much more convenient and can be used satisfactorily for low temperature measurements provided the element used is absolutely pure. Pure metals show a regular decrease of resistance with falling temperature, but even a slight trace of any impurity causes them to give inconsistent results.

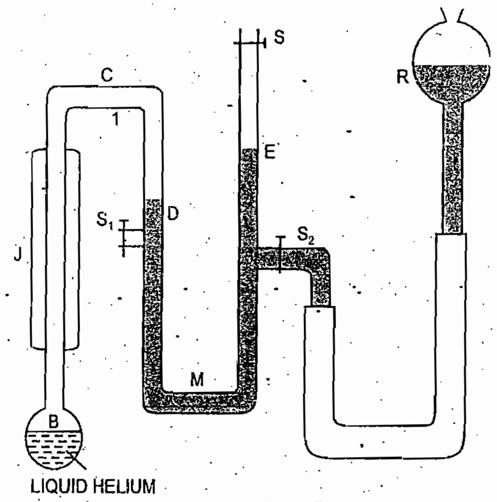
The most accurate method of measuring temperature *down to* – 100°C is to use a platinum resistance thermometer but below it, the thermometer becomes insensitive. Below – 190°C, the platinum thermometer can be used but is to be calibrated in terms of the gas thermometers at a number of points. Kammerlingh Onnes has shown that it is better to use a resistance thermometer of lead than one of platinum. He actually used a lead thermometer down to – 259°C. Below it, pure metal resistance thermometers become insensitive and so alloys are used instead of metals. An alloy of 5% lead in silver can be used from 7K to 3K. For still lower temperatures (upto 1K), constantan and phosphor-bronze have been emlpoyed. Actually unanealed phosphor-bronze is the best material to use in this region on account of its change of resistance with temperature being linear. The semi-conducting element germanium has also been used between 25K and 1K. *Carbon resistors have recently been found to be highly sensitive from 4K to below 1K.*

These thermometers, however suffer from two defects at very low temperatures. Firstly, they are disturbed by magnetic fields and secondly the super-conducting impurities cause the material to give inconsistent results.

**(iv) Thermoelectric Thermometers :** These too are quite sensitive and can be used for accurate measurement right down to very low temperatures. The iron.constantan and copper constantan couples are ordinarily used which develop a fairly large e.m.f. even at low temperatures. Iron-constantan couple, though sensitive, is not preferred as the iron is likely to be oxidized. Copper-constantan couple is frequently employed for temperatures upto – 255°C (18K), the accuracy being 0·05°C. Below 18K, couples of gold and silver are found to be better and much more sensitive. Using a thermo couple of an alloy of gold (with 2% cobalt) and an alloy of silver (with copper), temperatures *upto* 2K have been measured.

**(v) Vapour Pressure Thermometers :** For the measurement of extremely low temperatures, vapour pressure thermometers have been of great service. These are simple and highly sensitive and are indispensable *for the measurement of temperatures below* 2 K (the boiling point of helium). They are based on the principle that the vapour pressure of a liquid varies uniquely with temperature and increases as the temperature rises. Hence if the vapour pressure of a liquid could be measured at an unknow temperature, it may be found by applying theoretical formula or using a calibration curve.

The choice of the vapour dapends upon the temperature to be measured. Oxygen may be used for the tempetature range between 123K and 23K; neon between 27K and 24K; hydrogen between 20K and 11K and helium for temperatures below 5K. In fig 10.8 is shown a simple form of a *helium vapour pressure thermometer.* The apparatus which is constructed of glass, consists of a glass bulb *B*, containing liquid helium and helium vapour, connected by means of capillaries *C* to a mercury manometer *M*. An evacuated glass jacket *J* is attached to the tube *C* in order to prevent loss of heat. The level of the mercury in the manometer can be adjusted by raising or lowering the reservoir *R* containing mercury. Initially the reservoir *R* is moved until the mercury levels in limbs *D* and *E* of the manometer stand ~~below~~ the level of the ~~stop-cock~~ $S_1$. $S_1$ is then opened and connected to the vacuum pump to remove air form bulb *B* and capillary *C*. After some time $S_1$ is closed so that there is only liquid helium in *B* and its saturated vapour in capillary *C*. The bulb *B* is now put in a bath at a constant low temperature to be measured. The difference in mercury level of the two arms *D* and *E* gives the pressure of the saturated helium vapour in *C* from which corresponding temperature can be found by formulae which represent the vapour pressure as a function of temperature. *For temperatures above* 2·19K Schmidt and Keesom, in 1959, put forward the following formulae :



(Fig. 10.8)

$$\log_{10} p = \frac{4{\cdot}7921}{T} + 0{\cdot}00783\,T + 0{\cdot}0017601\,T^2 + 2{\cdot}6730$$

$$\log_{10} p = \frac{4{\cdot}7948}{T} + 0{\cdot}0343 \log_{10} T + 0{\cdot}018024\,T^2 + 2{\cdot}6775,$$

where *p* (cm. of Hg) is the vapour pressure at the ice point. For the temperature ranges *between* 2·19 K and 16 K, Lignac suggested the following formula

$$\log_{10} p = -\frac{3{\cdot}1189}{T} + 2{\cdot}5 \log_{10} T - 5{\cdot}9981 \times 10^{-5}\,T^2 + 1{\cdot}1958$$

To calculate the *temperatures below* 1·6 K, Bleaney and Simon obtained the following formula

$$\log_{10} p = -\frac{3{\cdot}117}{T} + 2{\cdot}5 \log_{10} T + 1{\cdot}196 + \Delta,$$

where the quantity $\Delta$ represents a small correction term and its value is given by a graphical representation.

Another method to determine the temperature corresponding to any value of the vapour pressure is to draw a graph between temeprature and vapour pressure of helium which can be extrapolated either way to give the required temperature. In this way temperatures upto 0·75 K have been measured.

Thus a vapour pressure thermometer is very sensitive and when used properly is an instrument of high precision but it suffers from the disadvantage that a given vapour pressure thermometer can be used only for a small range.

**(vi) The Magnetic Thermometers** *(For measuring temperature below* 1 K*)*. The measurement of the temperature below 1 K is a matter of great difficulty, beacuse, it becomes impossible to use a helium gas thermometer in this range. Moreover, the vapour pressure of helium decreases exponentially to a very small value and consequently it can no longer serve as a standard of measurement. The principal temperature measuring device below 1 K is a magnetic thermometer whose action is based on *Curie's law* according to which the susceptibility $\chi$ of a paramagnetic substance is inversely proportional to its absolute temperature *T i.e.*, $\chi = \frac{C}{T}$ which C is a constant.

Although this rule is at best only a first approximation, yet it has got a great advantage that the method employed increases in sensitiveness with a fall in temperature. Hence if the susceptibility $\chi$ which becomes very high at extremely low temperatures be measured, the corresponding temperature can be obtained.

The *principle underlying the method* is as follows : Certain salts of the iron group and the rare earth, *e.g.*, gadolinium sulphate $[Gd_2(SO_4)_3, 8H_2O]$ and chromium-potassium alum, are paramagnetic *i.e.*, they may be considered to be made up of a large number of elementary molecular magnets lying inside them in a disorderly fashion in neutralizing groups. When a magnet is brought near to them, the axes of the elementary magnetic atoms tend to set themselves parallel to the force applied or in other words they tend to become magnetising magnets. This, however, is resisted by the molecular rigidity of the substance ~~which decreases, with a fall in~~ temperature. Thus as the temperature is lowered, the resistance to magnetization decreases or in other words its susceptibility to magnetization increases. In this way, other conditions remaining the same, *the degree of magnetization of the substance is a measure of its temperature.* If we can determine the susceptibility of the substance, its temperature may be read from the graph obtained experimentally before hand.

*The experiment* consists in measuring the susceptibility of a suitable paramagnetic salt by surrounding the apparatus containing it by two cells–a primary and a secondary. An alternating current is passed through the primary coil. Consequently a current is induced in the secondary which depends upon the suceptibility of the salt. This current is then amplified and recorded by a sensitive galvanometer which gives a measure of the susceptibility. The measured susceptibility above 1 K is directly plotted against temperature as read by helium vapour thermometer. The curve is then extrapolated below 1 K and thus the temperatures can be read directly from the experimental value of the susceptibility. Alternatively, sometimes the galvanometer used to detect secondary current is calibrated to read the temperature of the substance directly. The temperature will, however, be accurate only when the susceptibility scale is some how related to the gas thermometer scale at the low temperatures.

The temperature obtained by the application of Curies's law in the manner described above, do not give the exact values of temperature because the law itself does not hold in this region. From these measurements, assuming the truth of Curie's law, a so-called magnetic temperature $T^*$ is obtained which is then, converted to the thermodynamic or Kelvin temperature as discussed in the next section.

## 10.6. Conversion of Magnetic Temperature to Kelvin Temperature

It is important to determine the relation between the magnetic temperature $T^*$ and the thermodynamic temperature *T*. Experiments have been done and a number of methods have been proposed to determine this relation between the Curie scale and the Kelvin scale. We shall discuss here a method used by Kurti and Simon the principle of which is to take a paramagnetic salt through a thermodynamic cycle and actually measure the heat absorbed by the metal when it is irradiated with $\gamma$-rays in order to raise its temperature. The method is as follows :

From eqn. (5) § 10·3, for negligible change in volume for small change in temperature, we have

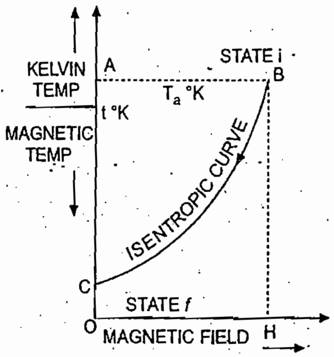
$$dQ = T\,dS = dU - H\,dI. \qquad \text{...(1)}$$

Suppose the field is zero ($H = 0$) and kept constant, then

$$T = \left(\frac{\partial U}{\partial S}\right)_{H=0} = \frac{(\partial U/\partial T*)_{H=0}}{(\partial S/\partial T*)_{H=0}}, \qquad \text{...(2)}$$

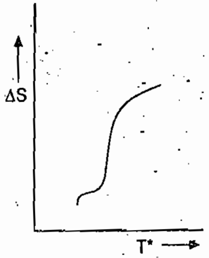
where $T$ is the temperature expressed on Kelvin scale. Its value is obtained by determining the quantities involved in equation . It is accomplished by performing three experiments in the following way :

(1) A quantity of a paramagnetic substance is taken at a known temperature $T_i$ (above 1 K) measured with the help of a helium vapour-pressure thermometer. The paramagneitc substance is slowly (isothermally) magnetized during which the entropy increases from $S_A$ (at point $A; T = T_i, H = 0$) to $S_B$ (at point $B, T = T_i, H = H_i$) as shown in fig. 10.9. The increases in entropy $S_B - S_A \left(= \frac{\Delta Q}{T_i}\right)$ can be measured directly by determining the heat evolved $\Delta Q$ in the magnetisation.



(Fig. 10.9)

(2) Then the substance is demagnetized adiabatically from the state $i$ at $B$ ($T = T_i; H = H$) to the state $f$ when the point $C$ is reached when $H = 0$. The process is isentropic ($BC$ in fig. 10.9) but there is a fall in temperature. Let the temperature at point $C$ be $TK$ or $T_f*$ (magnetic) as calculated from susceptibility measurement. This temperature $T_f*$ as well as the entropy change $S_C - S_A = S_B - S_A = \Delta S$ would depend upon the applied field $H$. Using different initial fields $H_i$, the quantity $S_C - S_A = \Delta S$ is determined for different $T_f*$ as shown in fig. 10.10. The enables the calculations of $\left(\frac{\partial S}{\partial T*}\right)_{H=0}$ required in equation (2).



(Fig. 10.10)

(3) Finally the paramagnetic substance is heated by $\gamma$-rays from $T_f*$ at zero field ($H = 0$) to some other $T*$ and the heat absorbed is measured. Then from equation (1), since $H = 0$, we have

$$\left(\frac{\partial Q}{\partial T*}\right)_{H=0} = \left(\frac{\partial U}{\partial T*}\right)_{H=0}$$

Thus knowing $\delta Q$ and $\delta T*$ the quantity $\left(\frac{\partial U}{\partial T*}\right)_{H=0}$ is found out. By substituting of these quantities in equation (2), the magnitude of Kelvin temperature $T$ is known.

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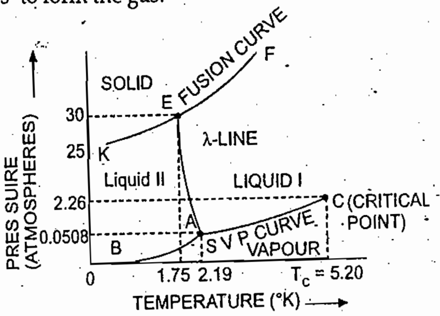
## 10.7 Helium I and II.

Helium was the last gas to be liquefied on account of having the lowest critical temperature (–268°C) of all known gases. It is a colourless transparent very volatile liquid and has the lowest boiling point of 4·2 K at a pressure of 1 atmosphere. It has no normal freezing point and shows quite a few other properties which single it out as almost an exceptional and unique substance.

A peculiarity arising in the helium system is that the solid can not be obtained merely by lowering the temperature of the liquid. Kamerlingh Onnes failed to solidify helium despite the fact that he reached a temperature of 0·84 K. Solid helium was first obtained by Keesom who subjected liquid helium to very high pressure. The solid is obtained at a pressure of 250 atmospheres at 4·2 K while only under 23 atmospheres at 1·1 K. Thus it is necessary to increase the pressure simultaneously while lowering the temperature of the liquid. Later investigations revealed that at high enough pressure, solid helium could be obtained in equilibrium with the vapour at temperatures well above the critical point of the gas. Thus at 5800 atmospheres, solid helium is obtained at a temperature as high as 42 K. This is the curious property of the helium system that although liquid can not exist above the critical temperature (5·2 K). solid can exist if sufficiently great pressure is applied. Hence at high enough pressure, the melting point exceeds the critical temperature and so the solid helium 'melts' to form the gas.

The phase equilibria of helium are represented diagrammatically in fig. 10.11 in which all portions are not on the same scale. A study of the plase diagram shows that it is entirely different from that of all other substances. The fusion curve (or the solid-liquid phase ~~line)~~ and the saturated vapour pressure curve (or the liquid-vapour phase line) do not meet in a point, as in the case of other substances and if we pursue the vapour pressure curve down to lower temperature it is found that the vapour and the liquid continue in equilibrium down to the absolute zero. Thus the three phases solid, liquid and vapour are never found to coexist or in other words *helium has no triple point* in the conventional sense of terms. This is certainly an extraordinary thing and shows that helium is a unique liquid.

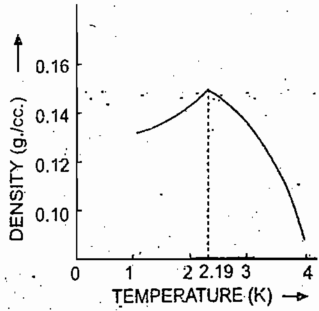


(Fig. 10.11)

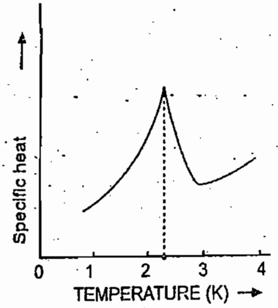
The curve *FEK* (Fig. 10.11) shows the influence of pressure on the melting point. It proceeds upwards to the right, takes a sharp bend at $E$ and flattens out at low temperatures meeting the pressure axis at 25 atmospheres indicating that *helium will not solidify even at* 0 K *if it is not subjected to pressures exceeding 25 atmotpheres.* The S.V.P. curve, on the other hand, appears to proceed normally to the left towards the origin ($p = 0, T = 0$) but to the right it terminates at critical point C corresponding to a temperature of 5·2 K and a pressure of 2·26 atmospheres. The point $A$ (2·19 K) is known as the $\lambda$ *point* of liquid helium under its own pressure.

For helium in the liquid phase, tnere is a *phase transition* called the $\lambda$– transition, which divides the liquid state into two phases, helium I and helium II. The fusion curve and S.V.P. curve are joined by the $\lambda$*–line* running between the points $E$ ($T = 1·75$ K, $p = 30$ atmos) and $A$ ($T = (2·19$ K and $p = 0·05$ atoms) with helium I to its right and helium II to its left. Thus helium is present in the liquid form on either side of the $\lambda$–line. Kamerlingh Onnes, in the course of his investigations found that liquid helium shows an extremely interesting behaviour if it is cooled below its boiling point (4·2 K) to about 2·18 K. He found that the density passes through an abrupt maximum at 2·19 K decreasing slightly thereafter as shown in fig. 10.12. The density first rises with the fall of temperature from 4·2 K upto 2·19 K reaches a maximum value of 0·1462 at 2·19 K and then decreases with the decrease of temperature. Thus below 2·19 K, the liquid helium which was contracting when cooled now begins to expand.

The specific heat of liquid helium at constant volume $C_v$ has been plotted in fig. 10.13 . The specific heat increases, upto 2·19 K, and at this temperature there is a sudden and abnormal increase in its value. Beyond 2·19 K the specific heat first decreases and then increases. The dielectric constant also behaves in a similar manner. The specific heat temperature graph at 2·19 K looks like the Greek letter lambda (λ) and hence this *temperature* (2·19 K) *at which specific heat changes abruptly is called the λ–point.* There is a fundamental ~~difference~~ between ~~the natures~~ of the liquid above and below the λ– point (2·19 K). Liquid helium above 2·19 K which behaves in a normal way is called liquid helium *I* and that exiting below this temperature is called the liquid helium *II* because of its abnormal properties. No heat is evolved or absorbed during the transition from one form of helium to another. In other words, no latent heat is involved in the transition *He I* ⟶ *He II* which suggests that :



(Fig. 10.12 (a))



(Fig. 10.12 (b))

(a) the entropy is continuous across the curve *i.e.*, the entropy of *He II* is practially the same as that of the *He I* and

(b) there is no change of density during transitions, *i.e.*, the density of both types of liquid is about the same.

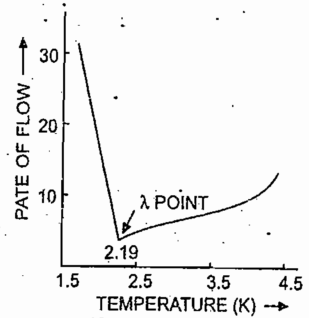
While the viscosity of liquids increases with decrease in temperature, that of liquid helium *I* decreases, in this respect *He I* resembles a gas. The viscosity of *He II* is almost zero and it can flow rapidly through a narrow capallaries. Liquid helium *I* is a normal liquid while helium *II* presents a very anomalous behaviour in the sense that its thermal couduetivity is abnormally high, its internal friction is practically zero and that when it is forced through a capillary, the emerging liquid cools while that which remains behind warms up. The densites of the two liquids are about the same, somewhere in the neighbourhood of 0·1462 K which is far less than that of the lightest of other liquids like ether and gasoline.

## 10.8. Some Peculiar Properties of Helium II.

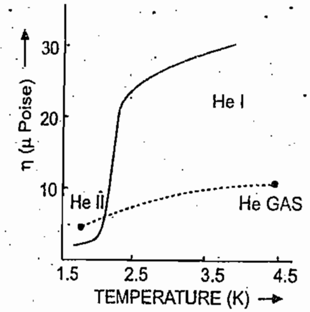
In many of its properties, the behaviour of liquid helium *II* is quite unlike that of any other substance. It behaves strongly and shows some very unique properties. Some of the more interesting ones are given below :

(1) **Extreme fluidity.** One of the most significant properties of liquid helium *II* is that its viscosity is abnormally low even less than that of hydrogen gas and that its rate of flow through capillaries is independent of the pressure difference across them. According to Poiseuille's law the rate of flow of liquid through a capillary tube or an annular space is inversely proprtional to the viscosity. If the rate of flow of liquid helium through a fine annulus is measured as a function of temperature, the curve poltted in Fig. 10.14 (a) is obtained. At the λ–point the rate of flow increases abruptly and below it the flow is found to be extra-ordinary large thus proving the experimental evidence of a very low viscosity of liquid helium *II*. The values of the viscosity coefficient are plotted in Fig 10.14 (b) as obtained by the oscillating disc method It may be noted that there is a sharp discontinuity at the λ–point and in course of the curve on the two sides of it is different. The viscosity falls by a factor of about ten on passing through the λ–point. In fact Kapitza found that

$$\frac{\eta \text{ for liquid } He\ II}{\eta \text{ for liquid } He\ I} \approx 10^{-3}.$$



(Fig. 10.13)



(Fig. 10.15)

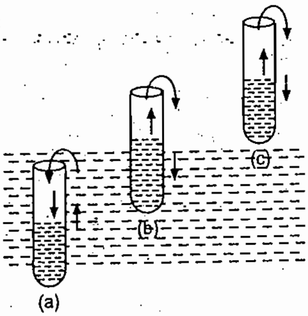
Thus liquid *He II* has practically zero viscosity and can flow rapidly, almost without resistance, through narrow tubes. that is why the liquid *He II* is called a *superfluid*, a new frictionless state of matter. The properties associated with it have been characterised as *superfluidity*.

(ii) **High heat conductivity.** Heat conductivity of liquid helium I is quite normal of the order of $10^4$, which in turn is of the same order as for gases at ordinary temperatures. But *He II* is found to have an extra ordinary high coefficient of thermal conductivity. The heat transported per unit temperature gradient is several 10 times as great as that in copper at room temperature, *He II* is said to be about 800 times more conducting than copper and about $13{\cdot}5 \times 10^6$ times more than liquid *He I*, the absolute value being 820 cals $cm^{-1}\ deg^{-1}\ second^{-1}$. It is also found that the heat flow is not proportional to the temperature gradient.

Daunt and Mendelssohn, in 1947, pointed out the striking analogy between the unimpeded flow of helium atoms in liquid helium *II* and phenomenon of *super conductivity*. No trace of electrical resistance is observed in a material which is in a superconducting state, *i.e.*, the electrons move freely in the conductor unimpeded by any electrical resistance.

(iii) **Formation of films over solid surfaces.** Liquid helium *II* can creep along solid surfaces in the form of a highly mobile film generally known as the Rollin (sometimes also called Rollin-Simon) film which is of the order of several hundred atoms thick. The properties of the film were investigated by Daunt & Mendelssohn who observed the following remarkable behaviour of helium.

If a tube containing helium *II* be placed in a helium *II* bath, it is observed that :



(Fig. 10.15)

(a) If the liquid level inside the tube is lower than that outside, the liquid helium from outside starts creeping into the tube along its surface in the direction of arrows shown in Fig. 10.15 (a) The process continues till the levels, inside and outside the tube, are equalized.

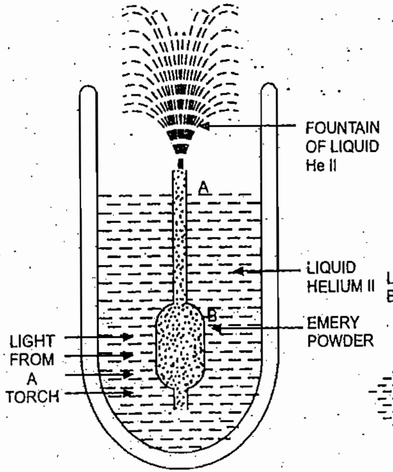
(b) If the tube be raised up so that the level of helium inside it is higher than that outside it, the liquid from inside the tube starts creeping out of it along its surface in the direction of arrow [Fig. 10.15 (b)] till the two levels again become the same.

(c) If the tube is lifted entirely out of the *He* bath, the liquid inside the tube now creeps out along the surface of the tube, collects at its bottom in the form of drops and falls into the liquid below till the whole liquid inside the tube is drained out [Fig. 10.15 (c)] and the tube is empty.

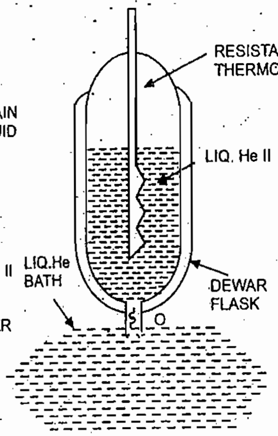
All these experiments indicate that the liquid helium II seeks the lowest level, but the rate of transfer of the liquid is independent of the difference in level and the nature of the surface. It, however, depends upon the temperature and the perimeter of the surface over which it has to pass.

Thus liquid, *He II* seems to defy gravity by creeping out of the containing vessel by coating the walls with a thin film of the liquid.

**(iv) The 'Fountain' and 'Mechano-caloric' Effect.** Another set of peculiar properties of liquid *He II* is manifested in the 'Fountain' and 'Mechano-caloric' effects. The fountain effect, which is illustrated ~~in Fig.~~ 10.16 shows that heat locally supplied to the system produces a pressure difference. The phenomenon was discovered by Allen and Jones, in 1938 but the apparatus shown in Fig. 10.16 is one due to Allen and Misener. In the apparatus, *He II* is taken in a tube *AB* open at both the ends and kept inside a Dewar flask also containing liquid helium II. The upper part *A* of the tube is in the form of a capillary and kept projecting out of the liquid bath while the lower part *B* with a small opening *O* at the bottom is packed with fine *emery powder*. The interspaces between the powder particles provide fine *capillaries* for the liquid *He II* to flow into the tube. When heat radiations from an ordinary torch are allowed to fall on the powder, liquid *He* is found to spurt out of the capillary tube in the form of a fountain which has been observed as high as 30 cm. This is a consequence of absorption of energy by emery powder.



(Fig. 10.16)



(Fig. 10.17)

The mechano-caloric effect is illustrated in Fig. 10.17 which is opposite to the fountain effect and shows that the flow of liquid gives rise to a temperature difference. A Dewar flask is filled partly with the liquid helium II and provided with a small hole *O* at the bottom which is plugged by fine powder. A resistance thermometer is introduced in the Dewar flask and then its top is closed. If now the flask is above the level of the liquid *He* bath, the liquid from the flask drains out through the power and its temperature is found to increase by about 0·1°C If on the other hand, the Dewar flask is dipped into the bath and the liquid helium is allowed to flow into it through the opening *O* via the powder, the temperature inside the flask is observed to decrease.

## 10.9. Attempted Explanation of the Properties of Liquid Helium II :

In order to account for the peculiar properties of liquid helium II, it is generally regarded as a mixture of two different kinds of liquids. One of these is composed of normal atoms with normal viscosity while the other is composed of those atoms which are in the state of lowest energy (zero point energy) with zero entropy and capable of moving through the normal atoms without friction or viscosity. According to the current views, this part of the liquid consists of 'condensed' atoms and markes its first appearance at λ point. Such a liquid is called a *superfluid* and its property to flow through capillary tubes without showing any resistance is called *superfiuidity.* On the lowering the temperature, the superfluid grows in quantity at the expense of normal component until at absolute zero, the whole liquid is made up of super fluid.

Let us now discuss the different theories put forward to explain the behaviour of liq. *He II* :

## 10.10. Landau's Theory

A theory of liquid helium II was put forward by Landau in 1941 in order to account for its extra ordinary properties. He postulated that the energy levels of liquid helium II (liquid as a whole, not of individual helium atoms) consisted of two sets of overlapping energy states one representing the quanta of sound or *phonons* and the other for quanta of vortex (whirling) motion or *rotons*. These quanta behave like gases and interchange energy with the walls. The lowest phonon levels is assumed to be below the lowest roton level separated from it by a finite energy gap. On the basis of these assumptions. Landau set up a quantum hydrodynamics and could explain the anomalous results of liquid *He II*.

According to Classical Mechanics all bodies must be solid at absolute zero temperature but in practice helium can remain liquid down to absolute zero. This is no account of the fact that the interaction between the helium atoms is unusually weak and it has got a large zero point energy. Morever at very low temperatures at which quantum effect become very important*, it may be called a *quantum liquid* and it is not necessary that solidification must take place. Accordingly Landau proposed the theory of a quantum liquid by considering its departure from the known theory of solids rather than that of an ideal gas.

As the temperature is increased above 0K thermal agitation begins to appear and the *elementary excitations* arise in liquid helium. These elementary excitations behave like *quasi particles* moving in the volume occupied by the body and possessing definite energies and momenta. For example, the excited states of a crystal whose atoms perform small vibrations about equilibrium position can be considered as a set of phonons moving inside the system. Phonons are quanta of

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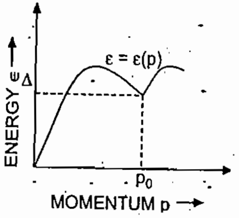
*Quantum effects become important when the de Broglie wavelength corresponding to the thermal motions of the atoms becomes comparable with the interatomic spaces. In liquid helium this takes place at 2·3 K.

sound waves which in a crystal can be either longitutinal or transverse. We shall, however, assume that liquids can support only longitudinal vibrations. We also assume that these waves propagating through the fluid constitute the lowest excited states, they carry energy and momentum and have their amplitudes quantized. They vaguely resemble the photons, the light quanta and can be treated mathematially in the same way as particles.

Now, when the temperature is low, the number of elementary excitations is sufficiently small and we can neglect the interactions between these quasi particles. It means that their energies combine additively and the assembly of these quasi particles may be regarded as an ideal gas. One of the possible types of energy spectrum of low excited states of a quantum liquid (a Bose-type spectrum) is characterized by the fact that the elementary excitations may appear and disappear one by one. But the angular momentum of any quantum system (here the liquid as a whole) can change only by a whole number. Hence the elementary excitations which occur singly must have an integral quantum number and so obey Bose-Einstein statistics. Based on these ideas, Landau postulated the energy spectrum of excitations to have the form as shown in fig. 10.18. Every quantum liquid consisting of particles which obey Bose statisties will have an energy spectrum of this type.



(Fig. 10.18)

The elementary excitations with small momenta $p$ or large wavelength $\left(\lambda = \frac{h}{p}\right)$ correspond to the longitutinal sound waves in the liquid and are known as *phonons*. These are the excitation of lowest energy and are simply quantized sound waves. These energy $\varepsilon(p)$ near the origin (*i.e.*, with small $p$) is a linear function of the momentum $p$ *i.e.*,

$$\varepsilon(p) = up$$

where $u$ is the speed of sound is the liquid.

For large values of momentum, the function $\varepsilon(p)$ cases to be linear. It first rises, reaches a maximum, then decreases for a certain value $p = p_0$, becomes minimum and again increases. The shape of the curve after the first maximum, may not be the same for all the liquids as it depends upon the law and nature of interaction between the molecules in the liquid. For very large momenta, the function $\varepsilon(p)$ can not exist at all since elementary excitations with too large momenta are unstable and decompose into several excitations with smaller momenta and energies.

The elementary excitations in the neighbourhood of $p = 0$ are called as *phonons* and those in the neighbourhood of $p = p_0$ are called as *rotons*. There is a finite energy gap $\Delta$ between the phonons and rotons levels. The energy of rotons is given by

$$\varepsilon = \Delta + \frac{(p - p_0)^2}{2\mu}.$$

where $p_0$ is a constant and $\mu$ is the effective mass of rotons. The empirical values of the constants $\Delta$, $p_0$ and $\mu$ are

$$\Delta = 8{\cdot}5\ K, p_0 = 2{\cdot}5 \times 10^{-19} \text{ g-cm./s. and } \mu = 2{\cdot}1 \times 10^{-24} \text{ g.}$$

Now knowing the energy spectrum of excitations, we can calculate the various thermodynamic quantities of liquid helium at different temperatures. At temperatures close to absolute zero, all the elementary excitations in the liquid have low energies and are practically phonons. Debys's theory can then be used directly for calculating the specific heat of the quantum liquid $He^4$. The only difference in this case in that wheras there are three possible directions of polarization of elastic waves in a solid (one longitudinal and two transverse), there exists only one (longitudinal) in case of liquid. Thus while applying Debye's theory we shall consider only the longitudinal component and write the expression for $\nu_m$ (the maximum of all the possible frequencies) as

$$\nu_m^3 = \frac{9N}{4\pi V} c_l^3$$

So that
$$\frac{\Theta}{T} = \frac{h\nu_m}{kT} = \frac{h'}{kT}\left(\frac{9N}{4\pi V}\right)^{1/3} c_l$$

Putting this value of $\frac{\Theta}{T}$ in the equation for specific heat;

$$C_v = 3\,Nk \, . \, \frac{12\pi^4}{15}\left(\frac{T}{\Theta}\right)^3$$

we get,
$$C_v = \frac{12\,Nk\,\pi^4}{4}\left(\frac{kT}{h}\right)^3 . \frac{4\pi V}{9N} . \frac{1}{c_l^3} = \frac{16}{15}\pi^5 k\left(\frac{kT}{h}\right)^3 V \frac{1}{c_l^3}.$$

Replacing $c_l$ by $u$ in case of helium and putting $(h/2\pi = \hbar)$, we get the specific heat of liquid helium at low temperatures

$$Cv = \frac{2\pi^2 k}{15(\hbar u)^3} V (kT)^3.$$

Thus, the specific heat is proportional to the cube of the temperature. But actually above 0·7 **K** the specific heat increases much more rapidly and hence phonons are supposed to be supplemented by some other modes of excitations which set in as the temperature increases. Classical hydrodynamics provides such a mechanism in vortex motion. The vortices in a non-viscous liquid have a high stability and travel in straight lines at constant speed. The quasi-particles corresponding to this type of motion are called rotons. They have a certain minimum energy of formation and can not be excited at the lowest temperatures. The roton energy always includes the quantity $\Delta$ which is large compared to $kT$ at very low temperatures for a 'roton gas' to be considered. Hence in the description of rotons, Boltzmann distribution (instead of Bose distribution) can be applied with sufficient accuracy. Accordingly, the roton contribution to the specific heat is calculated to be

$$C_r = k\,N_r\left[\frac{3}{4} + \frac{\Delta}{kT} + \left(\frac{\Delta}{kT}\right)^2\right]$$

Thus the temperature dependence of the roton part is essentially exponential. Hence at very low temperatures, the roton part is less than the phonon part, while at high temperatures the situation is much opposite and the roton contribution is greater than that of the phonons.

On the basis of this theory many of the properties of liquid helium II have been explained. It has provided an account of the thermodynamical properties of liquid helium but it does not provide a satisfactory explanation of the phenomenon at the lambda point. A new form of wave motion in liquid helium called the *second sound* postulated by Landau was demonstrated in 1944 by Pesh Kov and the variation with temperature of the speed of second sound, its attenuation and the viscosity of liquid helium have been explained on this basis. Various experiments made in the last two decades have shown without doubt the existence of rotons in helium and proved the Landau's approach is a correct one.

## 10.11 London's Theory.

An equally reasonable point of view was developed from quantum statistical mechanics by London. He suggested that the unusual properties of the liquid helium II can be explained in terms of the condensation of a Bose-Einstein gas. At low temperatures, there is a tendency of helium atoms to cluster in low energy states. This is the so called condensation phenomenon representing a peculiar type of quantum condensation and is known as *Bose–Einstein condensation*. This is a phenomenon that occurs not in ordinary space like the familiar condensation but in a momentum space where the condensed particles possess zero-point energy and momentum. London visualizes the formation of liquid helium II from liquid helium I at the λ–point as a Bose-Einstein condensation. Thus according to him, helium II is a liquid analogous to a Bose-Einstein gas and the λ–transtion in liquid helium is the counterpart of the Bose-Einstein condensation.

The condensed particles in the lowest state have no heat content as they possess only the zero-point kinetic energy and no extra energy. These particles have the property of zero entropy and zero viscosity and have been identified by London as the *superfluid*. The particles which lie in the excited states have been identified by him as the *normal* fluid. The critical temperature at which Bose-Einstein condensation occurs is given by

$$T_0 = 3{\cdot}528\, n^{2/3} \left(\frac{2\pi\hbar}{m}\right)^2$$

In this expression, if we substitute the values of $n$ (number of particles per unit volume) and $m$ (~~molecular~~ mass) correspond~~ing to He~~ *II*, we get $T_c = 3{\cdot}12$ K which is of the same order of mangnitude as the observed lambda point (2·19 *K*) of helium.

London calculated the specific heat due to such a condensation. It shows a peak which does not resemble the λ–point but as London rightly pointed out that liquid helium is not an ideal gas because it exerts Vander Waal's forces and its molecules interact with each other continuosly.

Attempts have been made to introduce modifications in London's theory in order to achieve a better agreement with the observed peculiar properties of liquid helium.

## 10.12 Tiszas's two fluid model.

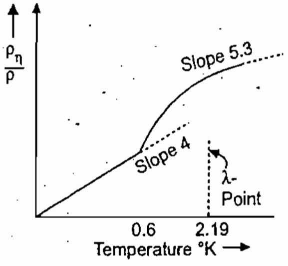
The phenomenological theory of Tisza redescribes both Landau's and London's points of view in picturesque language. Tisza introduced the two-fluid hypothesis according the which liquid helium consists of two independent components, normal fluid and a super fluid. *The normal fluid has energy in excess of the zero point energy, behaves as an ordinary liquid and possesses no unusual properties except that it is still liquid at low temperatures. The super fluid, on the other hand, possesses only the zero point energy and shows some very peculiar properties. The super fluid has zero entropy and viscosity and flows without resistance through channels.* If fact, the narrower the bore, the freer its flow through it. This the reason for calling it superfluid. the normal component is identical with helium I but the super fluid one consists of 'condensed' atoms. It begins to be formed at the λ–point but its percentage goes on increasing as the temperature is lowered until at absolute zero all the atoms go into the superfluid phase. Thus relative concentrations of normal and superfluid components varies with temperature.

The exact nature of these fluids is not specified in Tisza's two fluid model. The total mass density ρ and the mass current ρ*V* of the system are defined by

$$\rho = \rho_n + \rho_s,$$

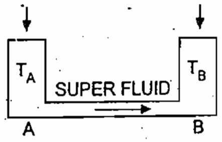
$$\rho V = \rho_n v_n + \rho_s v_s,$$

where the subscripts $n$ and $s$ refer to normal fluid and superfluid respectively. At the λ–point all the atoms are normal and hence $\rho_n/\rho = 1$, while at absolute zero whole liquid is made up of superfluid and $\rho_n/\rho = 0$. Thus, $\rho_n/\rho$ increases markedly as the temperature rises. The variation of normal fluid concentration $(\rho_n/\rho)$ with temperature has been plotted in fig. 10.19 on the basis of measurements made by Andronikashvilli and others. It may be seen that $\rho_n/\rho$ varies as the fourth power of $T$ upto 0·6 K beyond which the variation is more complicated. The heat capacity and the thermal conductivity of liquid helium II also change abruptly their temperature dependence at 0·6 K. It leads to supposition that at temperatures below 0·6 K, only phonons play a significant role.



(Fig. 10.19)

With these assumptions and thermodynamics many properties of liquid helium II can be explained. As a matter of fact, the existence of mechano-caloric effect, the fountain effect and second sound were predicted by Tisza before they were experimentally established. For example, if two vessels *A* and *B* in fig 10.20 are connected through such a thin tube that only the superfluid can pass, then on applying pressure on the liquid in *A* some superfluid will flow to *B*. As there is no entropy transport, it will increase the entropy in *A* and decrease in *B*. As a result $T_A$ will increase and $T_B$ will decrease. This is *mechano caloric effect*. Moreover a decrease $T_B$ results in a *fountain* of super fluid from *A*. This is the so called *fountain effect*.



(Fig. 10.20)

As $\rho_n/\rho$ increases with an increase in temperature, a temporary scarcity of superfluid atoms may be produced in a small region of a vessel having liquid *He II* by raising the temperature of that region. Consequently, super fluid atoms diffuse into the medium. This motion of super fluid atoms relative to normal atoms explains the abnormally high heat conductivity of *He II*.

Equally an explanation can also be given for the anomalous results on viscosity. When liquid He II flows through a capillarly, it is only the superfluid that pass (because it is non-viscous $\eta = 0$) and the normal liquid is held stationary by the walls and does not take part in the flow. Consequently, the fluid that comes out in these experiments is colder than that which remains behind, which is actually the case. Moreover, as there is no gradient in the velocity of the normal fluid, no viscous effects are observed and thus the viscosity becomes abnormally low.

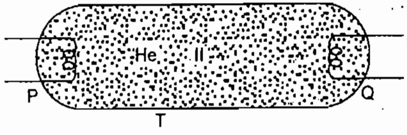
Although the ideas developed by Tisza have proved to be of great importance for the ultimate understanding of the problem, it is unsatifactory for two reasons :

(a) It has yet no molecular basis to explain the nature of the two fluids.

(b) It is incomplete (even phenomenologically) as it does not provide hydrodynamic equations. The description of Andronikashvilli experiment is also not unambiguous.

## 10.13 Second Sound

The usual sound (first) is a pressure wave; but *second sound is a thermal* (or entropy) wave. It was first predicted by L. Tisza and observed by V.P. Peshkor using a continuous wave resonance technique. In the arrangement consists of a tube *PQ* containing helium II. The periodic heat is produced



(Fig. 10.21)

at end $P$ and detected by the thermometer coil at end $Q$.

Tisza assumed the two types of interpenetrating fluids (normal fluid and superconducting fluid) do not resist the motion of each other. Due to heat wave produced, a temperature gradient is established across the helium column. Tisza further assumed that this temperature gradient tends to reduce by a current of normal fluid ($\varepsilon > 0$) in the direction of falling temperature and a current of superfluid ($\varepsilon = 0$) in the opposite direction, such that the total mass density remains constant *i.e.*, if $\rho$ is fluid density and $v$ is fluid velocity, then

$$\rho v = 0 \Rightarrow \rho_n v_n + \rho_s v_s = 0 \qquad \ldots(1)$$

This implies that then is no net transport of mass across any plane in the liquid. This possible mode of motion in which to normal fluid and superfluid oscillate out of phase by 180° leads to the **thermal waves or second sound.**

**Velocity of Second wave :** The entropy of superfluid component is zero. Therefore the total entropy '$S$' per unit mass of liquid He II is given by

$$\rho S = \rho_n S_n \qquad \ldots(2)$$

For simplicity we assume that the transport of entropy is only along one direction. We consider a parallelopiped of unit cross-section and length $\Delta x$ inside the liquid with one pair of opposite faces vertical. The amount of entropy entering the volume per second at one face is

$$\rho S\, v_n = \rho_n S_n v_n \qquad \ldots(3)$$

and that leaving the opposite face is

$$\rho S v_n + \frac{\partial}{\partial x}(\rho S\, v_n)\, \Delta x$$

Therefore the net transport of entropy per second is

$$\rho S\, v_n + \frac{\partial}{\partial x}(\rho S\, v_n)\, \Delta x - \rho S\, v_n$$

$$= \frac{\partial}{\partial x}(\rho S\, v_n)\, \Delta x$$

Net transport of entropy per unit volume is $= \frac{\partial}{\partial x}(\rho S\, v_n)$ ...(4)

The initial entropy within the volume was $\rho S$

$\therefore$ The mass of entropy per unit time will be

$$= -\frac{\partial}{\partial t}(\rho S) \qquad \ldots(5)$$

Equating (4) and (5), we get continuity equation

$$-\frac{\partial}{\partial t}(\rho S) = \frac{\partial}{\partial x}(\rho S\, v_n) \qquad \ldots(6)$$

If mass density $\rho$ remains constant, we get

$$-\rho \frac{\partial S}{\partial t} = \rho \left[ S \frac{\partial v_n}{\partial x} + v_n \frac{\partial S}{\partial x} \right]$$

If $v_n$ is very small then the smaller term $v_n \frac{\partial S}{\partial x}$ may neglected so above equation becomes

$$S \frac{\partial v_n}{\partial x} = -\frac{\partial S}{\partial t} \qquad \ldots(7)$$

Let the temperatures of opposite faces be $T$ and $T + \Delta T$. The quantity of heat transferred across the thickness $\Delta x$ per second from second law of thermodynamics is

$$\Delta Q = T \Delta S$$

Here

$$\Delta S = \rho S\, v_n$$

$$\Delta Q = T\,(\rho S v_n) \qquad \ldots(8)$$

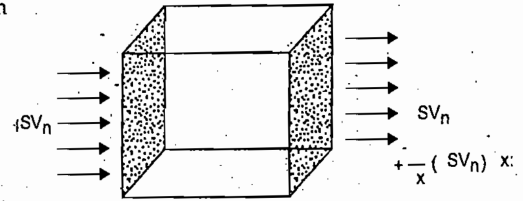
In reversible heat transfer (as in Carnot cycle) work done $\Delta W$ is given by

$$\frac{\Delta W}{\Delta Q} = \frac{\Delta T}{T}$$

$$\Rightarrow \quad \Delta W = \Delta Q \left( \frac{\Delta T}{T} \right)$$

Using (8), we get

$$\Delta W = (\rho S v_n)\, \Delta T \ \ldots \qquad (9)$$



(Fig. 10.22)

The work done will cause a change in kinetic energy. The kinetic energy of fluid per unit volume

$$E_k = \frac{1}{2}(\rho_n v_n^2 + \rho_s v_s^2)$$

From (1), $v_s = -\frac{\rho_n v_n}{\rho_s}$

$$\therefore \quad E_k = \frac{1}{2}\left\{ \rho_n v_n^2 + \rho_s \left( -\frac{\rho_n v_n}{\rho_s} \right)^2 \right\}$$

$$= \frac{1}{2}\rho_n v_n^2 \left[ 1 + \frac{\rho_n}{\rho_s} \right] = \frac{1}{2}\rho_n v_n^2 \left( \frac{\rho_s + \rho_n}{\rho_s} \right)$$

But $\rho_s + \rho_n = \rho$ (total mass density)

$$\therefore \quad E_k = \frac{1}{2}\frac{\rho \rho_n v_n^2}{\rho_s}$$

$\therefore$ Rate of change of kinetic energy per unit volume

$$\frac{d}{dt}(E_k) = \frac{\rho \rho_n}{\rho_s} v_n \frac{\partial v_n}{dt}$$

Rate of change of kinetic energy in volume $\Delta x$ will be

$$\left( \frac{d}{dt} E_k \right) \Delta x = \frac{\rho \rho_n}{\rho_s} v_n \frac{\partial v_n}{dt} \Delta x \qquad \ldots(10)$$

Comparing (9) and (10), we get

$$-\rho S v_n \Delta T = \frac{\rho \rho_n}{\rho_s} v_n \cdot \frac{\partial v_n}{\partial t} \Delta x$$

$$\Rightarrow \quad \frac{\rho_n}{\rho_s} \frac{\partial v_n}{\partial t} = -S \frac{\partial T}{\partial x} \qquad \ldots(11)$$

From first and second laws of thermodynamics

$$\Rightarrow \quad \delta Q = T \delta S \ \text{ and } \ \delta Q = C_V\, \delta T + p\, \delta V$$

where $C_v$ is specific heat at constant volume when volume $V$ is kept constant $\delta V = 0$.

$$T \delta S = C_v\, \delta T$$

$$\Rightarrow \quad \frac{\partial T}{\partial S} = \frac{T}{C_v}$$

$$\Rightarrow \qquad \frac{\partial T}{\partial x}\cdot\frac{\partial x}{\partial S}=\frac{T}{C_v}$$

$$\Rightarrow \qquad \frac{\partial T}{\partial x}=\frac{T}{C_v}\frac{\partial S}{\partial x} \qquad ...(12)$$

Substituting this value in (11), we get

$$\frac{\rho_n}{\rho_s}\frac{\partial v_n}{\partial t}=-\frac{TS}{C_v}\frac{\partial S}{\partial x}$$

Diff. w.r.t. to $x$, we get

$$\frac{\rho_n}{\rho_s}\frac{\partial^2 v_n}{\partial x\,\partial t}=-\frac{TS}{C_v}\frac{\partial^2 S}{\partial x^2}$$

$$\Rightarrow \qquad \frac{\rho_n}{\rho_s}\frac{\partial}{dt}\left(\frac{\partial v_n}{\partial x}\right)=-\frac{TS}{C_v}\frac{\partial^2 S}{\partial x^2}$$

Using equation (7), we get

$$-\frac{\rho_n}{\rho_s}\frac{1}{S}\frac{\partial}{\partial t}\left(\frac{\partial S}{\partial t}\right)=-\frac{TS}{C_v}\frac{\partial^2 S}{\partial x^2}$$

or

$$\frac{\partial^2 S}{\partial x^2}=\left(\frac{\rho_n}{\rho_s}\cdot\frac{C_v}{TS^2}\right)\frac{\partial^2 S}{\partial t^2} \qquad ...(13)$$

This is in the form of wave equation where entropy is undergoing periodic changes. Standard equation of wave motion is

$$\frac{\partial^2 S}{\partial x^2}=\frac{1}{u_2^2}\frac{\partial^2 S}{\partial t^2} \qquad ...(14)$$

Comparing (13) and (14), the speed of thermal (or second) wave is

$$u_2=\sqrt{\left[\frac{\rho_s}{\rho_n}\frac{TS^2}{C_v}\right]}$$

or

$$u_2=\sqrt{\left[\left(\frac{\rho-\rho_n}{\rho_n}\right)\frac{TS^2}{C_v}\right]} \qquad ...(15)$$

The Tisza's two fluid model concludes the when $T \to 0,\ u_2 \to 0$

and when $\qquad T \to T_\lambda = 2{\cdot}19\ \text{K},\ \rho_s \to 0$

The prediction that for $T \to 0,\ u_2 \to 0$ is wrong. But it may be said that at λ-point, where $\rho_s \to 0$, the velocity of thermal wave rapidly falls to zero.

## 10.14 Feynmann's Theory

Many of the statements of both Landau's and London's theories rest on arguments rather than derivation from quantum theory. Their situation has been improved to a considerable extent by the researches of Feynman who has given a very interesting discussion of Landau's theory while trying to relate it to the London's approach. Feynman could succeed in deriving quantum statistically the energy levels and energy gas picture of Landau retaining the Bose-Einstein condensation idea of London.

Feynman's work begins with an analysis of the types of motion which can be possible in a condensed Bose-Einstein system. He has shown that no excitations other that the phonons and rotons of Landau's theory are possible. Excitations near the minimum have been shown to behave in all essential ways like the rotons.

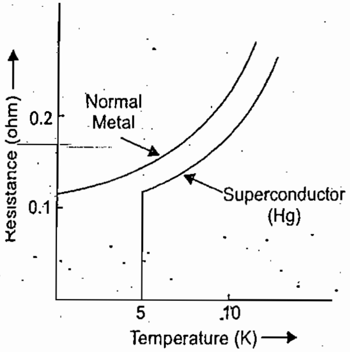
Onsager and Feynman, from this point of view discussed the thermodynamic and hydrodynamic equations of the two fluid model. They postulated that the super fluid is capable of forming eddies and that these large vortices, every one containing a large number of atoms is to be quantized. When these vortices interact with phonons and rotons, dissipation of energy can take place. As an enormous numbers of atoms take part in the formation of these large scale quantum eddies, the energy per atom is much smaller than that required for the creation of a single phonon or roton. Thus the vortices allow energy to be abstracted from the flow of super fluid at much smaller velocities than those predicted by the Landau's theory.

Feynman has also suggested that the energy spectrum for excitations in liquid helium should be computed by examining the inelastic scattering of thermal neutrons which have been passed through a polycrystalline filter. The energy momentum relation so determined confirms the validity of the energy spectrum proposed by Landau in his theory.

## 10.15 Superconductivity

It was known a long time ago that the resistance of a metal decreases with temperature and attains a minimum residual value. Further decrease in temperature does not produce appreciable change in resistance as shown in Fig. 10.23.

Kamerling Onnes in 1911, while studying the electrical resistance of mercury at very low temperatures, observed that the *resistance* of mercury first decreases regularly like that of any metal but at 4·2 K it *suddenly decreases to zero* (actually becomes about a millionth of its orginal value at the melting point) as shown in Fig. 10.23 The temperature, at which this phase transition occurs and the resistance suddenly drops to zero, is called the *critical temperature* ($T_c$). The transition temperature of helium is 2·19 K. He-II is a superconductor. Similar results were obtained by using various other metals like Al, Pb, Sn, In, Zn, Cd etc. *This phenomenon of disappearance of electrical resistance of material below a certain temperature is called superconductivity and the material in this state is called a superconductor.*



(Fig. 10.23)

The discovery of superconductivity attracted a large number of workers because the materials with no electrical resistance (negligible heat losses) could be exploited to fabricate powerful and economical devices which consume negligible amount of electrical energy. For example, if a magnet is inserted into or withdrawn out of a coil rapidly, a momentary current flows in the coil but only for the duration when magnetic flux through the coil is changing. If, however, the temperature of the coil is brought down so that if becomes superconducting, then the current will continue to flow for days and even months after the removal of the magnet. Thus, an electromagnet made up of a superconducting material can function for years together even after the removal of the supply voltage. However, due to requirement of very low temperatures, it was not feasible to manufacture such devices. Therefore, a lot of research work was undertaken to develop superconducting materials at high temperatures.

In 1977, a critical temperature ($T_c$) of 23·2 K was observed in $Nb_3$(Ge) (an intermediate compound of niobium and germanium). In 1986, Bednorz and Miller Discovered that the superconducting transition temperature in case of $La_{1\cdot85}Sr_{0\cdot15}CuO_4$ was about 40 K. In 1987, a ceramic superconductor of the composition $YBa_2Cu_3O_7$ was discovered which showed $T_c$ equal to 90 K. The value of $T_c$ was found to be 125 K for thallium cuprates. However, the highest superconducting transition temperature reported till date is 150 K.

Superconducting state is a distinct phase of matter having characteristic electrical, magnetic, thermodynamic and other physical properties. When a metal becomes superconductor, its thermal conductivity decreases considerably and approaches zero approximately as the cube of the temperature. In the superconducting state the *magnetic permeability is also zero.* Superconductors have zero electrical resistance and the *perfect diamagnetism.* This phenomenon is known as *Meissner effect.*

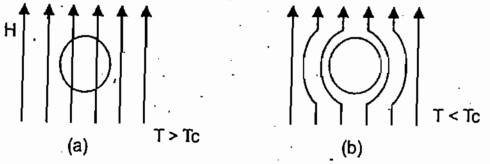


**Fig. 10.24**

Superconductivity is destroyed by a magnetic field. Even the magnetic field due to the current flowing in the superconductor itself may destroy the superconductivity provided the current is large enough. If by switching on a magnetic field, the superconducting state is suddenly removed, the metal becomes a good heat conductor. This phenomenon has actually been utilized in magnetic refrigerator.

## EXERCISES

### SHORT ANSWER QUESTIONS

1. Name four methods for producing low temperatures.
2. Explain the method of regenerative cooling coupled with Joule Thomson effect. *(Kanpur 2001, Rohilkhand 2005)*
3. Explain the phenomenon of adiabatic demagnetisations. Explain how low temperature can be attained using this phenomenon.
4. Describe the properties of He I and He II. What is meant by $\lambda$-point ? *(Kanpur 2005, 2001)*
5. Explain why the solidification of helium is difficult. *(Kanpur 1999)*
6. Explain why the temperature of a gas drops in adiabatic demagnetisation. *(Kanpur 2004)*
7. Describe to principle to liquefy hydrogen with a neat labelled diagram.
8. What do you mean by photons, phonons and rotons ?
9. What do you mean by Bose Einstein condensation ? Discuss liquid helium as example of Bose-Einstein condensation.
10. Mention four unusual properties of liquid helium II.
11. Give a brief account of London's theory to explain unusual properties of liquid helium II.
12. How will you measure temperatures below 1 K.

### LONG ANSWER QUESTIONS

1. Explain with the help of necessary theory, how extremely low temperatures can be produced in the laboratory. How can these temperatures be measured ?
2. (a) Give the theory of cooling due to adiabatic demagnetization.
   (b) Outline the broad facts known about superconductivity. *(Rohilkhand 2002)*

3. Give the theory of production of very low temperatures, in the neighbourhood of absolute zero by the adiabatic magnetisation of a suitable paramagnetic salt. *(Rohilkhand 2000, 1987)*
4. Explain with necessary theory how extremely low temperatures have been produced by the method of adiabatic demagnetization. How have these temperatures been measured and reduced to absolute scale? Deduce the mathematical relation. *(Agra 1991)*
5. How are temperatures in the range below 1 K measured ? Comment on the validity of these measurements. *(Agra 1994)*
6. What do you mean by adiabatic demagnetisation ? How is it used to produce lowest temperature ? Obtain an expression for to coolling produced by this method. *(Kanpur 2006, 2003 Meerut 2000, Rohilkhand 2004)*
7. Discuss the principle of colling by adiabatic demagnetisation of a paramagnetic salt. Give its experimental details. Derive an expression for the final temperature of the salt in terms of initial temperature and the strength of magnetic field applied. Show your cooling results by drawing curves for change of entropy against temperature at constant magnetic fields. *(Rohilkhand 2006, 2001)*
8. Give a brief account of production and measurement of temperature near absolute zero. *(Rohilkhand 1993, 86)*
9. Give the theory of producing milli-degree temperatures by adiabatic demagnetization of paramagnetic salt. How magnetic temperatures are converted into absolute temperatures to measure such low temperatures.
10. Discuss the theories for production of very low temperatures near absolute zero by adiabatic demagnetisation . Explain experimental arrangement used for this method. *(Mumbai 2004, 2003)*
11. Give the theory of adiabatic demagnetization method for the production of very low temperatures near absolute zero. Describe a method for converting the magnetic temperature into Kelvin temperature. *(Rohilkhand 1985, 81)*
12. Mention the distinguishing features of liquid helium II. Discuss the nature of transition between helium I and helium II.
13. Distinguish between liquid helium I and liquid helium II. How can you explain the strange behaviour of liquid helium II in particular its property of super-fluidity ?
14. What is the energy spectrum of liquid helium II proposed by Landau ? How does this spectrum explain the temperature of the quantum liquid ? *(Agra 1989)*
15. (a) Distinguish clearly between helium I and helium II. What do you understand by lambda-points ? Describe some important properties of helium II.
    (b) Describe a suitable method for producing temperatures below 1 K. *(Agra 1982)*
    (c) Explain how temperature below 1 K are measured and reduced to absolute scale ? Give necessary details. *(Agra 1982)*
16. Discuss the various properties of liquid helium which undergo sudden changes when it is cooled below 2·2 K. What experiments would you perform to demonstrate the strange behaviour of the liquid below this temperature ? Discuss the significance of this temperature.

17. Discuss Bose-Einstein condensation. How it differs from ordinary condensation ? Discuss the anomalous properties of liquid helium at the transition temperature. *(Meerut 1973)*

18. Distinguish between liquid helium I and liquid helium II. Explain the the theories which have been put forward to account for the peculiar behaviour of liquid helium II. *(Agra 1986; Rohilkhand 2004)*

19. Describe some of the properties of liquid Helium II which distinguish it from ordinary liquid helium. How are they explained ? *(Rohilkhand 1988)*

20. Distinguish between liquid helium I and liquid helium II. Explain the theories which have been put forward to account for the peculiar behaviour of liquid helium II. *(Agra 1986; Rohilkhand 80)*

21. What type of elementary excitations have been assumed for liquid helium problem by Landau ? How has Landau's theory been successful in explaining some important properties of liquid helium below 1·6 K. *(Rohilkhand 1986)*

22. What do you mean by second wave ? Find an expression for velocity of second wave on the basis of Tisza's two fluid model.

23. Write short explanatory notes on :
    (i) Production and measurement of extremely low temperatures. *(Agra 1983, 65)*
    (ii) March towards absolute zero temperature. *(Rohilkhand 1982; Agra 71)*
    (iii) Production of temperatures below 4 K. *(Agra 1975)*
    (iv) Measurement of Temperatures near the absolute zero. *(Rohilkhand 1977)*
    (v) Adiabatic demagnetisation. *(Agra 1983)*
    (vi) *BE* condensation. *(Agra 1976)*
    (vii) Liquid Helium I and Helium II. *(Agra 1977)*
    (viii) Landau theory of liquid He II. *(Rohilkhand 1982, 78)*
    (ix) Liquid He II. *(Agra 1818; Rohilkhand 84, 81)*
    (x) Super conductors of type I and type II. *(Agra 1983)*
    (xi) The λ–transition in Helium. *(Rohilkhand 1987)*

## NUMERICALS

1. Calculate the cooling produced by adiabatic demagnetization of a paramagnetic salt as the field is reduced from 5000 oersted to zero at initial temperature of 2 K. Given Curie constant per gm mole per c.c.= 0·06 C.G.S units and $C_H = 0{\cdot}42$ joules $gm^{-1} K^{-1}$.

   [Ans. 0·18 K]

2. One gram of paramagnetic substance obeying Curie's law is in a magnetic field of 20,000, oersted and at a temperature of 20°C. Assuming the specific hear capacity at constant field to remain constant at 0·10 cal/g K and the Curie constant to be 0·05 cal K/g, calculate the change in temperature if the field is reduced reversibly and adiabatically to zero.

## MULTIPLE CHOICE QUESTIONS

1. Using adiabatic demagnetisation, the minimum temperature produced is :
   (a) 10 K (b) 1 K (c) 0·25 K (d) 0 K

2. When a magnetised permagnetic salt is suddenly demagnetised, it will :
   (a) absorb heat (b) evolve heat (c) get liquefied (d) get evaporated.

3. The susceptibility (χ) of a paramagnetic substance depends on temperature as :
   (a) $\chi \propto T$ (b) $\chi \propto T^2$ (c) $\chi \propto \frac{1}{T}$ (d) $\chi \propto T^0$

4. The last gas to be liquefied was :
   (a) oxygen (b) hydrogen (c) nitrogen (d) helium

5. Solid helium :
   (a) can be obtained merely by lowering the temperature of liquid helium :
   (b) melts to form liquid
   (c) melts to form gas if melting point exceeds the critical temperature
   (d) can not exist above the critical temperature

6. The critical temperature of helium is
   (a) 0·3 K (b) 2·19 K (c) 5·2 K (d) 42 K

7. Lambda point of liquid helium is :
   (a) 0·3 K (b) 2·19 K (c) 5·2 K (d) 42 K

8. Helium has :
   (a) unique triple point (b) no triple point
   (c) two triple points (d) three triple points

9. Which of the following statements is wrong for liquid helium II :
   (a) the viscosity of He II is almost zero
   (b) the thermal conductivity of He II very low
   (c) the density of He II is almost same as that of He I
   (d) the flow of He II through capillaries is independent of pressure difference

10. The ratio of coefficients of viscosity of He II to He I is : *(Garhwal 2001)*
    (a) 10 (b) $10^{-1}$ (c) $10^{-3}$ (d) $10^3$

11. Which thermometer can be used to measure temperatures below 1 K :
    (a) Vapour pressure thermometer (b) Alcohol thermometer
    (c) Thermocouple thermometer (d) Magnetic thermometer

12. Helium II is a :
    (a) Conductor (b) Semiconductor
    (c) Insulator (d) Superconductor

13. Second sound is :
    (a) pressure wave (b) volume wave
    (c) thermal wave (d) sound having velocity more than

### ANSWERS

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. (c) | 2. (b) | 3. (c) | 4. (d) | 5. (c) | 6. (c) | 7. (b) | 8. (b) |
| 9. (b) | 10. (c) | 11. (d) | 12. (d) | 13. (c) | | | |

# 11

# TRANSPORT THEORY

## [Outline of an Exact Kinetic Theory of Gases]

## 11.1 Introduction

Statistical physics deals with the relation between the macrosopic laws of a system and the dynamics of the interactions of its microscopic constituents. So far we have considered the systems to be in equilibrium and have applied the statistical microscopic laws *e.g.* the derivation of thermodynamic relations by equilibrium statistical mechanics. For *non equilibrium systems* the derivation of macroscopic laws, such as those of hydrodynamics from the microscopic laws has not been generally developed. However for the particular cases of dilute gases the microscopic analysis of non-equilibrium phenomenon has been done successfully to a considerable degree of extent by *kinetic theory or transport theory* which allows us to relate the transport of matter or of energy for example (as in case of diffusion or heat flow respectively) to the mechanics of the particles making up the system.

In kinetic theory, the macroscopic quantities are found as averages over the motion of many molecules, each molecular event being assumed to take place a macroscopic time interval so that a measurement that is made over a microscopic time interval involves many molecules. The kinetic theory description is *probabilistic* because the assumptions are made about the motion of one molecule and the results of this motion are averaged over all the molecules of the gas, giving proper weight to the prabability that the various molecules of the gas can have the assumed motion.

In its most elementary aspect, kinetic theory is developed on the basis of a *hard sphere model of particles* making up the gas. It assumes that the particles are uniformly distributed in space and that all have the same speed and there are equal number of particles moving parallel to each co-ordinate axis. This assumption allows us to take the averages over the direction of motion of the particles and to obtain a statistical description of gross effect. This simple model is found to give results that are reasonable approximations to the macroscopic laws they attempt to describe. However this simple model gives the statisfactory results in many phenomenan of interest due to the unrealistic assumptions and the very simplicity of the model prevents calculation of many such phenomena.

In its more advanced aspects the kinetic theory is based upon description of the gas in terms of the probability of a particle having certain values of coordinates and velocity at a given time. The interactions among particles are developed by the ordinary laws of mechanics and the results of these averaged over the probability distribution. The probability distribution function that is used for a given macroscopic physical situation is determined by means of an equation known as *Boltzmann transport equation,* which describes the space, velocity and time changes of the distribution function in terms of the collisions between particles. This equation is usually solved to give the distribution function in terms of certain macroscopic functions. The transport equation

method is very useful in dealing with few processes and in many circumstances the method is easy to use. In this chapter we shall consider its applications to electrical and thermal conductivities and to viscosity.

## 11.2 Distribution Function :

Consider a six dimensional phase space. The coordinates of a point in this space is represented by $(x, y, z, v_x, v_y, v_z)$ where $x, y, z$ are the position coordinates and may be denoted by $\mathbf{r}$ while $(v_x, v_y, v_z)$ are velocity coordinates and may be denoted by $v$. Hence the coordinates of a point in six dimensional phase space may be denoted by $(\mathbf{r}, \mathbf{v})$. The differential volume element about the point $(\mathbf{r}, \mathbf{v})$ in this phase space will be represented by,

$$d\Gamma = dx\,dy\,dz\,dv_x\,dv_y\,dv_z = d\mathbf{r}\,d\mathbf{v}.$$

If $dn$ represents the number of particles which are in the differential volume element $d\Gamma = d\mathbf{r}\,d\mathbf{v}$ (*i.e.*, whose coordinates lie within ranges $x$ to $x + dx, y$ to $y + dy, z$ to $z + dz, v_x$ to $v_x + dv_x, v_y$ to $v_y + dv_y, v_z$ to $v_z + dv_z$); then the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ is defined by :

$$dn = f(\mathbf{r}, \mathbf{v}, t)\,d\mathbf{r}\,d\mathbf{v}. \qquad \text{...(1)}$$

The differentials lengths $d\mathbf{r}$ and velocities $d\mathbf{v}$ must be small compared with the macroscopic distances and velocity intervals over which there are significant changes in the gross properties of the gas. On the other hand they must be sufficiently large so that there are a large number of particles contained in the differential volume element of phase space.

## 11.3 Boltzmann Transport Equation

Consider a system of particles acted upon by external forces. For example the system may consists of electrons in a metal that is acted upon by electric and magnetic fields. In order to derive the Boltzmann transport equation consider a region of six dimensional space about the point $(x, y, z, v_x, v_y, v_z)$ *i.e.*, $(\mathbf{r}, \mathbf{v})$. An element of volume in this six dimensional space is written as $dx\,dy\,dz\,dv_x\,dv_y\,dv_z$ or $d\mathbf{r}\,d\mathbf{v}$. The number of particles having coordinates within ranges $\mathbf{r}$ to $\mathbf{r} + d\mathbf{r}$ and $\mathbf{v}$ to $\mathbf{v} + d\mathbf{v}$ can be represented as

$$dn = f(\mathbf{r}, \mathbf{v}\; t)\,d\mathbf{r}\,d\mathbf{v}, \qquad \text{...(1)}$$

where $f(\mathbf{r}, \mathbf{v}\; t)$ is the *distribution function.*

At point $(\mathbf{r}, \mathbf{v})$ the variation of distribution function $f$ (with time may be caused by two independent ways :

(i) Drift-variation : The function $f$ may vary because of the drift of particles from one region of space to another. This variation per unit time is represented by $\left(\frac{\partial f}{\partial t}\right)_{\text{drift}}$.

(ii) Collision or scattering interactions : The function $f$ may vary because of the collisions among the particles. This variation per unit time is represented by $\left(\frac{\partial f}{\partial t}\right)_{\text{collisions}}$.

Hence the time rate of change of the function $f$ may be expressed as :

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\text{drift}} + \left(\frac{\partial f}{\partial t}\right)_{\text{collisions}}. \qquad \text{...(2)}$$

Here we have assumed that *the number of particles in the system is conserved.* If it is not so, then we must add the terms representing the generation and recombination of particles to the right hand side of equation (2). Such additional terms are required in the theory of nuclear and junction transistor.

To derive the Boltzmann transport equation, we proceed as follows :

Let the particles in the differential phase space volume $d\mathbf{r}\,d\mathbf{v}$ around $(\mathbf{r}, \mathbf{v})$ move to a new position by virtue of their velocities in a short time interval $dt$. The velocity of the particles may change due to the external force acting upon them and the collisions among themselves. Let the new position be represented by $(\mathbf{r}', \mathbf{v}')$ such that

$$\mathbf{r}' = \mathbf{r} + \mathbf{v}\,dt, \quad \mathbf{v}' = \mathbf{v} + \mathbf{a}\,dt$$

where a is the acceleration of the particle.

If we consider that no collision occurs during the time interval $dt$, then all of particles will move to the new volume $d\mathbf{r}'\,d\mathbf{v}'$ and so we may write,

$$f(\mathbf{r} + \mathbf{v}\,dt, \mathbf{v} + \mathbf{a}\,dt, t + dt)\,d\mathbf{r}'\,d\mathbf{v}' = f(\mathbf{r}, \mathbf{v}, t)\,d\mathbf{r}\,d\mathbf{v}. \qquad \ldots(3)$$

Furthermore, according to Liouville's theorem, we can write

$$d\mathbf{r}'\,d\mathbf{v}' = d\mathbf{r}\,d\mathbf{v}. \qquad \ldots(4)$$

Then eqn. (3) gives

$$f(\mathbf{r} + \mathbf{v}\,dt, \mathbf{v} + a\,dt, t + dt) = f(\mathbf{r}, \mathbf{v}, t). \qquad \ldots(5)$$

Now, using Taylor's series expansion on L.H.S. and retaining terms linear in $dt$ in the limit $dt \to 0$, above equation becomes

$$f(\mathbf{r}, \mathbf{v}, t) + \mathbf{v}\,dt \cdot \text{grad}_r f + \mathbf{a}\,dt \cdot \text{grad}_v f + \frac{\partial f}{\partial t}\,dt = f(\mathbf{r}, \mathbf{v}, t)$$

*i.e.,*

$$\mathbf{v} \cdot \text{grad}_r f + \mathbf{a} \cdot \text{grad}_v f + \frac{\partial f}{\partial t} = 0 \qquad \ldots(6)$$

This is *Bolztmann's transport equation* when no collisions are taken into account.

In this equation $\text{grad}_r = \nabla_r$ is the usual del operator and $\text{grad}_v = \nabla_v$ is the del operator in velocity space. ……

$$\left.\begin{aligned} \nabla_r &= \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z} \\ \text{and} \qquad \nabla_v &= \mathbf{i}\frac{\partial}{\partial v_x} + \mathbf{j}\frac{\partial}{\partial v_y} + \mathbf{k}\frac{\partial}{\partial v_z} \end{aligned}\right\} \qquad \ldots(7)$$

$$\left.\begin{aligned} \text{so that} \qquad \mathbf{v} \cdot \text{grad}_r f &= v_x\frac{\partial}{\partial x} + v_y\frac{\partial}{\partial y} + v_z\frac{\partial}{\partial z} \\ \text{and} \qquad \mathbf{a} \cdot \text{grad}_v f &= a_x\frac{\partial}{\partial v_x} + a_y\frac{\partial}{\partial v_y} + a_z\frac{\partial}{\partial v_z} \end{aligned}\right\} \qquad \ldots(8)$$

However, when we take collisions into account, then due to collisions among the particles some particles leave the volume element $d\mathbf{r}\,d\mathbf{v}$ and some pass from $d\mathbf{r}'_1\,d\mathbf{v}'_1$ to $d\mathbf{r}\,d\mathbf{v}$. This is equivalent to a loss or gain in the number of particles in volume element $d\mathbf{r}\,d\mathbf{v}$ owing to collisions. Now the change in number of particles in volume element $d\mathbf{r}\,d\mathbf{v}$ during the time interval from $t$ to $t + dt$, using Liouville's theorem is given by

$$f(\mathbf{r} + \mathbf{v}\,dt, \mathbf{v} + \mathbf{a}\,dt, t + dt)\,d\mathbf{r}\,d\mathbf{v} - f(\mathbf{r}, \mathbf{v}, t)\,d\mathbf{r}\,d\mathbf{v} = \left(\frac{\partial f}{\partial t}\right)_{collisions} dt\,d\mathbf{r}\,d\mathbf{v}$$

*i.e.,*

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \text{grad}_r f + \mathbf{a} \cdot \text{grad}_v f = \left(\frac{\partial f}{\partial t}\right)_{collisions} \qquad \ldots(9)$$

This is the *Bolzmann's transport equation* in general form.

Comparing equations (2) and (9), we have

$$\left(\frac{\partial f}{\partial t}\right)_{drift} = -\mathbf{v} \cdot \text{grad}_r f - \mathbf{a} \cdot \text{grad}_{\mathbf{v}} f \qquad \ldots(10)$$

If $J_{gain}$ and $J_{lost}$ represent the number of particles gained and lost per unit volume element per unit time as a consequence of collisions, then the Boltzmann's transport equation (9) may be written as

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \text{grad}_r f + \mathbf{a} \cdot \text{grad}_v f = J_{gain} - J_{loss}. \qquad \ldots(11)$$

The collisions term $\left\{\frac{\partial f}{\partial t}\right\}_{collisions}$ in eqn. (9) or $(J_{gain} - J_{loss})$ in eqn. (11)

may require special treatment; but in many problems it is possible to justify approximately the introduction of a parameter $\tau_c$ called the *relaxation time* or *mean free time* defined by the equation

$$\left\{\frac{\partial f}{\partial t}\right\}_{collisions} = -\frac{f - f_0}{\tau_c}, \qquad \ldots(12)$$

where $f_0$ *is the distribution function in thermal equilibrium.*

Noting that by definition $\frac{\partial f_0}{\partial t} = 0$, eqn. (12) may be written as

$$\frac{\partial (f - f_0)}{\partial t} = \frac{f - f_0}{\tau_c} \qquad \ldots(13)$$

This equation represents the rate at which distribution function approaches the equilibrium condition (when external forces such as electric field or temperature gradient are suddenly removed) as being proportional to the deviation from equilibrium condition at a given time.

Equation (13) has the solution

$$(f - f_0)_t = (f - f_0)_{t=0}\, e^{-t/\tau_c}. \qquad \ldots(14)$$

This equation indicates that $(f - f_0)_l$ is proportional to $e^{-t/\tau_c}$, *i.e.* the distribution towards equilibrium decays exponentially.

Using equation (12) the *Boltzmann's transport equation* (9) in relaxation time approximation is written as

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \text{grad}_r f + \mathbf{a} \cdot \text{grad}_{\mathbf{v}} f = -\frac{f - f_0}{\tau_c} \qquad \ldots(15)$$

In the steady state $\frac{\partial f}{\partial t} = 0$.

In the problems where the introduction of the relaxation time is not justified, we have to calculate the collision term in detail with the laws of elastic collisions by introducing the transtion probabilities for processes which remove the particles from the volume element $d\mathbf{r}\,d\mathbf{v}$ and for processes which bring the particles into this volume element. This leads in general to an integro differential equation.

## 11.4 Kinetic Formulation of Transport Problems : Chamber's Equation

Chambers has given a simple and general kinetic formulation of transport problems, which is now widely used. The number of particles in volume element $d\mathbf{r}\,d\mathbf{v}$ in equilibrium state is expressed as $f_0(\mathbf{r}, \mathbf{v})\,d\mathbf{r}\,d\mathbf{v}$, where $f_0(\mathbf{r}, \mathbf{v})$ is the equilibrium distribution function at point $(\mathbf{r}, \mathbf{v})$.

Chambers assumed that for non-equilibrium situations $f_0$ describes the distribution immediately after collision.

The particles passing through any point $(\mathbf{r}_0, \mathbf{v}_0)$ in phase space with energy $W$ will have followed a certain trajectory, since their last collision. This trajectory may be determined by the external force acting on the particle. Often the force acting on the charged particle moving with velocity $\mathbf{v}$ is given by the general Lorentz relation,

$$\mathbf{F} = q\mathbf{E} + q\mathbf{v} \times \mathbf{B} \qquad \ldots(1)$$

where $q$ is the change on the particle, $\mathbf{E}$ is the electric field strength and $\mathbf{B}$ is the magnetic field induction.

The distribution function $f(\mathbf{r}_0, \mathbf{v}_0, t_0)$ is evaluated by integrating the number of particles scattered into the trajectory at preceding point along it, the particles having energy $W - \Delta W$ at scattering Here $\Delta W$ is the energy gained by particles from the applied fields before reaching $\mathbf{r}_0$. The number of particles scattered is weighed by probability of reaching $\mathbf{r}_0$, *i.e.*

$$f(\mathbf{r}_0, \mathbf{v}_0, t_0) = \int_{-\infty}^{t_0} f_0 (W - \Delta W) \exp \{t_0 - t / \tau_c\} \cdot \left(\frac{dt}{\tau_c}\right) \qquad \ldots(2)$$

where $\tau_c$ is the relaxation time and the factor $\exp \{-(t_0 - t)/\tau_c\}$ represents the probability that a particle scattered at time $t$ will reach time $t_0$ without further scattering.

Now assuming isothermal conditions and uniform charge distribution expanding $f_0 (W - \Delta W)$ to the first order in $\Delta W$, *i.e.*

$$f_0 (W - \Delta W) = f_0 (W) - \left(\frac{\partial f_0}{\partial W}\right) \Delta W. \qquad \ldots(3)$$

So the equation (2) may be written as

$$f(\mathbf{r}_0, \mathbf{v}_0, t_0) = \int_{-\infty}^{t_0} f_0 (W) \exp \{-(t_0 - t)/\tau_e\} \cdot \frac{dt}{\tau_c} - \left(\frac{\partial f_0}{\partial W}\right) \int_{-\infty}^{t_0} \exp \{- t_0 - t)/\tau_c\} \cdot \Delta W \cdot \frac{dt}{\tau_c}$$

$$= f_0 (\mathbf{r}_0, \mathbf{v}_0, t_0) - \left(\frac{\partial f_0}{\partial W}\right) \int_{-\infty}^{t_0} \exp \{-(t_0 - t)/\tau_c\} \cdot \Delta W \cdot \left(\frac{dt}{\tau_c},\right)$$

Above equation may be written as

$$\delta f = f(\mathbf{r}_0, \mathbf{v}_0, t_0) - f_0 (\mathbf{r}_0, \mathbf{v}_0, t_0)$$

$$= -\left(\frac{\partial f_0}{\partial W}\right) \int_{-\infty}^{t_0} \exp \{-(t_0 - t)/\tau_c\} \cdot \Delta W \cdot \frac{dt}{\tau_c} \qquad \ldots(4)$$

Integrating R.H.S, by parts, we get

$$\delta f = \left(\frac{\partial f_0}{\partial W}\right) \int_{-\infty}^{t_0} \left(\frac{d\Delta W}{dt}\right) \exp \{-(t_0 - t)/\tau_c\} \, dt.. \qquad \ldots(5)$$

Noting that the magnetic fields have no direct effect on the energy, we may write

$$\Delta W (t) = q \int_{t}^{t_0} \mathbf{E}(r, t) \cdot \mathbf{v}(t) \, dt, \qquad \ldots(6)$$

where $\mathbf{E}(\mathbf{r}, t)$ is the applied electric field.

Then

$$\frac{d(\Delta W)}{dt} = q\mathrm{E}(\mathrm{r}, t) \cdot \mathrm{v}(t) \qquad \ldots(7)$$

Therefore equation (5) takes the form

$$\delta f = q \left(\frac{\partial f_0}{\partial W}\right) \int_{-\infty}^{t_0} \mathrm{E}(\mathrm{r}, t) \cdot \mathrm{v}(t) \exp \{-(t_0 - t)/\tau_c\} \, dt. \qquad \ldots(8)$$

This is *Chamber's equation.*

If $\tau_e = \tau_\epsilon (0) = \tau_c (t)$, then we may replace $\exp \{-(t_0 - t)/\tau_c\}$ by

$$\exp \left\{ -\int_{t}^{t_0} \frac{dt}{\tau_c (t)} \right\}$$

Therefore in this case Chamber's equation takes the form

$$\delta f = q \left(\frac{\partial f_0}{\partial W}\right) \int_{-\infty}^{t_0} \mathrm{E}(\mathrm{r}, t) \cdot \mathrm{v}(t) \exp \left\{ -\int_{t}^{t_0} \frac{dt}{\tau_c (t)} \right\} dt. \qquad \ldots(9)$$

## 11.5 Electrical and Thermal Conductivities of an Electron gas

We shall now calculate the electrical and thermal conductivities of metals by *Boltzmann's transport equation.* If a temperature gradient or an electrical field is applied to the metal, the *electron gas* is not in complete equilibrium. The distribution function $f(\mathbf{r}, \mathbf{v}, t)$ which will be written simply $f$ giving the number of electrons per cell of velocity $\mathbf{v}$ at the position $\mathbf{r}$ can no longer be assumed to have the form $f_0 = \frac{1}{e^{(\varepsilon - \mu)/kT} + 1}$ which was derived for complete equilibrium.

However, we may determine the function $f$ under the perturbing influence of the temperature gradient and the field by *two conditions* which it must fulfill. These conditions are :

(i) The distribution function $f$ must approach $f_0$ as the field and temperature gradient become zero.

(ii) The distribution function $f$ is independent of time, *i.e.* the system is in a steady state. Mathematically $\partial f/\partial t = 0$.

**Electrical Conductivity :** The electrical conductivity in an electron gas in computed in the following steps :

(a) The distribution function is calculated in the presence of the applied electric field.

(b) The current density $\mathbf{J}$ is computed in terms of the distribution function.

(c) As $\mathbf{J} = \sigma\mathbf{E}$, where $\sigma$ is the electrical conductivity, therefore the proportionality constant between the current density and applied electric field gives the electrical conductivity.

Let us consider and metallic specimen with an electric field $E$ in the X-direction. If no magnetic field is present, then the components, of the force on the electron of charge $(-e)$ are given by

$$F_x = -eE, \quad F_y = 0, \quad F_z = 0.$$

If $m$ is the mass of the electron and $a_x, a_y, a_z$ are the components, of acceleration $\mathbf{a}$, then

$$a_x = -\frac{eE}{m}, \; a_y = 0, \; a_z = 0,$$

*i.e.*

$$\mathbf{a} = -\frac{eE}{m} \mathbf{i}.$$

As the specimen is considered to be in steady state [condition (ii)] $\partial f/\partial t = 0$ and the distribution function is independent of $y$ and $z$, the *Boltzmann's transport equation* (2) of section 11.3 takes the form

$$(\mathbf{i}v_x + \mathbf{j}v_y + \mathbf{k}v_z) \cdot \left(\mathbf{i}\frac{\partial f}{\partial x} + \mathbf{j}\frac{\partial f}{\partial y} + \mathbf{k}\frac{\partial f}{\partial z}\right) + \left(-\frac{eE}{m}\mathbf{i}\right) \cdot \left(\mathbf{i}\frac{\partial f}{\partial v_x} + \mathbf{j}\frac{\partial f}{\partial v_y} + \mathbf{k}\frac{\partial f}{\partial v_z} = -\frac{f - f_0}{\tau_c}\right)$$

*i.e.*

$$v_x \frac{\partial f}{\partial x} - \frac{eE}{m}\frac{\partial f}{\partial v_x} = -\frac{f - f_0}{\tau_c} \qquad \ldots(1)$$

This is the *Boltzmann's transport equation* for electron gas is the steady state

$$f = f_0 - \tau_c \left\{ v_x \frac{\partial f}{\partial x} - \frac{eE}{m} \frac{\partial f}{\partial v_x} \right\} \qquad \ldots(2)$$

It the *electric field is very weak*, then we may write

$$\frac{f - f_0}{\tau_c} \ll 1 \text{ i.e. } f \approx f_0$$

To this approximation (2), we may write as

$$f = f_0 - \tau_c \left\{ v_x \frac{\partial f_0}{\partial x} - \frac{eE}{m} \frac{\partial f_0}{\partial v_x} \right\} \qquad \ldots(3)$$

Now $f_0$ is the function of the temperature $T$, chemical potential $\mu$ and energy $\varepsilon$, then energy $\varepsilon$ is the function of $v_x$ since $\varepsilon = \frac{1}{2} m v_x^2$. So we have

$$\left.\begin{aligned} \frac{\partial f_0}{dx} &= \frac{\partial f_0}{\partial T} \frac{\partial T}{\partial x} + \frac{\partial f_0}{\partial \mu} \cdot \frac{\partial \mu}{\partial x} \\ \text{and} \qquad \frac{\partial f_0}{\partial v_x} &= \frac{\partial f_0}{\partial \varepsilon} \cdot \frac{\partial \varepsilon}{\partial v_x} = \frac{\partial f_0}{\partial \varepsilon} \cdot \frac{\partial}{\partial v_x} \left( \frac{1}{2} m v_x^2 \right) = m v_x \frac{\partial f_0}{\partial \varepsilon} \end{aligned}\right\} \qquad \ldots(4)$$

The electric conductivity $\sigma$ is usually defined under the conditions $\frac{\partial T}{\partial x} = 0$ and $\frac{\partial f_0}{\partial \mu} = 0$. Then equations (4) reduce to

$$\frac{\partial f_0}{\partial x} = 0 \text{ and } \frac{\partial f_0}{\partial v_x} = m v_x \frac{\partial f_0}{\partial \varepsilon} \qquad \ldots(5)$$

Using equation (5), equation (3) takes the form

$$f = f_0 + \tau_c e E v_x \frac{\partial f_0}{\partial \varepsilon} \qquad \ldots(6)$$

Taking into account the electronic spin, the number of states per unit volume associated with a momentum space element $dp_x \, dp_y \, dp_z$ or velocity space element $dv_x \, dv_y \, dv_z$

$$\frac{2}{h^3} dp_x \, dp_y \, dp_z = 2 \left( \frac{m}{h} \right)^3 dv_x \, dv_y \, dv_z. \qquad \ldots(7)$$

In thermal equilibrium and in the absence of the electric field the average number of occupied electronic states is

$$(dn)_{equlibrum} = 2 \left( \frac{m}{h} \right)^3 f_0(\varepsilon) \, dv_x \, dv_y \, dv_z$$

where $f_0(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/kT} + 1}$ is the Fermi-Dirac distribution function and represents the probability that a state at energy $\varepsilon$ is occupied.

Here $\mu$ is often referred as chemical potential or the Fermi energy $\varepsilon_F$ for a free electron gas.

When the electric field $E$ along X-axis is applied, the electron gas is in non-equilibtium state, then the average number of occupied electronic states is given by

$$dn = 2 \left( \frac{m}{h} \right)^3 f(\varepsilon) \, dv_x \, dv_y \, dv_z. \qquad \ldots(8)$$

Therefore, the current density is given by

$$\therefore \quad J_x = -nev_x = -\int dn \cdot e \, v_x$$

$$= -e \iiint_{-\infty}^{+\infty} v_x \cdot 2 \left( \frac{m}{h} \right)^3 f(\varepsilon) \, dv_x \, dv_y \, dv_z \qquad \ldots(9)$$

Using equation (6),

$$J_x = -2e \left( \frac{m}{h} \right)^3 \iiint_{-\infty}^{+\infty} v_x f_0 \, dv_x \, dv_y \, dv_z - 2e^2 \left( \frac{m}{h} \right)^3 \iiint_{-\infty}^{+\infty} \tau_c \cdot E v_x^2 \left( \frac{\partial f_0}{\partial \varepsilon} \right) dv_x \, dv_y \, dv_z .$$

As $f_0$ is symmetrical function in $v_x$, the integral

$$\int_{-\infty}^{+\infty} v_x f_0 \, dv_x = 0$$

Therefore,

$$J_x = -2e^2 E \left( \frac{m}{h} \right)^3 \iiint_{-\infty}^{+\infty} \tau_c \cdot v_x^2 \frac{\partial f_0}{\partial \varepsilon} dv_x \, dv_y \, dv_z. \qquad \ldots(10)$$

Now averaging over the angle $\theta$, we obtain $\langle v_x^2 \rangle = v^2 \overline{\cos^2 \theta} = \frac{1}{3} v^2$ and we may write $dv_x \, dv_y \, dv_z = 4\pi v^2 \, dv$.

Also relaxation time $\tau_c = \frac{\lambda}{v}$, where $\lambda$ is the mean free path.

Then equation (10) takes the form

$$J_x = -\frac{16\pi}{3} e^2 E \left( \frac{m}{h} \right)^3 \int_0^\infty \lambda v^3 \left( \frac{df_0}{\partial \varepsilon} \right) dv. \qquad \ldots(11)$$

We know $\varepsilon = \frac{1}{2} m v^2$, therefore using $v = \sqrt{\left( \frac{2\varepsilon}{m} \right)}$

and $\qquad dv = \left( \frac{2\varepsilon}{m} \right)^{-1/2} \frac{1}{m} d\varepsilon$ in eqn. (11),

we get $\qquad J_x = -\frac{16\pi m}{3h^2} e^2 \cdot E \int_0^\infty \lambda \, \varepsilon \frac{\partial f_0}{\partial \varepsilon} d\varepsilon. \qquad \ldots(12)$

As $\frac{\partial f_0}{\partial \varepsilon} = \frac{\partial}{\partial \varepsilon} \left( \frac{1}{e^{(\varepsilon - \mu)/kT} + 1} \right)$ is negative, therefore $J_x$ is positive.

The integration over the energy $\varepsilon$ is performed by limiting ourselves to the zeroth order approximation. As $\partial f_0 / \partial \varepsilon$ has a sharp maximum at $\varepsilon = \mu$, which is approximation $\varepsilon = \mu_0$, and

$$\int_0^\infty \frac{\partial f_0}{\partial \varepsilon} d\varepsilon = f_0(\infty) - f(0) = -1,$$

we may write equation (12) as

$$J_x \simeq \frac{16\pi m}{3h^3} \cdot e^2 \cdot E \lambda_0 \mu_0, \qquad \ldots(13)$$

where $\lambda_0$ is the mean free path of the electrons having the energy $\varepsilon = \mu_0$.

Now eliminating $h^3$ in equation (13) by the equation

$$\mu_0 = \varepsilon_F(0) = \frac{h^2}{8\pi^2 m}(3\pi^2 n)^{2/3} \qquad \ldots(14)$$

we get

$$J_x = \frac{e^2 E \lambda_0}{m} n \left(\frac{m}{2\mu_0}\right)^{1/2}$$

Here $n$ is the number of electrons per unit volume.

But $\left(\frac{2\mu_0}{m}\right)^{1/2} = v_F$ is the velocity of electrons at the Fermi surface *i.e.*, the upper edge of field bands, therefore

$$J_x = \frac{ne^2}{m} \cdot \frac{\lambda_0}{v_F} E$$

But $\frac{\lambda_0}{v_F} = \tau_F$ is the relaxation time at the Fermi surface there-fore finally, we have

$$J_x = \frac{ne^2 \tau_F}{m} E. \qquad \ldots(15)$$

Hence the electrical conductivity $\sigma$ is given by

$$\sigma = \frac{J_x}{E} = \frac{ne\tau_F}{m} \qquad \ldots(16)$$

**Thermal Conductivity :** Let us consider a metallic specimen with a temperature gradient $\frac{dT}{dx}$ along $X$-axis. In the measurement of thermal conductivity the experimental conditions are such that the electric current is zero, but not the electric field. The temperature gradient in the metal establishes as electric field such that the electric current in the metal is zero. Thus the *Boltzmann's transport equation* beside the thermal gradient $(dT/dx)$ includes a term containg an electric field.

As in the case of electrical conductivity, the *Boltzmann's transport equation* under the steady state $\left(\frac{\partial f}{\partial t} = 0\right)$ is given by

$$v_x \frac{\partial f}{\partial x} - \frac{eE}{m}\frac{\partial f}{\partial v_x} = -\frac{f - f_0}{\tau_c} \qquad \ldots(17)$$

This equation yields

$$f = f_0 - \tau_c\left(v_x \frac{\partial f}{\partial x} - \frac{eE}{m}\frac{\partial f}{\partial v_x}\right) \qquad \ldots(18)$$

When the temperature gradient and electric field are very weak, then we may write $f \approx f_0$ in the bracketed expansion; thus we get

$$f = f_0 - \tau_c\left(v_x \frac{\partial f_0}{\partial x} - \frac{eE}{m}\frac{\partial f_0}{\partial v_x}\right) \qquad \ldots(19)$$

As electron gas in metal obey Fermi-Dirac statistics, the *equilibrium distribution function* $f_0$ is given by

$$f_0 = \frac{1}{e^{(\varepsilon - \mu)/kT} + 1} \qquad \ldots(20)$$

Carrying out its differentiation w.r.t. to we get

$$\frac{\partial f_0}{\partial x} = \frac{\partial f_0}{\partial T} \cdot \frac{\partial T}{\partial x} = \frac{\partial f_0}{\partial \varepsilon}\left[\frac{\mu}{T} - \frac{\varepsilon}{T} - \frac{\partial \mu}{\partial T}\right] \cdot \frac{\partial T}{\partial x} \qquad \ldots(21)$$

Substituting this value in equation (19) and using

$$\frac{\partial f_0}{\partial v_x} = mv_x \frac{\partial f_0}{d\varepsilon}, \text{ we get}$$

$$f = f_0 - \tau_c \cdot v_x \frac{\partial f_0}{\partial \varepsilon}\left[\frac{dT}{dx} - \frac{\varepsilon}{T} - \frac{\partial \mu}{\partial T} - eE\right] \qquad \ldots(22)$$

In the presence of the electric field and the temperature gradient, the electron gas is non-equilibrium state; then the average number of occupied electronic states per unit volume in the velocity space element $dv_x\,dv_y\,dv_z$ is given by

$$dn = \frac{2}{h^3} f\,dp_x\,dp_y\,dp_z = 2\left(\frac{m}{h}\right)^3 f \cdot dv_x\,dv_y\,dv_z. \qquad \ldots(23)$$

The heat flow $Q_x$ due to electrons is the kinetic energy $\varepsilon$ carried by them along $X$-axis. This is the product $v_x\,\varepsilon$, integrated for the electrons in unit volume, over all velocities, *viz.*

$$Q_x = 2\left(\frac{m}{h}\right)^3 \iiint_{-\infty}^{+\infty} v_x\,\varepsilon \cdot f\,dv_x\,dv_y\,dv_z. \qquad \ldots(24)$$

In order to determine the heat transported under conditions of no electric current, the field $E$ is determined in such a way that $J_x$ calculated by equation (9) is zero for a given temperature gradient ~~$(dT/dx)$. The heat flow $Q_x$ of~~ equation (24) ~~is then~~ calculated with the given $(dT/dx)$ and the electric field $E$.

It is clear that under all conditions the contributions of the first term $f_0$ or equation (22) to both $Q_x$ and $J_x$ are zero, since, $f_0$ is symmetrical in $v_x$. So for orbitrary tield and temperature gradient $(dT/dx)$, the general equations for *current density and heat flow* are

$$J_x = -e \iiint_{-\infty}^{+\infty} v_x \cdot 2\left(\frac{m}{h}\right)^3 \cdot f\,dv_x\,dv_y\,dv_z$$

$$= -2e\left(\frac{m}{h}\right)^3 \iiint_{-\infty}^{+\infty} \tau_c v_x^2 \frac{\partial f_0}{d\varepsilon}\left\{eE - \frac{dT}{dx}\left(\frac{\mu}{T} - \frac{\varepsilon}{T} - \frac{\partial \mu}{\partial T}\right)\right\} \times dv_x\,dv_y\,dv_z, \qquad \ldots(25)$$

and

$$Q_x = -2\left(\frac{m}{h}\right)^3 \iiint_{-\infty}^{+\infty} \tau_c v_x^2 \frac{\partial f_0}{\partial \varepsilon}\left\{-eE + \frac{dT}{dx}\left(\frac{\mu}{T} - \frac{\varepsilon}{T} - \frac{\partial \mu}{\partial T}\right)\right\} \times dv_x\,dv_y\,dv_z. \qquad \ldots(26)$$

Now averaging over the angle $\theta$, we obtain

$$< v_x^2 > = v^2 \overline{\cos^2 \theta} = \frac{1}{3} v^2,$$

and we may write $dv_x\,dv_y\,dv_z = 4\pi v^2\,dv$.

Also relaxation time (or mean free time) $\tau_c = \frac{\lambda}{v}$, where $\lambda$ is the *mean free path.*

Then equation (25) and (26) take the form

$$J_x = -\frac{3}{2}\pi e\left(\frac{m}{h}\right)^3 \lambda v^3 \frac{\partial f_0}{d\varepsilon}\left\{eE - \frac{\partial T}{\partial x} \times \left(\frac{\mu}{T} - \frac{\varepsilon}{T} - \frac{\partial \mu}{\partial T}\right)\right\} dv \qquad \ldots(27)$$

$$Q_x = -\frac{8}{3}\pi\left(\frac{m}{h}\right)^3 \int_0^\infty \lambda v^2 \varepsilon \frac{\partial f_0}{\partial \varepsilon}\left\{-eE + \frac{\partial T}{\partial x} \times \left(\frac{\mu}{T} - \frac{\varepsilon}{T} - \frac{\partial \mu}{\partial T}\right)\right\} dv \quad \ldots(28)$$

Since $\varepsilon = \frac{1}{2} mv^2$, therefore using

$$v = \sqrt{\left(\frac{2\varepsilon}{m}\right)} \text{ and } dv = \left(\frac{2\varepsilon}{m}\right)^{-1/2} \frac{1}{m} d\varepsilon$$

in equations (27) and (28), we get

$$J_x = -\frac{16\pi m}{3h^3} \cdot e \int_0^\infty \lambda \varepsilon \frac{\partial f_0}{\partial \varepsilon}\left\{eE - \frac{\partial T}{\partial x}\left(\frac{\mu}{T} - \frac{\varepsilon}{T} - \frac{\partial \mu}{\partial T}\right)\right\} d\varepsilon \quad \ldots(29)$$

and

$$Q_x = -\frac{16\pi m}{3h^3} \int_0^\infty \lambda \varepsilon^2 \frac{\partial f_0}{\partial \varepsilon}\left\{-eE + \frac{\partial T}{\partial x}\left(\frac{\mu}{T} - \frac{\varepsilon}{T} - \frac{\partial \mu}{\partial T}\right)\right\} d\varepsilon \quad \ldots(30)$$

Now using the abbreviation,

$$-\frac{16\pi m}{3h^3} \int_0^\infty \lambda \varepsilon^\nu \frac{\partial f_0}{\partial \varepsilon} d\varepsilon = J_\nu \quad \ldots(31)$$

Equations (29) and (30) take the form

$$J_x = \left[e^2 E - e\frac{\partial T}{\partial x}\left(\frac{\mu}{T} - \frac{\partial \mu}{\partial T}\right)\right] J_1 + \frac{e}{T}\frac{\partial T}{\partial x} J_2 \quad \ldots(32)$$

$$Q_x = \left[-eE - \frac{dT}{dx}\left(\frac{\mu}{T} - \frac{\partial \mu}{\partial T}\right)\right] J_2 - \frac{1}{T}\frac{\partial T}{\partial x} J_3 \quad \ldots(33)$$

As the electric current density must be equal to zero, therefore equating $J_x$ in equation (32) to zero; the electric field $E$ in the metal must be given by

$$eE = -\frac{1}{T}\frac{\partial T}{\partial x}\frac{J_2}{J_1} + \frac{\partial T}{\partial x}\left(\frac{\mu}{T} - \frac{\partial \mu}{\partial T}\right). \quad \ldots(34)$$

Substituting this value of $eE$ in equation (33). we get

$$Q_x = -\frac{1}{T}\frac{\partial T}{\partial x}\frac{J_3 J_1 - J_2^2}{J_1}. \quad \ldots(35)$$

The integral

$$J_\nu = \frac{16\pi m}{3h^3}\left[(\lambda\varepsilon^\nu)_{\varepsilon=\mu} + \frac{\pi^2}{6}(kT)^2\left(\frac{d^2(\lambda\varepsilon^\nu)}{d\varepsilon^2}\right)_{\varepsilon=\mu}\right]$$

$$= \frac{16\pi m}{3h^3}\left[\lambda\mu^\nu + \frac{\pi^2}{6}(kT)^2\left\{\nu(\nu-1)\lambda\sigma^{\nu-2} + 2\nu\lambda'\mu^{\mu-1} + \lambda''\mu^\nu\right\}\right] \quad \ldots(36)$$

where $\lambda$, $\lambda'$ and $\lambda''$ signify zeroth, first and second derivatives of $\lambda$ with respect to $\varepsilon$ *at* $\varepsilon = \mu$ respectively.

Using integrals for $J_\nu$ from equation (36), we get

$$\frac{J_3 J_1 - J_2^2}{J_1} = \frac{16\pi^3 m}{9h^3}(kT)^2 \lambda\mu. \quad \ldots(37)$$

Now we may replace $\lambda$ and $\mu$ by their values $\lambda_0$ and $\mu_0$ at absolute zero. Then equation (35) gives

$$Q_x = -\frac{16\pi^3 m}{9h^3}(\lambda_0\mu_0)\frac{(kT)^2}{T}\frac{dT}{dx} \quad \ldots(38)$$

Now eliminating $h^3$ with the help of equation (14) *viz.*

$$\mu_0 = \varepsilon(0) = \frac{h^2}{8m}\left(\frac{3n}{\pi}\right)^{2/3} \quad \ldots(39)$$

we get

$$Q_x = -\frac{1}{3}\frac{\pi^2 n\lambda_0}{m}\left(\frac{m}{2\mu_0}\right)^{1/2} \cdot k^2 T \cdot \frac{dT}{dx} \quad \ldots(40)$$

If $v_x$ is the velocity of the electrons at the Fermi surface, *i.e.*, at the upper edge of the filled bands, then we have

$$v_F = \left(\frac{2\varepsilon_F(0)}{m}\right)^2 = \left(\frac{2\mu_0}{m}\right)^{1/2} \quad \ldots(41)$$

The equation (40) may be written as

$$Q_x = -\frac{1}{3}\frac{\pi^2 n\lambda_0}{m} \cdot k^2 T \cdot \frac{dT}{dx} \quad \ldots(42)$$

But $\frac{\lambda}{v_F} = \tau_F$ is the relaxation time at the Fermi's surface, therefore finally equation (42) may be written as

$$Q_x = -\frac{1}{3}\frac{\pi^2 n\tau_F}{m} \cdot k^2 T \cdot \frac{dT}{dx} \quad \ldots(43)$$

The thermal conductivity $K$ is given by

$$K = -\frac{Q_x}{dT/dx} = \frac{1}{3}\frac{\pi^2 n\tau_F}{m} k^2 T \quad \ldots(44)$$

The ratio of thermal conductivity to electrical conductivity is

$$\frac{K}{\sigma} = \frac{1}{3}\frac{\pi^2 k^2}{e^2} T. \quad \ldots(45)$$

This equation represents the mathematical form of *Wiedmann Franz law*. This quantity $\frac{\pi^2 k^2}{3e^2}$ is termed as *Lorentz number*.

## 9.6 Magneto-Resistance

The phenomenon of change of resistance of metals under the influence of a magnetic field is called the *magneto-resistance effect*. The magneto-resistance effect is produced due to the fact that when the magnetic field is applied, the paths of the electrons become curved and do not follow exactly the direction of the superimposed electric field. The magneto-resistance is measured by the ratio of the change in the resistance (resistivity) under the influence of the magnetic field to the resistane in the absences of the magnetic field. When the magnetic field is applied normal to the current flow, the effect is termed as ***transverse magneo-resistance*** and when field is applied along the current flow, the effect is termed as ***longitudinal magneto-resistance.***

If $R$ is the resistance of the metal in the absence of the magnetic field and $\Delta R$ is the change in the resistance due to the application of the magnetic fielf $B$, then it is found that the magnetoresistance $\Delta R/R$ varies as $B^2$ for comparatively low values; but varies as $B$ for higher values of the magnetic field. We shall consider here the transverse magneto-resistance which is of much greater interest.

Let us consider a long thin wire directed along $X$-axis. Let the wire be subjected to an electric field $E_x$ along $X$-axis and a uniform magnetic field $B_z$ along $Z$-axis, thus normal to axis of the wire.

Now the Lorentz force exerted on an electron of charge $-e$ and velocity v is

$$\mathbf{F} = e\,[\mathbf{E} + \mathbf{v} \times \mathbf{B}]$$

or
$$(\mathbf{i}F_x + \mathbf{j}F_y + \mathbf{k}F_z) = -e\,[\mathbf{i}E_x + (\mathbf{i}v_x + \mathbf{j}v_y + \mathbf{k}v_z) \times (\mathbf{k}B_z)]$$

or
$$\mathbf{i}\,F_x + \mathbf{j}F_y + \mathbf{k}F_z = -e\,[\mathbf{i}E_x - \mathbf{j}v_x\,B_z + \mathbf{i}v_y\,B_z].$$

Comparing coefficients of **i**, **j** and **k**, we get

$$F_x = -e\,[E_x + v_y\,B_z]$$
$$F_y = ev_x\,B_z,$$
$$F_z = 0,$$

i.e.
$$\left.\begin{aligned} m\frac{d^2x}{dt^2} &= -eE_x - eB_z\frac{dy}{dt} &&\ldots(a)\\ m\frac{d^2y}{dt^2} &= eB_z\frac{dx}{dt} &&\ldots(b)\\ m\frac{d^2z}{dt^2} &= 0. &&\ldots(c)\end{aligned}\right\} \qquad \ldots(1)$$

Integrating equations (1$a$) and (1$b$), we get

$$m\frac{dx}{dt} = -eE_xt - eB_z\,y + C_1,$$
$$m\frac{dy}{dt} = eB_zx + C_2,$$

where $C_1$ and $C_2$ constants of integration.

Let the initial conditions be:

At $t = 0$, $x = y = 0$, $\quad \dfrac{dx}{dt} = v_{ox}$, $\dfrac{dy}{dt} = v_{oy}$.

Then, we have $\quad C_1 = mv_{ox}$ and $C_2 = mv_{oy}$.

Therefore,
$$m\frac{dx}{dt} = -eE_x\,t - eB_z\,y + mv_{ox}$$
$$m\frac{dy}{dt} = eB_z\,x + mv_{oy}.$$

or
$$\frac{dx}{dt} = -\frac{eE_x}{m}t - \frac{eB_z}{m}y + v_{ox} \qquad \ldots(2)$$
$$\frac{dy}{dt} = \frac{eB_z}{m}x + v_{oy}. \qquad \ldots(3)$$

Integrating equation (2), we have

$$x = -\frac{eE_x}{m}\frac{t^2}{2} - \frac{eB_z}{m}yt + v_{ox}\,t + C_3.$$

As at $t = 0$, $x = 0$, therefore $C_3 = 0$

Then
$$x = -\frac{eE_x}{m}\cdot\frac{t^2}{2} - \frac{eB_z}{m}yt + v_{ox}\,t. \qquad \ldots(4)$$

Substituting this value of $x$ is equation (3), we get

$$\frac{dy}{dt} = \frac{eB_x}{m}\left[-\frac{eE_x}{m}\frac{t^2}{2} - \frac{eB_z}{m}yt + v_{ox}\,.\,t\right] + v_{oy}.$$

Substituting this value of $\dfrac{dy}{dt}$ in equation (1$a$), we get

$$m\frac{d^2x}{dt^2} = -eE_x - eB_z\left[\frac{eB_z}{m}\left\{-\frac{eE_x}{m}\frac{t^2}{2} - \frac{eB_z}{m}yt + v_{ox}\,t\right\} + v_{oy}\right]$$

or
$$\frac{d^2x}{dt^2} = -\frac{e}{m}\left[E_x + B_z \times \left\{\frac{eB_z}{m}\left(-\frac{eE_x}{m}\frac{t^2}{2} - \frac{eB_z}{m}yt + v_{ox}\,t\right) + v_{oy}\right\}\right] \qquad \ldots(5)$$

Integrating this equation, we get

$$\frac{dx}{dt} = -\frac{e}{m}\left[E_x\,t + B_z \times \left\{\frac{eB_z}{m}\left(-\frac{eE_x}{m}\frac{t^3}{6} - \frac{eB_z}{m}\frac{yt^2}{2} + \frac{v_{ox}\,t^2}{2}\right) + v_{oy}\,t\right\}\right]$$

If $\tau_c$ is the mean free time between two successive collisions, we have

$$<\frac{dx}{dt}> = \frac{1}{\tau_c}\int_0^{\tau_c}\frac{dx}{dt}\,dt$$
$$= -\frac{e}{m\tau_c}\left[\int_0^{\tau_c} E_xt\,dt + B_z\left\{\frac{eB_z}{m}\times\left(\int_0^{\tau_c} -\frac{eE_x}{6m}\right)t^3\,dt + \right.\right.$$
$$\left.\left.\int_0^{\tau_c}\left(-\frac{eB_z}{m}\right)\frac{yt^2}{2}\,dt + \left(\int_0^{\tau_c}\frac{v_{ox}\cdot t^2}{2}\,dt\right) + \int_0^{\tau_c} v_{oy}\,t\,dt\right\}\right]$$
$$= -\frac{e}{m\tau_c}\left[\frac{E_x\tau_c^2}{2} + B_z\left\{\frac{eB_z}{m}\left(-\frac{eE_x}{24m}\tau_c^4 - \frac{eB_z}{6m}y\tau_c^3 + \frac{v_{ox}\,\tau_c^3}{6}\right) + \frac{v_{oy}\,\tau_c^2}{2}\right\}\right] \qquad \ldots(6)$$

In the case of weak magnetic field the terms containing $B_z$ alone may be neglected. Moreover, the average values of $v_{ox}$ and $v_{oy}$ are also zero because the electrons have the same probability of moving along positive and negative axes.

Therefore, equation (6) reduce to

$$<\frac{dx}{dt}> = <\dot{x}> = \bar{\dot{x}} = -\frac{1}{2}\frac{eE_x}{m}\cdot\tau_c + \frac{e^3B_z^2E_x}{24m^3}\tau_c^3. \qquad \ldots(7)$$

Now, the current density

$$J_x = -ne\bar{v} = -ne\bar{\dot{x}}$$
$$= -ne\left[-\frac{1}{2}\frac{eE_x}{m}\tau_c + \frac{e^3B_z^2E_x}{24m^3}\tau_c^3\right]$$
$$\Rightarrow\; J_x = \frac{ne^2E_x}{2m}\left[\tau_c - \frac{1}{12}\frac{e^2B_z^2}{m^2}\tau_c^3\right] \qquad \ldots(8)$$

Therefore the *electrical conductivity* σ is given by

$$\sigma = \frac{J_x}{E_x} = \frac{ne^2}{2m}\left[\tau_c - \frac{1}{12}\frac{e^2B_z^2}{m^2}\tau_c^3\right] \qquad \ldots(9)$$

In the absence of the magnetic field $B_z = 0$, then *electrical conductivity* $\sigma_0$ is given by

$$\sigma_0 = \frac{ne^2}{2m}\tau_0. \qquad \ldots(10)$$

From equations (9) and (10) the ratio $\frac{\sigma - \sigma_0}{\sigma}$ is given by

$$\frac{\sigma - \sigma_0}{\sigma_0} = \frac{\tau_c - \tau_0}{\tau_0} - \frac{1}{12} \frac{e^2 B_z^2}{m^2} \frac{\tau_c^3}{\tau_0} \qquad \ldots(11)$$

Using the approximation $\tau_c = \tau_0$, we get

$$\frac{\Delta\sigma}{\sigma_0} = \frac{\sigma - \sigma_0}{\sigma_0} = \frac{\Delta\tau}{\tau_0} - \frac{1}{12} \frac{e^2 B_z^2}{m^2} \tau_0^2. \qquad \ldots(12)$$

Using (10), *i.e.* $\tau_0 = \frac{2m\sigma_0}{ne^2}$, above equation may be written as

$$\frac{\Delta\sigma}{\sigma_0} = \frac{\Delta\tau}{\tau_0} - \frac{1}{12} \frac{e^2 B_z^2}{m^2} \left( \frac{2m\sigma_0}{ne^2} \right)^2 = \frac{\Delta\tau}{\tau_0} - \frac{1}{3} \frac{B_z^2 \sigma_0^2}{n^2 e^2} \qquad \ldots(13)$$

The change in resistivity is given by

$$\frac{\Delta\rho}{\rho_0} = -\frac{\Delta\sigma}{\sigma_0} = -\frac{\Delta\tau}{\tau_0} + \frac{1}{3} \left( \frac{\sigma_0}{ne} \right)^2 B_z^z. \qquad \ldots(14)$$

If $\Delta\tau/\tau_0$ is very small, then

$$\frac{\Delta\rho}{\rho_0} = \frac{1}{3} \left( \frac{\sigma_0}{ne} \right)^2 B_z^2 = AB_z^2. \qquad \ldots(15)$$

where $A = \frac{1}{3} (\sigma_0 / ne)^2$,

*i.e.*,

$$\frac{\Delta\rho}{\rho_0} = \frac{\Delta R}{R_0} \propto B_z^2. \qquad \ldots(16)$$

Obviously, for weak magnetic fields the magneto-resistance is proportional to the square of the magnetic field. This result has been deduced for electrons as charge carriers. But in general there may be two groups of charge carriers *i.e.*, electrons and holes.

In such a general case

$$\frac{\Delta\rho}{\rho_0} = \frac{\rho - \rho_0}{\rho_0} = \frac{\sigma_1 \sigma_2 (\beta_1 - \beta_2) B_z}{(\sigma_1 + \sigma_2) + B_z^2 (\beta_1 \sigma_1 + \beta_2 \sigma_2)^2}, \qquad \ldots(17)$$

where

$$\beta_1 = \frac{q_1 \tau_1}{m_1}, \; \beta_2 = \frac{q_2 \tau_2}{m_2}$$

where $q_1, \tau_1, m_1$ are respectively the charge, mean free time, mass of each electron and $q_2, \tau_2, m_2$ are the corresponding quantities for each hole. It is obvious from equation (17) that the magnetoresistance essentially increases (since $\Delta\rho/\rho_0$ is positive) and vanishes only if $\beta_1 = \beta_2$.

## SOLVED EXAMPLES

**Ex. 1.** *Use Boltzmann's transport equation to obtain the distribution function for magneto-resistance effects. Hence show that if the relaxation time is independent of time, there is no magnetoresistance.*

**Solution :** We shall consider the influence on the static electrical conductivity of a magnetic field transverse to the current flow for a Maxwellian electron gas at constant temperature.

The Boltzmann's transport equation in the steady state is written as

$$a \cdot \nabla_v f = \frac{f - f_0}{\tau_c} \qquad \ldots(1)$$

This equation gives

$$f = f_0 + \tau_c \, \mathbf{a} \cdot \nabla_v f \qquad \ldots(2)$$

Let

$$f = f_0 (1 + \phi), \qquad \ldots(3)$$

where $\phi$ is yet undermined function.

We have

$$\nabla_v f = \nabla_v \{ f_0 (1 + \phi) \} = (1 + \phi) \nabla_v f_0 + f_0 \nabla_v \phi. \qquad \ldots(4)$$

Now for a Maxwellian distribution

$$\nabla_v f_0 = \nabla_v \left[ n \cdot \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT} \right] = -\frac{m\mathbf{v}}{kT} f_0. \qquad \ldots(5)$$

The Lorentz force acting on an electron of charge $-e$ and moving with velocity v is given by

$$\mathbf{F} = -e [\mathbf{E} + \mathbf{v} \times \mathbf{B}], \qquad \ldots(6)$$

where **B** is the magnetic induction and **E** is the electric field.

Therefore, the acceleration **a** is given by

$$\mathbf{a} = -\left( \frac{e}{m} \right) [\mathbf{E} + \mathbf{v} \times \mathbf{B}].$$

Then

$$\begin{aligned} \mathbf{a} \cdot \nabla_v f_0 &= -\left( \frac{e}{m} \right) [\mathbf{E} + \mathbf{v} \times \mathbf{B}] \cdot \left( -\frac{m\mathbf{v}}{kT} f_0 \right) \\ &= \frac{ef_0}{kT} \mathbf{E} \, . \, \mathbf{v} + \frac{ef_0}{kT} \mathbf{v} \, . \, \mathbf{v} \times \mathbf{B} \\ &= \frac{ef_0}{kT} \mathbf{E} \, . \, \mathbf{v} \qquad (\text{since } (\mathbf{v} \, . \, \mathbf{v} \times \mathbf{B} = 0). \qquad \ldots(7) \end{aligned}$$

Further

$$\begin{aligned} \mathbf{a} \, . \, \nabla_v \phi &= -\left( \frac{e}{m} \right) [\mathbf{E} + \mathbf{v} \times B] \, . \, \nabla_v \phi \\ &= -\left( \frac{e}{m} \right) [\mathbf{E} \, . \, \nabla_v \phi + \mathbf{v} \times \mathbf{B} \, . \, \nabla_v \phi]. \qquad \ldots(8) \end{aligned}$$

But the first term on R.H.S. is order $E^2$, as $\mathbf{E} = -\nabla \phi$, hence it may be neglected for weak fields

$$\mathbf{a} \, . \, \Delta_v \phi = -\left( \frac{e}{m} \right) \mathbf{v} \times \mathbf{B} \, . \, \nabla_v \phi. \qquad \ldots(9)$$

Now, using equations (2), (7) and (9) and neglecting smaller terms, we get

$$\phi f_0 = \frac{ef_0 \tau_c}{m} \mathbf{v} \times \mathbf{B}. \; \nabla_v \phi - \frac{ef_0 \tau_c}{kt} \mathbf{E} \cdot \mathbf{v}$$

or

$$\phi / \tau_c + (e/kT) \, \mathbf{E} \, . \, \mathbf{v} - (e/m) \, \mathbf{v} \times \mathbf{B} \, . \, \nabla_v \phi = 0. \qquad \ldots(10)$$

Let us now write the solution of equation (10) of the form

$$\phi = \mathbf{M} \, . \, \mathbf{v} + \mathbf{N} \, . \, \mathbf{v} \times \mathbf{B}, \qquad \ldots(11)$$

where **M**, **N** are constant vectors perpendicular to **B** and of magnitude to be determined by equation (10).

From equations (10) and (11), we have

$$\frac{\mathbf{M} \, . \, \mathbf{v}}{\tau_c} + \frac{\mathbf{N} \, . \, \mathbf{v} \times \mathbf{B}}{\tau_c} + \frac{e}{kT} \mathbf{E} \, . \, \mathbf{v} - \frac{e}{m} \mathbf{v} \times \mathbf{B} \, . \, \nabla_v (\mathbf{M} \, . \, \mathbf{v} + \mathbf{N} \, . \, \mathbf{v} \times \mathbf{B}) = 0. \qquad \ldots(12)$$

Now using the results

$$\nabla_v (\mathbf{M} . \mathbf{v}) = \mathbf{M},$$

and

$$\nabla_v [\mathbf{N} . \mathbf{v} \times \mathbf{B}] = -\mathbf{N} \times \mathbf{B}.$$

equation (12) becomes

$$\frac{\mathbf{M} . \mathbf{v}}{\tau_c} + \frac{e}{kT} \mathbf{E} . \mathbf{v} + \frac{\mathbf{N} . \mathbf{v} \times \mathbf{B}}{\tau_c} - \frac{1}{m} (\mathbf{v} \times \mathbf{B}) . (\mathbf{M} - \mathbf{N} \times \mathbf{B}) = 0. \qquad ...(13)$$

But $(\mathbf{v} \times \mathbf{B}) . (\mathbf{N} \times \mathbf{B}) = (\mathbf{v} . \mathbf{N}) B^2 - (\mathbf{B} . \mathbf{N}) (\mathbf{v} . \mathbf{B}). = (\mathbf{v} . \mathbf{N}) B^2,$ ...(14)

Since N is assumed perpendicular to B.

Therefore equation (13) may be satisfied by two equations

$$\left.\begin{aligned} \frac{\mathbf{M} . \mathbf{v}}{\tau_c} + \frac{e}{kT} \mathbf{E} . \mathbf{v} + \frac{eB^2}{m} (\mathbf{v} . \mathbf{N}) = 0 \\ \frac{\mathbf{N} . \mathbf{v} \times \mathbf{B}}{\tau_c} - \frac{e}{m} \mathbf{N} . \mathbf{v} \times \mathbf{B} = 0 \end{aligned}\right\} \qquad ...(15)$$

Now equating the coefficient of v and v × B rseparately to zero, we get

$$\left.\begin{aligned} \frac{\mathbf{M}}{\tau_c} + \frac{e}{kT} \mathbf{E} + \frac{eB^2}{m} \mathbf{N} = 0 \\ \text{and} \qquad \frac{\mathbf{N}}{\tau_c} - \frac{e}{m} \mathbf{M} = 0. \end{aligned}\right\} \qquad ...(16)$$

Solving this pair of equation for M and N, we get

$$\mathbf{M} = -\frac{e\, \mathbf{E}\, \tau_c}{kT} \left[ 1 + \left( \frac{eB\tau_c}{m} \right)^2 \right]^{-1} \qquad ...(17)$$

and

$$\mathbf{N} = -\frac{e^2 \tau_c^2}{mkT} \mathbf{E} \left[ 1 + \left( \frac{eB\tau_c}{m} \right)^2 \right]^{-1} \qquad ...(18)$$

Now using the notation

$$\xi = \left[ 1 + \left( \frac{eB\tau_c}{m} \right)^2 \right]^{-1} \qquad ...(19)$$

Thus,

$$f = f_0 + f\phi = f_0 + f_0 (\mathbf{M} . \mathbf{v} + \mathbf{N} . \mathbf{v} \times \mathbf{B})$$

$$= f_0 - \frac{f_0 e \tau_c \xi}{kT} \mathbf{E} . \mathbf{v} - \frac{f_0 e^2 \tau_c^2}{mkT} \mathbf{E} . \mathbf{v} \times \mathbf{B} \qquad ...(23)$$

to order E . B or $B^2$

If B is along z direction, then

$$f = f_0 \left[ 1 - \frac{e\tau_c \xi}{kT} (E_x v_x + E_y v_y) - \frac{e^2 \tau_c^2 B}{mkT} (E_x v_y - E_y v_x) \right] \qquad ...(21)$$

This is the required expression for the distribution function.

Eqn. (21) can be used to obtain the coefficients in the equations.

$$\left.\begin{aligned} J_x = \sigma_{xx} E_x + \sigma_{xy} E_y \\ J_y = \sigma_{yx} E_x + \sigma_{yy} E_y \end{aligned}\right\} \qquad ...(22)$$

If the specimen is in the form of a slab with the current flowing down along X-axis and with the face of the slab normal to the Y-axis, and if the relaxation time $\tau_c$ is independent of velocity, then the conduction that there is no current flow along Y-axis requires the coefficient of $v_y$ in equation (21) to be zero. This gives

$$f = f_0 \left( 1 + \frac{e\tau_c}{kT} v_x E_x \right) \text{to order } B^2. \qquad ...(23)$$

This equation is independent of $B$ to order $B^2$. Thus we may say *there is no magneto-resistance if the relaxation time is independent of velocity.*

## 11.7 Viscosity form Boltzmann Equation

We shall now apply Boltzmann's transport equation

$$\frac{\partial f}{\partial t} \mathbf{v} . \text{grad}_r f + \mathbf{a} . \text{grad}_{\mathbf{v}} f = -\frac{f - f_0}{\tau_c} \qquad ...(1)$$

of find an expression for the viscosity of a gas obeying classical (Maxwell-Boltzmann) statistics with flow velocity in $x$-direction. If the velocity field in the gas is such that there is a velocity gradient $\gamma \left( = \frac{\partial v_x}{\partial y} \right)$ in the $y$-direction, then *flow velocity* **v** can be represented as

$$v_x = \gamma y, \; v_y = v_z = 0. \qquad ...(2)$$

The viscosity of the gas in now computed in the following steps :

(i) The Boltzmann's transport equation is written for the gas in the steady state in the absence of external body forces acting on the molecules.

(ii) The steady state distribution function is set up to give the postulated velocity field.

(iii) The shear force required to maintain the flow is calculated.

(iv) Finally, *we find the viscosity coefficient* η *which is defined as the shear per unit velocity gradient transverse to the flow.*

If $f_0 (v_x, v_y, v_z)$ denotes the thermal equilibrium distribution function for the gas at rest, then zero order approximation to the distribution function in the gas moving according to equation (2) would be expected to be

$$F_0 (v_x, v_y, v_z) = f_0 (v_x - \gamma y, v_y, v_z). \qquad ...(3)$$

Now assuming no external body forces acting on the molecule the Boltzmann transport equation (1) in the steady state takes form

$$\mathbf{v} . \text{grad}_r F (\mathbf{v}, \mathbf{r}) = -\frac{F - F_0}{\tau_c} \qquad ...(4)$$

$$\left( \text{Since here } \frac{\partial f}{\partial t} = 0 \text{ and } \mathbf{a} = 0 \right)$$

The equation gives

$$F = F_0 - \tau_c . \mathbf{v} . \text{grad}_r F (\mathbf{r}, \mathbf{v}). \qquad ...(5)$$

If the gas under consideration is not much deviated from equilibrium condition, we may use the first order approximation for $F(\mathbf{r}, \mathbf{v})$ and write $F (\mathbf{r}, \mathbf{v}) \approx F_0 (\mathbf{r}, \mathbf{v})$ on R.H.S. of equation (5).

Therefore equation (5) takes the form

$$F = F_0 - \tau_c \mathbf{v} . \text{grad}_r F_0 (\mathbf{r} . \mathbf{v})$$

$$= F_0 - \tau_c v_y \frac{\partial}{\partial y} f_0 \{ v_x - \gamma y, (v_y, v_z) \}$$

$$= F_0 + \tau_c \gamma v_y \frac{\partial}{\partial v_x} f_0 (v_x - \gamma y, v_y, v_z) \qquad ...(6)$$

If **v**′ denotes the molecular velocity relative to the flow velocity, then

$$v_x' = v_x - \gamma y, \; v_y' = v_y, \; v_z' = v_z \qquad \ldots(7)$$

and we have

$$F = F_0 + \tau_c \gamma v_y' \frac{\partial}{\partial v_x'} f_0 (v_x', v_y', v_z'). \qquad \ldots(8)$$

Now to compute the shear stress in $x$-direction across the plane normal to $y$-direction we have to calculate the net rate of transport of $x$-component of momentum across unit area in the $x$-$z$ plane from the region of smaller to greater $y$. This net rate of momentum transport is obtained by multiplying the distribution function $F$ with $mv_x' v_y'$ and integrated over **v**′, *i.e.* the net rate of transport of $x$-component of momentum across unit area in $x$-$z$ plane from the region of smaller to greater $y$ is given by

$$\int F \, . \, mv_x' \, . \, v_y' \, d\mathbf{v}'.$$

The quantity is equal to $-X_y$, the shear stress in the $x$-direction across the plane normal to the $y$-direction (the $x$-$z$ plane). Thus, we have

$$\begin{aligned} X_y &= -\int F \, . \, mv_x' \, . \, v_y' \, d\mathbf{v}' \\ &= -\int \left\{ F_0 + \tau_c \gamma v_y' \frac{\partial}{\partial v_x'} f_0 (v_x', v_y') \right\} mv'_x v_y' \, d\mathbf{v}' \\ &= -m \int F_0 v_x' \, . \, v_y' \, d\mathbf{v}' - m\tau_c \gamma \int v_x' v_y'^2 \frac{\partial}{\partial v_x'} f_0 (v_x', v_y', v_z') \, d\mathbf{v}'. \end{aligned}$$

Since $F_0$ is symmetrical function of $v_x'$ and $v_y'$, the integral

$$\int F_0 \, v_x' v_y' \, d\mathbf{v}' = 0.$$

So, we have

$$X_y = -m\tau_c \gamma \int v_x' v_y'^2 \frac{\partial}{\partial v_x'} f_0 (v_x' v_y', v_z') \, d\mathbf{v}'. \qquad \ldots(9)$$

Now integrating by parts we get

$$X_y = m\tau_c \gamma \int v_y'^2 f_0 (v_x', v_y', v_z') \, . \, d\mathbf{v}'. \qquad \ldots(10)$$

This may be written as

$$\begin{aligned} X_y &= 2\tau_c \gamma \int \left( \frac{1}{2} m v_y'^2 \right) f_0 (v_x'; v_y', v_z') \, d\mathbf{v}' \\ &= 2\tau_c \gamma \times (\text{Mean kinetic energy density in } y\text{-direction}). \end{aligned} \qquad \ldots(11)$$

In Maxwell-Boltzmann statistics the mean kinetic energy density in $y$ direction $= \frac{1}{2} nkT$, where $n$ is the number of molecules per unit volume.

Therefore, in Maxwell-Boltzmann statistics

$$X_y = 2\tau_c \gamma \cdot \frac{1}{2} nkT = n\tau_c kT\gamma.$$

The coefficient of viscosity, $\eta$, according to definition, is given by

$$\eta = \frac{X_y}{\gamma} = n\tau_c kT. \qquad \ldots(13)$$

## EXERCISES

### SHORT ANSWER QUESTIONS

1. Write Boltzmann's transport equation, standing the meaning of each term.
2. Write Chamber's equation. What does it describe ?
3. Express Boltzmann's transport equation for electron gas.
4. State Wiedmann-Franz law. On what factors does the ratio $\left( \frac{\text{Thermal Conductivity}}{\text{Electrical Conductivity}} \right)$ depend ?
5. What is Lorentz number ?
6. What do you mean by magneto-resistance effect ?
7. What is meant by magneto resistance ? How is it measured ?
8. How does magneto resistance depend on magnetic field if the field is weak ?
9. What is the value of coefficient of viscosity as derived by Boltzmann's transport equation ?

### LONG ANSWERS QUESTIONS

1. What is distribution function? Derive Maxwell-Boltzman's transport equation in the form
$$\frac{\partial f}{\partial t} + \mathbf{v} \, . \, \text{grad}_r f + \mathbf{a} \, . \, \text{grad}_v f = -\frac{f - f_0}{\tau_c}$$
where the symbols have their usual meaning
2. Derive the Boltzmann's transport equation and discuss the collision term.
3. Deduce the Boltzmann's transport equation. Prove that for a hetrogeneous medium
$$\left( \frac{\partial f}{\partial t} \right)_{\text{collision}} \neq 0.$$
4. What do you mean by a classical gas? Starting from Boltzmann's transport equation derive an expression for the coefficient of viscosity of a classical gas.
5. Derive Boltzmann transport equation and hence obtain an expression for the viscosity for a gas having Maxwellian velocity distribution.
6. Obtain the Boltzmann's transport equation in the relaxtion time aproximation. Use it to obtain the electrical conductivity in an electron gas assuming Maxwellian distribution.
7. Define electrical conductivity. Derive an expression for the electrical conductivity of electron gas in a metal using Boltzmann's equation.
8. (a) Derive Chamber's equation for the change in the distribution function of a system due to the applied fields.
   (b) Obtain an expression for the thermal conductivity of electron gas in a metal assuming that electron gas obey's Fermi-Dirac statistics.
9. Explain the term magneto-resistance. Obtain an expression for measurement of the transverse magneto-resistance and discuss it.

10. Use Maxwell-Boltzmann's equation to derive expressions for the electrical conductivity and thermal conductivity of electron gas in a metal, assuming that electron gas obeys Fermi-Dirac statistics. Hence derive Wiedmann-Franz law.
11. What do you menn by magneto-resistance? Derive an expression for the increase of resistivity of a metal to order $B^2$ when magnetic field $\vec{B}$ is applied perpendicular to the direction of current flow.
12. Calculate the thermal conductivity of a classical gas with a maan free path λ independent of the particle velocity, so that
$$\tau_c = \frac{\lambda_0}{v}.$$
13. Calculate the fractional change $(\Delta f/f)$ in the distribution function of Maxwellian electrons at 300K, using $E = 3 \times 10^4$ volt/metre and $\tau = 10^{-14}$ second.

## MULTIPLE CHOICE QUESTIONS : SELECT THE RIGHT CHOICE

1. The time rate of change of distribution function $f(\vec{r}, \vec{v})$, when number of particles is held constant, is given by :

(a) $\frac{\partial f}{\partial t} = \frac{d\vec{r}}{dt} + \frac{d\vec{v}}{dt}$

(b) $\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\text{drift.}}$ + constant

(c) $\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\text{collision}}$ + constant

(d) $\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\text{drfit.}} + \left(\frac{\partial f}{\partial t}\right)_{\text{collision}}$

2. Boltzmann's transport equation is :

(a) $\frac{\partial f}{\partial t} + \vec{v} \cdot \text{grad}_r f + \vec{a} \cdot \text{grad}_v f = \left(\frac{\partial f}{\partial t}\right)_{\text{collision}}$

(b) $\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau_c}$, $\tau_c$ is relaxation time

(c) $\delta f = q \frac{\partial f_0}{\partial W} \int_{-\infty}^{t_0} E(\vec{r}, t) \cdot \vec{v}(t) \exp\left\{-\int_t^{t_0} \frac{dt}{\tau_c(t)}\right\} dt$

(d) $\frac{K}{\sigma} = \frac{1}{3} \frac{\pi^2 k^2}{e^2} \cdot T$

3. Chamber's equation is :

(a) $\frac{\partial f}{\partial t} + \vec{v} \cdot \text{grad}_r f + \vec{a} \cdot \text{grad}_v f = \left(\frac{\partial f}{\partial t}\right)_{\text{collision}}$

(b) $\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau_c}$, $\tau_c$ is relaxation time

(c) $\delta f = q \frac{\partial f_0}{\partial W} \int_{-\infty}^{t_0} E(\vec{r}, t) \cdot \vec{v}(t) \exp\left\{-\int_t^{t_0} \frac{dt}{\tau_c(t)}\right\} dt$

(d) $\frac{K}{\sigma} = \frac{1}{3} \frac{\pi^2 k^2}{e^2} \cdot T$

4. Wiedmann-Franz law is :

(a) $\frac{\partial f}{\partial t} + \vec{v} \cdot \text{grad}_r f + \vec{a} \cdot \text{grad}_v f = \left(\frac{\partial f}{\partial t}\right)_{\text{collision}}$

(b) $\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau_c}$, $\tau_c$ is relexation time

(c) $\delta f = q \frac{\partial f_0}{\partial W} \int_{-\infty}^{t_0} E(\vec{r}, t) \cdot \vec{v}(t) \exp\left\{-\int_t^{t_0} \frac{dt}{\tau_c(t)}\right\} dt$

(d) $\frac{K}{\sigma} = \frac{1}{3} \frac{\pi^2 k^2}{e^2} \cdot T$

5. The Magneto resistance is defined as :
(a) the resistance offered by magnetic field to the flow of current
(b) the change of resistance of metals in external magnetic field
(c) the motion of charge in external magnetic field
(d) the disappearance of resistance in the magnetic field

6. The resistance of a metal changes by magnetic field if :
(a) the magnetic field is applied along the direction of current flow
(b) the magnetic fild is applied perpendicular to the direction of current flow
(c) both (a) and (b)
(d) neither (a) nor (b)

7. For weak magnetic field (B), the magneto-resistance of a metal when magnetic field is perpendicular to direction of current flow varies as :

(a) $B$ (b) $B^2$ (c) $B^4$ (d) $B^0$

8. The coefficient of viscosity according to Boltzmann's transport equation is given by η =

(a) $\eta\, \tau_c kT$ (b) $\frac{1}{2} \eta\, \tau_c kT$ (c) $\frac{1}{3} \eta\, \tau_c kT$ (d) $\frac{1}{2} \frac{\eta\, \tau_c}{kT^2}$

**ANSWERS**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. (d) | 2. (a) | 3. (c) | 4. (d) | 5. (b) | 6. (c) | 7. (b) | 8. (a) |

# 12

# FLUCTUATIONS AND IRREVERSIBLE PROCESSES

## 12.1 Introduction

In statistical mechanics, the equilibrium does not mean a rigrously unchanging state. Under the specific constraints, the assembly of molecules is free to take up all possible states. Therefore the given thermodynamic property of a system varies with time about the mean of equilibrium value. Such a variation of a system from its mean equilibrium value is called the fluctuation.

The fluctiations from equilibrium state are assumed to be small. It is useful to study the conditions for small fluctuations. If the fluctuations are small, then the three ensembles become equivalent. For example if fluctuation in energy $E$ in the systems of a canonical ensemble are small, it is equivalent to a microcanonical ensemble. If the fluctuations in energy ($E$) and number of particles ($N$) in systems of grand cenonical ensemble are quite small, then all the three ensembles are equivalent. A rough measure of fluctuations is provided by the *mean square–deviation*.

### Measure of Fluctuation : The Standard Deviation.

Consider a quantity $n$. Its average value is $\bar{n}$.

The deviation $\delta n$ is defined as

$$\delta n = n - \bar{n}$$

Clearly

$$\overline{\delta n} = \bar{n} - \bar{n} = 0$$

A first rough measure of fluctuations is provided by the mean square deviation.

$$\overline{(\delta n)^2} = \overline{(n-\bar{n})^2} = \overline{n^2} - 2\bar{n}\,\bar{n} + (\bar{n})^2$$

$$= \overline{n^2} - (\bar{n})^2$$

where $\overline{n^2}$ is the **second moments** of the distribution. The fluctuations is usually measured by standard deviation. The standard deviation $\Delta n$ is defined as **the root mean square deviation from the mean** and is given by

$$\Delta n = [\overline{(n-\bar{n})^2}]^{1/2}$$

If $P_i$ is the probability of a system in $i$th state and $f_i$ is value of physical quantity $f$ when the system is in $i$th state, then the average value of $f$ is defined as

$$\bar{f} = \sum_i P_i f_i \text{ with } \sum_i P_i = 1$$

Then

$$\overline{f - \bar{f}} = \Sigma P_i (f - \bar{f})$$

$$= \sum_i P_i f_i - \bar{f} \sum_i P_i = \bar{f} - \bar{f} = 0$$

and

$$\overline{(f-\bar{f})^2} = \sum_i P_i (f_i - \bar{f})^2$$

$$= \sum_i P_i f_i^2 - 2\bar{f} \sum_i P_i f_i + \overline{f^2} ) \sum_i P_i$$

$$= \overline{f^2} - 2(\bar{f})^2 + (\bar{f})^2$$

$$= \overline{f^2} - (\bar{f})^2$$

$\therefore$

$$\Delta f = [\overline{f^2} - (\bar{f})^2]^{1/2}$$

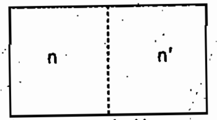
## 12.2 An illustaration of fluctuation : Molecules in two halves of a box

Consider an assembly of $N$ molecules in a box divided by some arbitrary partition into two equal parts.

Let the number of molecules in the two halves be denoted by $n$ and $n'$. Then $n + n' = N$.

If $N$ is large, we would ordinarily find $n \approx n'$. *i.e.*, half of the molecules will occupy roughly half of the box.

But this statement is roughly true because with the passage of time the number of molecules in each of the box fluctuates constanity due to collision with each other and with the walls of the box. Ordinarily these fluctuations are small so that $n$ does not differ too much from $(N/2)$, which ~~occurs~~ most frequently.



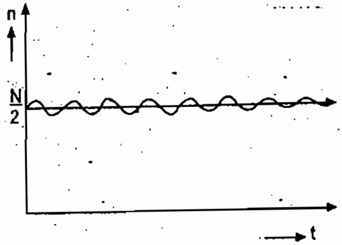
n + n' = N

(Fig. 12.1)

The frequency of occurrence of a particular value of $n$ decreases rapidly if value of $n$ differs more from $(N/2)$. *i.e.,* greater is to difference $|\Delta n|$.

$$\Delta n = \left| n - \frac{N}{2} \right|$$

If $N$ is large only values of $n$ with $|\Delta n| << N$ occurs with significant frequency. Positive and negative values of $\Delta n$ are equally probable.



(Fig. 12.2)

**Density fluctuation is a gas**

Consider $N$-molecules in volume $V$ of the box. Let $n_S$ be the number of molecules inside a specific volume $V_S$ of the box. This number $n_S$ fluctuates in time about an average value

$$\bar{n}_S = \frac{V_S}{V} N$$

The magnitude of fluctuation at any time being given by

$$\Delta n_S = n_S - \bar{n}_S$$

If we consider the volume $V_S$ as the left half the box, then

$$V_S = \frac{V}{2} \text{ and } \bar{n}_S = \frac{N}{2}$$

when $V_S$ is large, the average number $n_S$ of the molecules is also large, then the fluctuations from average value are sufficiently small.

In order to derive an expression for the probability of fluctuations, let $N = 2n$ so that $(n + s)$ particles be in left half and $(n - s)$ particles in right half.

As $N = 2n$ is very large number

$$\left( s << n \text{ i.e., } \frac{s}{n} << 1 \right)$$

Then probability of $(n+s, n-s)$ distribution

$$P\left( (n+s, n-s) = \frac{2n\,!}{(n+s)\,!\,(n-s)\,!} \cdot \frac{1}{2^n} \right) \qquad \ldots(1)$$

The most probable distribution has probability

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

The ratio of probability of $[(n+s), (n-s)]$ and $[n, n]$ distribution is

$$R = \frac{P\,(n+s, n-s)}{P\,(n, n)} = \frac{n\,!\,n\,!}{(n+s)\,!\,(n-s)\,!}$$

$$= \frac{(n-s+1)\,(n-s+2)\ldots n}{(n+1)\,(n+2)\ldots(n+s)} \approx \left\{ 1 - \frac{s}{n} \right\}^s \qquad \text{(since } s << n)$$

$$\therefore \qquad \log_e R = s \log_e \left( 1 - \frac{s}{n} \right) \approx s \cdot \left( \frac{-s}{n} \right)$$

$$= \frac{-s^2}{n^2} \cdot n$$

$$= -f^2 n$$

where $f = s/n$ is the fractional deviation from most probable distribution

$$\therefore \qquad R = e^{-f^2 n}$$

In terms of probability this result takes the form

$$P\,(f) = \alpha\, e^{-f^2 n}$$

where $\alpha$ is normalisation constant and is determined by the conditions that

$$\int_{-1}^{+1} P\,(f)\, df = 1$$

or

$$\int_{-1}^{+1} \alpha\, e^{-f^2 n}\, df = 1$$

$$\alpha \cdot \sqrt{\left( \frac{\pi}{n} \right)} = 1 \quad \text{or} \quad \alpha = \sqrt{\left( \frac{n}{\pi} \right)}$$

$$\therefore \qquad P\,(f) = \sqrt{\left( \frac{n}{\pi} \right)}\, e^{-f^2 n} \qquad \ldots(3)$$

This equation represents that With thereare of $f$, the probability of distribution decreases and for large values of $n$, $\left( \frac{n}{2}, \frac{n}{2} \right)$ state is most likely to occur.

## 12.3 Fluctuations in Ensemles

1. **Canonical Ensemble :** In canonical ensemble the systems are in thermal equilibrium with the reservoir, so *energy fluctuations* take place.

For a canonical ensemble, partition function

$$Z = \sum_i e^{-\beta E_i} \qquad \ldots(1)$$

$$\left( \text{where } \beta = \frac{1}{kT} \right)$$

Mean energy, $$\bar{E} = \sum_i P_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \qquad \ldots(2)$$

$$\overline{E^2} = \frac{\sum_i E_i^2 e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \qquad \ldots(3)$$

$$\frac{\partial \bar{E}}{\partial \beta} = -\frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = -\left[ \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 \right]$$

$$= -[\overline{E^2} - (\bar{E})^2] = -\overline{(\delta E)^2}$$

$$\Rightarrow \qquad \overline{(\delta E)^2} = -\frac{\partial \bar{E}}{\partial \beta} \qquad \ldots(4)$$

Molar heat at constant volume

$$C_v = \left( \frac{\partial \bar{E}}{\partial T} \right)_V = \frac{\partial \bar{E}}{\partial \beta} \cdot \frac{\partial \beta}{\partial T} = -k\beta^2 \left( \frac{\partial \bar{E}}{\partial \beta} \right)_V$$

$$= k\beta^2\, \overline{\partial E^2}$$

$$\Rightarrow \qquad C_V = \frac{1}{kT^2} (\overline{\delta E^2})$$

The energy fluctuation is measured by the ratio

$$\therefore \frac{\Delta E}{E} = \frac{\overline{(\delta E^2)}}{\bar{E}} = \frac{T}{\bar{E}} (k\, C_V)^{1/2}$$

For large values of $T$, the extensive quantities $C_v$ and $\bar{E}$ are proportional to the number of molecules $N$, so fluctuation is proportional to $N^{-1/2}$.

For an ideal gas $\bar{E} \approx NkT, C_v = Nk$. For a macroscopic system $N = 10^{22}$, so the fluctuations are very small of the order of $10^{-11}$; Therefore in a canonical ensemble, the distribution of energies is so peeked about the ensemble average energy that in practice the ensemble in regarded as a microcanonical ensemble.

2. **Grand Canonical Ensemble :** In grand canonical ensemble the fluctuations take place in concentration as well as energy. The energy fluctuations an calculated as for canonical ensemble.

For a grand **canonical ensemble,**

**Partition function,** $$Z = \sum_{N, i} e^{N\mu - E_{N_i}/\tau} \qquad (\text{where } \tau = kT) \qquad \ldots(1)$$

$$\bar{N} = -\left( \frac{\partial \Omega_E}{\partial \mu} \right)_{V,T} = \tau \frac{\partial}{\partial \mu} \log_e Z = \frac{\tau}{Z} \frac{\partial Z}{\partial \mu} \qquad \ldots(2)$$

$$\overline{N^2} = \frac{\sum\limits_{N,i} N^2 e^{(N\mu - E_{N_i})/\tau}}{\sum\limits_{N,i} e^{(N\mu - E_{N_i})/\tau}} = \frac{\tau^2}{Z}\frac{\partial^2 Z}{\partial \mu^2} \qquad \text{...(3)}$$

$$\overline{(\delta N)^2} = \overline{N^2} - (\overline{N})^2 = \tau^2\left[\frac{1}{Z}\frac{\partial^2 Z}{\partial \mu^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \mu}\right)^2\right]$$

$$= \tau\frac{\partial \overline{N}}{\partial \mu}$$

For an ideal classical (Maxwell's – Boltzmann) gas

$$\overline{N} = e^{\mu/\tau}\frac{(2\pi m\tau)^{3/2}}{h^3}V$$

$$\Rightarrow \qquad \frac{\partial \overline{N}}{\partial \mu} = \frac{\overline{N}}{\tau}$$

$$\overline{(\delta N)^2} = \overline{N}$$

For classical Maxwell Boltzmann gas

$$\frac{\Delta N}{N} = \left[\frac{\overline{(\delta N)^2}}{(\overline{N})^2}\right]^{1/2} = \left[\frac{\overline{N}}{(\overline{N})^2}\right]^{1/2} = \left(\frac{1}{\overline{N}}\right)^{1/2}$$

As $\qquad \overline{N} = \frac{PV}{kT}, \quad \frac{\Delta N}{N} = \left(\frac{kT}{PV}\right)^{1/2}$

For smaller volume of the gas, the greater is the **fractional fluctuation.**

## 12.4 Probability of one-Dimensional Random Walk

Consider a random walk in one dimension, as the motion of a drunk person. Suppose he takes $N$-steps of equal length $l$, each step being random which may be in forward or backward direction. Each step has probability $\frac{1}{2}$ of being in either direction. Let $P(m, N)$ be the probability that he is at a point $m$ steps away after $N$-steps. The probability of any given sequence of $N$ steps is $\left(\frac{1}{2}\right)^N$.

$$\therefore \qquad P(m, N) = \left(\frac{1}{2}\right)^N W(m) \qquad \text{...(1)}$$

where $W(m)$ is the number of distinct sequences that reach $m$ after $N$ steps. To arrive at $m$, some set of $n_1 = \frac{1}{2}(N+m)$ steps out of $N$ must be positive and $n_2 = \frac{1}{2}(N-m)$ steps must be negative. Therefore the number of distinct sequences that reach $m$ is

$$W(m) = \frac{N!}{\frac{1}{2}(N+m)!\,\frac{1}{2}(N-m)!} \qquad \text{...(2)}$$

$$\log_e P(m, N) = \log_e N! - \log_e\left(\frac{1}{2}N+m\right)! - \log_e\frac{1}{2}(N-m)!$$

Using Stirling approximation in its more exact form *i.e.*,

$$N! = (2\pi N)^{1/2} N^N e^{-N}$$

or $\qquad \log N! = N\log_e N - N + \frac{1}{2}\log_e(2\pi N)$

$$= \left(N + \frac{1}{2}\right)\log_e N - N + \frac{1}{2}\log_e 2\pi$$

then $\qquad \log_e P(m, N) = \left(N + \frac{1}{2}\right)\log_e N - \frac{1}{2}(N+m+1)\log_e\left(\frac{N+m}{2}\right)$

$$- \frac{1}{2}(N-m+1)\log_e\left(\frac{N-m}{2}\right) - \frac{1}{2}(\log_e 2\pi - N\log_e 2)$$

As $m \ll N$; $\qquad \log_e\left(1 \pm \frac{m}{N}\right) = \pm\frac{m}{N} - \frac{m^2}{2N^2} \pm \ldots$

Using $\log_e\frac{1}{2}(N \pm m) = \log_e\frac{N}{2} + \log_e\left(1 \pm \frac{m}{N}\right)$ we get after simplification

$$P(m, N) = \left(\frac{2}{\pi N}\right)^{1/2}\exp\left(\frac{-m^2}{2N}\right)$$

As $\qquad x = ml$ and $m = n_1 - n_2 = n_1 - (N - n_1) = 2n_1 - N$

In probability that the person is between $x$ and $x + dx$ after $N$-steps is

$$P(x, N)\,dx = P(m, N)\,dm = P(m, N)\frac{dx}{2l}$$

We write $dx = 2l\,dm$ since $m$ can take integral values separated by $\Delta m = 2$. The probability that a person is at a distance $x$ after $N$ steps is

$$P(x, N) = (2\pi l^2 N)^{-1/2}\exp\left(-\frac{x^2}{2Nl^2}\right)$$

which is same as normal distribution.

## 12.5 Motion Due to Fluctuating Force : Fokker Planck Equation

Brownian motion of a particle immersed in a liquid is an example of motion produced due to thermal fluctuation of pressure on the particle. Due to fluctuations in pressure, the net force on to particle is not always zero and the particle is forced to perform random motion.

As the force is rapidly fluctuating function of time, the velocity of particle also changes with time $t$. The Focker Planck equation is concerned with the time dependence of probability $P(v, t)$ which represents the probability of particle having velocity between $v$ and $v + dv$ at any time $t$.

This probability may be expressed as

$$P\,dv = P(v, t \mid v_0 t_0)\,dv$$

where $v_0$ is known velocity at earlier time $t_0$. As the probability does not depend on the past history of particle, therefore the probability depends only on the time difference $s = (t - t_0)$, so we can write

$$P(v, t \mid v_0 t_0)\,dv = P(v, s \mid v_0)\,dv \qquad \text{...(1)}$$

This equation implies that if $v = v_0$ is velocity at time $t_0$, then the probability takes a value between $v$ and $v + dv$ after time $s$. If $s \to 0$, $t \to t_0$ and $v = v_0$

This condition may be expressed as

when $\qquad s \to 0,\ P(v, s \mid v_0) \to \delta(v - v_0) \qquad \text{...(2)}$

when $\delta (v - v_0)$ is Dirac delta function which vanishes if $v \neq v_0$.

After a long long time *i.e.*, $s \to \infty$, the particle will definitely attain equilibrium with the surrounding at temperature $T$. It means that the probability will be independent of $v_0$ and time $t$.

In other words it reduces to canonical distribution The general conditions satisfied by the probability function $P (v, t \mid v_0, t_0)$ must express the complete probability distribution. Now we consider an intermediate time $t_1$ *i.e.*, $t_0 < t_1 < t$ when the velocity of particle is $v_1$ within a small range $dv_1$. This may be expressed as by the product.

$$\{P (vt \mid v_1t_1)\} \,.\, \{P (v_1t_1 \mid v_0t_0)\, dv_1\} \qquad \ldots(3)$$

Is intermediate velocity may range from $-\infty$ to $+\infty$, we have

$$P (vt \mid v_0t_0)\, dv = \int_{-\infty}^{+\infty} P (v, t \mid v_1t_1) \,.\, P (v_1t_1 \mid v_0t_0)\, dv_1 \qquad \ldots(4)$$

Now introducing the time differences

$$q = t_1 - t_0 \text{ and } \tau = t - t_1$$

$$q + \tau = t - t_0 = p$$

Equation (4) in terms of $q$ and $\tau$ may be expressed as

$$P (v, q + \tau \mid v_0) = \int_{-\infty}^{+\infty} P (v, \tau \mid v_1)\, P (v_1, q \mid v_0)\, dv_1 \qquad \ldots(5)$$

This is an integral equation satisfied by the probability $P$. Equation (5) may be converted into differential form by assuming $\tau$ to be very small Putting $v_1 = v - u$, we get

$$P (v, q \mid v_0) + \frac{\partial P}{\partial q} \tau = \int_{-\infty}^{+\infty} P (v_1 \tau \mid v - u)\, P (v - u, q \mid v_0)\, du \qquad \ldots(6)$$

As velocity $v$ can change by a small amount during small time interval $\tau$, the probability $P (v_1 \tau \mid v - u)$ can only be appreciable if $| u | = | v - v_1 |$ is infinitely small. Hence the integrand of (6) may be expanded in a Taylor's Series in powers of $u$ about the value $P (v, q \mid v_0)\, P (v + u, \tau \mid v)$ retaining only the lowest order terms. Then

$$P (v - u, q \mid v_0)\, P (v, \tau \mid v - u) = \sum_{n=0}^{\infty} \frac{(-u)^n}{n\,!} \frac{\partial^n}{\partial x^n} [P (v, q \mid v_0)\, P (v + u, \tau \mid v)]$$

In view of this equation (6) takes the form

$$\frac{\partial P}{\partial q} \tau = - P (v, q \mid v_0) + \sum_{n=0}^{\infty} \frac{(-1)^n}{n\,!} \frac{\partial^n}{\partial v^n} \left[ P (v, q \mid v_0) \int_{-\infty}^{+\infty} u^n P (v + u, \tau \mid v)\, du \right] \qquad \ldots(7)$$

For terms other than $n = 0$, let us introduce

$$M_n = \frac{1}{\tau} \int_{-\infty}^{+\infty} u^n\, P (v + u, \tau \mid v)\, du = \frac{< | \Delta v (\tau) |^n >}{\tau} \qquad \ldots(8)$$

where $<[\Delta v (\tau)]^n> = <[v (\tau) - v (0)]^n>$ in the $n$th moment of the velocity increment in time $\tau$. Equation (7) now becomes

$$\frac{\partial P (v, q \mid v_0)}{\partial q} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n\,!} \frac{\partial^n}{\partial v^n} [M_n\, P (v, q \mid v_0)] \qquad \ldots(9)$$

When $\tau \to 0, <(\Delta v)^n> \to 0$ rapidly if $n > 2$

Therefore retaining only terms for $n = 1$ and $n = 2$ in equation (9), we get

$$\therefore \frac{\partial P}{\partial q} = \frac{(-1)^1}{1\,!} \frac{\partial}{\partial v} [M_1\, P] + \frac{(-1)^2}{2\,!} \frac{\partial^2}{\partial v^2} [M_2\, P]$$

$$\Rightarrow \qquad \frac{\partial P}{\partial q} = - \frac{\partial}{\partial v} [M_1\, P] + \frac{1}{2} \frac{\partial^2}{\partial v^2} (M_2 P) \qquad \ldots(10)$$

This is called **Fokker-Planck equation.** It involves two moments $M_1$ and $M_2$ as coefficients which are evaluated for very small time interval. The values of these coefficients may be evaluated from Brownian motion through corelation function given by

$$M_1 = \frac{1}{\tau} <\Delta v (\tau)> = - \gamma v$$

$$M_2 = \frac{1}{\tau} <[\Delta v (\tau)]^2> = \frac{2kT}{m} \gamma$$

Substituting these values in (10), we get

$$\frac{\partial P}{\partial q} = \gamma \frac{\partial}{\partial v} (vP) + \gamma \frac{kT}{m} \cdot \frac{\partial^2 P}{\partial v^2}$$

or

$$\frac{\partial P}{\partial q} = \gamma P + \gamma v \frac{\partial P}{\partial v} + \gamma \frac{kT}{m} \frac{\partial^2 P}{\partial v^2}$$

This is final form of **Fokker-Planck equation**. This equation represents the time dependence probability distribution.

## 12.6 Fourier Analysis of Random Function : Wiener-Khintchine Theorem

A random process is one in which the variable parameter $x$ (say) does not depend on in a well defined may on the independent time ($t$) (say). If measurements are made on similar systems of an ensemble, we get different functions $x (t)$. As $x (t)$ can not be determined for various systems, therefore we shall try to study the problem by probability considerations. It is convenient to resolve the variables into components according to harmonic law, this is convenienlty achieved by Fourier analysis of the random function.

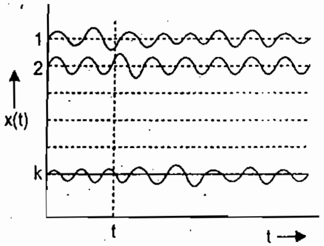
In a closed circuit, when no potential difference is applied, the heat variations may produce an irregular current (or emf). The temperature and concentration of charge carriers fluctuate in various parts of the circuit thereby producing variable emf and variable current of any sign in the circuit.

We consider a randomly fluctuating quantity $x (t) = F (t)$ say which varies with time and study its behaviour for particular system *e.g.*, $F (t)$ may represent electric current in unit resistance, so $F^2 (t)$ will represent the power dissipated.

Consider an ensemble containing a large number of systems. We arrange the systems one below the other and plot $x (t)$ versus $t$ for each system. The ensemble averages are taken in vertical direction and time average along horizontal direction (fug). We can find for example.

$p_1 (x, t)\, dx$ = probability of finding $x$ between $x$ and $x + dx$ at time $t$.

$p_2 (x_1, t_1, x_2, t_2)\, dx_1\, dx_2$ = probability of finding $x_1$ between $x_1$ and $x_1 + dx_1$ at time $t_1$ and between $x_2$ and $x_2 + dx_2$ at time $t_2$ and so on for $p_3, p_4, \ldots p_\infty$.



(Fig. 12.3)

Usually it is sufficient to find $p_2$. When it is so, the random process is called **Morkoff process.**

The random function $x(t) = F(t)$ can be expanded in a Fourier series in the interval. $0 < t < T$ i.e.,

$$F(t) = a_0 + \sum_{n=1}^{\infty} a_n \cos\omega_n t + \sum_{n=1}^{\infty} b_n \sin\omega_n t$$

When
$$a_0 = \frac{1}{T}\int_0^T F(t)\,dt$$

$$a_n = \frac{2}{T}\int_0^T F(t)\cos\omega_n t\,dt$$

$$b_n = \frac{2}{T}\int_0^T F(t)\sin\omega_n (t)\,dt$$

The time averages will be denoted by bracket of the form < >. We assume $<F(t)> = 0$, so above equation will take the form

$$F(t) = \sum_{n=1}^{\infty} a_n \cos\omega_n t + \sum_{n=1}^{\infty} b_n \sin\omega_n t \qquad \ldots(1)$$

As quoted earlier, let $F(t)$ be electric current per unit resistance, the instantaneous power dissipation is $F^2(t)$, then power in $n$th component is

$$P_n = (a_n \cos\omega_n t + b_n \sin\omega_n t)^2 \qquad \ldots(2)$$

Its time average over a complete period $0 < t < T$ is

$$<P_n> = a_n^2 <\cos^2\omega_n t> + b_n^2 <\sin^2\omega_n t> + 2a_n b_n <\cos\omega_n t \sin\omega_n t>$$

But
$$<\cos^2\omega_n t> = <\sin^2\omega_n t> = \frac{1}{2}$$

and
$$<\cos\omega_n t \sin\omega_n t> = 0$$

$$\therefore \quad <P_n> = \frac{1}{2}(a_n^2 + b_n^2) \qquad \ldots(3)$$

$$\therefore \quad <F^2(t)> = \frac{1}{2}\sum_n (a_n^2 + b_n^2) = \sum_n <P_n> \qquad \ldots(4)$$

If we take measurements on a large number of systems, the ensemble average of the time average is

$$\overline{<F^2(t)>} = \frac{1}{2}\sum_n (\overline{a_n^2} + \overline{b_n^2}) = \sum_n \overline{<P_n>} \qquad \ldots(5)$$

**Spectral Density or Power Spectrum :** As period 0 to $T$ is arbitrary, so $\omega_n$ is also arbitrary. Therefore it is useful to define the power dissipated $G(w_n)$ say in the frequency interval $\Delta\omega_n$ between two adjacent frequencies i.e.,

$$\Delta\omega_n = \omega_{n+1} - w_n = \frac{2\pi}{T}(n+1) - \frac{2\pi}{T}(n) = \frac{2\pi}{T}$$

i.e., Power dissipiated at $n$th component between frequency range $\Delta w_n$

$$\therefore \quad G(\omega_n)\,\Delta\omega_n = \frac{1}{2}(\overline{a_n^2} + \overline{b_n^2}) = \overline{<P_n>}$$

$$\therefore \quad \overline{<P(t)>} = \overline{<F^2(t)>} = \sum_n G(\omega_n)\,\Delta\omega_n \qquad \ldots(6)$$

Assuming frequency interval $\Delta\omega_n$ to be infinitely small, we may write

$$\overline{<P(t)>} = \overline{<F^2(t)>} = \int_0^{\infty} G(\omega)\,d\omega \qquad \ldots(7)$$

where $G(\omega)$ is the spectral density or power spectrum of the randomly fluctuating quantity $F^2(t)$. The integral over all possible frequencies represents the ensemble averaged total power which is independent of time.

**Correlation Function :** Let $x(t)$ be some displacement, so that it denotes the difference between its instantaneons value and the mean value $<x> = 0$. There exists a correlation between the values of $x(t)$ at different instants. The value of $x$ at time $t$ affects the probabilities of the various possible values at later instant $t + \tau$, provided $\tau$ is not very large. The correlation function is defined as the mean value of the product $<x(t)\,x(t+\tau)>$

Taking its ensemble average

$$C(\tau) = \overline{<x(t)\,x(t+\tau)>}$$

$$= \frac{1}{T}\int_0^T \sum_{n,m} \overline{[a_n\cos\omega_n t + b_n \sin\omega_n t]}\,.\,\overline{[a_m \cos\omega_m(t+\tau) + b_m \sin\omega_m(t+\tau)]}$$

Expanding $\cos\omega_m(t+\tau)$ and $\sin\omega_m(t+\tau)$, we get

$$C(\tau) = \frac{1}{2}\sum_n \overline{(a_n^2 + b_n^2)}\cos\omega_m\tau \qquad \ldots(8)$$

Using result (7), we get

$$C(\tau) = \int_0^{\infty} G(\omega)\cos\omega\tau\,d\omega \qquad \ldots(9)$$

Clearly $C(\tau)$ is the Fourier cosine transform of $G(\omega)$

The inverse transform gives

$$G(\omega) = 4\int_0^{\infty} C(\tau)\cos\omega\tau\,d\tau \qquad \ldots(10)$$

Relations (9) and (10) are known as **Wiener-Khintchine Theorem**

## 12.7 Electrical Noise (NYQUIST THEOREM)

Consider a resistor of length $L$, cross-sectional area $A$ and resistance $R$. The fluctuating current $I(t)$ due to random thermal motion of electrons in the resistor gives rise to a random output across it; called the **electrical noise**. The effective fluctuating voltage $V$ is given by

$$V(L) = R\,I(t) = R\,ne\,A\,\overline{u} \qquad \ldots(1)$$

where $n$ is electron density, $e$ charge on electron and $\overline{u}$ is average velocity component of electrons along the length of resistor.

Total number of electrons in resistor, $N = n\,(AL)$.

The average velocity $\overline{u} = \dfrac{u_1 + u_2 + \ldots + u_N}{N} = \dfrac{\sum_i u_i}{nAL} \qquad \ldots(2)$

Substituting this value in (1), we get

$$V(t) = R\,ne\,A \times \frac{\sum_i u_i}{nAL}$$

$$\Rightarrow \qquad V(t) = \frac{\text{Re}}{L} \sum_i u_i \qquad \ldots(3)$$

This may be expressed as

$$V(t) = \sum_i V_i = \frac{\text{Re}}{L} \sum_i u_i \qquad \ldots(4)$$

$$\Rightarrow \qquad V_i = \frac{Re}{L} u_i \qquad \ldots(5)$$

$V_i$ and $u_i$ both are *i*th components of random variables. The electrons due to thermal agitation, collide with ions/atoms of lattice, so one can regard $\tau_c$ as time of free travel between successive collisions, called the *relaxation time.* The correlation function may be expressed as

$$C(\tau) = \overline{V_i(t).V_i(t+\tau)} = \overline{V^2}\, e^{-(\tau/\tau_c)}$$

By *Wiener-Khintchine theorem,* the spectral density function is

$$G(\omega) = 4 \int_0^\infty C(\tau) \cos \omega \tau \, d\tau$$

$$= 4\, \overline{V_i^2} \int_0^\infty e^{-(\tau/\tau_c)} \cos \omega \tau \, d\tau$$

$$-4\, \overline{V_i^2} \frac{\tau_c}{1+(\omega\tau_c)^2} \qquad \ldots(6)$$

In metals $\tau_c = 10^{-12}$ seconds at 300 K, therefore for usual frequencies (*dc* to microwaves), $w\tau_c << 1$)

$$\therefore \qquad G(\omega) = 4\, \overline{V_i^2}\, \tau_c \qquad \ldots(7)$$

Substituting value of $V_i$ from equation (5).

$$G(\omega) = 4 \left(\frac{Re}{L}\right)^2 \overline{u_i^2}\, \tau_c$$

$$G(\omega)\, \Delta\omega = 4 \left(\frac{Re}{L}\right)^2 \overline{u_i^2}\, \tau_c \Delta\omega \qquad \ldots(8)$$

If σ is electrical conductivity, then

$$\sigma = \frac{n e^2 \tau_c}{m} \text{ and } R = \frac{L}{\sigma A}$$

$$\Rightarrow \qquad \tau_c = \frac{mL}{RA\, ne^2}$$

From kinetic theory, the mean kinetic energy per component $\frac{1}{2} m \overline{u_i^2} = \frac{3}{2} kT$

Thas gives $\overline{u_i^2} = \frac{3kT}{m}$

Substituting these values in (8), we get

$$G(\omega)\, \Delta\omega = 4 \left(\frac{Re}{L}\right)^2 \left(\frac{3kT}{m}\right) \left(\frac{mL}{RA\, ne^2}\right) \Delta\omega$$

$$\Rightarrow \qquad G(\omega)\, \Delta\omega = \left(\frac{4kTR}{nAL}\right) \Delta\omega$$

This relation shows the spectral density $G(\omega)$ in frequency range $\omega$ and $\omega + \Delta\omega$ of the fluctuating voltage with resistance ($R$) of metal at given temperature is called the ***Nyquist's theorem.***

## 12.8 Thermodynamic Irreversible Processes

A reversible process is one in which the effect produced in a system by a cause is completely retraced after removal of cause. For example dielectric polarisation of a crystal by applying an electric field is a reversible process. The reversibles processes are completely described by the three laws of thermodyanics.

An irreversible process is one in which the effect produced in a system by a cause can not exactly be retraced by removal of cause. The heat flow due to a difference of temperature, current-flow due to a difference of potential are irreversible processes. For such processes the three laws of thermodynamics furnish only the qualitative description. It has been found if the system is close to equilibrium it is possible to describe its rate of approach to equilibrium in general terms by means of certain principles. The principles and their formulation are called the *Thermodynamics of irreversible processes.*

The thermodynamics of irreversible processes is based on the two importance concepts :

(i) The linear law and

(ii) ONSAGAR'S reciprocal relations

**(i) Linear Law :** The linear law is a generalisation of the empirical relations which are found to hold for these systems which are slightly deviated from equilirbium. The linear law is only empirical and has no foundation. It is accepted because it works. Linear relations apply only when the system is close to equilibrium. Therefore the postulate of linear relationship merely defines the range of applicability of thermodynamics of irreversible processes.

We have studied that a number of causes can give rise to irreversible phenomena. For example a temperature gradient causes heat flow, a concentration gradient causes diffusion flow, a potential difference causes current flow and so on. These causes are usually called driving forces (denoted by $X$) which produces fluxes or flows (denoted by $J$)

Thus the linear relation close to equilibrium is of the general form

$$J_i = \sum_{k=1} L_{ik} \cdot X_k \; (i = 1, 2, \ldots n) \qquad \ldots(1)$$

This equation simply states that the fluxes are the linear functions of the generalised forces. The linear relations of this type are called the phenomenological relations and the coefficients $L_{ik}$ are called the **phenomenological coefficients.** If there is only one irreversible process, the coefficient is represented by $L_{ii}$ (or $L_{kk}$). For example $L_{ii}$ may stand for electrical conductivity, thermal conductivity or diffusion coefficient. But the coefficient $L_{ik}$ ($i \neq k$) stands for interference of two irreversible process. For example if two processes are thermal conductivity and diffusion occuring simultaneously then the coefficient $L_{ik}$ is connected with **thermo-diffusion.** If we consider only two simultaneous irreversible processes, then equation (1) may be expressed as

$$\left.\begin{aligned} J_1 &= L_{11} X_1 + L_{12} X_2 \\ J_2 &= L_{21} X_1 + L_{22} X_2 \end{aligned}\right\} \qquad \ldots(2)$$

**(ii) ONSAGER RECIPROCAL Relations :** Onsager gave a fundamental theory of thermodynamics for irrversible processes. The theorem states.

If a proper choices of fluxes ($J_i$) and forces ($X_i$) has been made, the matrix of phenomenological coefficients $L_{ik}$ is symmetric *i.e.,*

$$L_{ik} = L_{ki} \; (i, k = 1, 2, \ldots n) \qquad \ldots(3)$$

These identities are called the **Onsager reciprocal relations.** These relations play a very important role in irreversible processes. We now explain what is meant by the proper choice of the fluxes and forces : Suppose that the state of the system is described by a number of parameters $(A_1 A_2, \ldots A_n)$ (*e.g.*, temperature, pressures etc.) and the values of these parameters are $(A_1^0, A_2^0, \ldots A_n^0)$ in equilibrium, then the deviations of state parameters from their equilibrium values viz, $\alpha_i = A_i - A_i^0$ with $i = 1, 2, \ldots n$ is called the ***state variable.*** The proper choice of fluxes and forces are respectively the time derivative of the state variable $\alpha_i$ *i.e.*,

$$J_i = \dot{\alpha}_i \,(i = 1, 2, 3 \ldots, n) \qquad \ldots(4)$$

and the generalised force $X_i = \dfrac{\partial (\Delta S)}{\partial \alpha_i}$ $(i = 1, 2, \ldots n)$ ...(5)

where $\Delta S$ is the deviation of entropy from its equilibrium value.

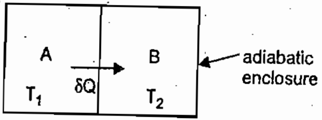
As entropy increases in all irreversible processes, therefore entropy change $\Delta S$ from equilibrium value may be expressed as a function of state variables $\alpha_i$, *i.e.*,

$$\dot{\Delta S} = \frac{\partial}{\partial \alpha_1}(\Delta S)\,\dot{\alpha}_1 + \frac{\partial (\Delta S)}{\partial \alpha_2}\,\dot{\alpha}_2 + \ldots = \sum_i \dot{\alpha}_i \frac{\partial (\Delta S)}{\partial \alpha_i}$$

Using (4) and (5), we get

$$\dot{\Delta S} = \sum_i J_i X_i \qquad \ldots(6)$$

Equations (1), (3), (4) and (6) represent a complete set upon which the satisfactory macroscopic theory of thermodynamics of irreversible processes may be formulated. Equation (3) may be assumed as a fundamental principle.



(Fig. 12.4)

To illustrate the method we consider a simple system composed of two parts A and B both enclosed within the same adiabatic enclosure. The temperatures of these parts are $T_1$ and $T_2$, assumed uniform with $T_1 > T_2$. Let a small quantity of heat flow from part A to part B. Then increase in entropy of system.

$$\delta S = \frac{\delta Q}{T_2} - \frac{\delta Q}{T_1} = \delta Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

The rate of change of entropy

$$\frac{\delta S}{\delta t} = \frac{\delta Q}{\delta t}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \Rightarrow \dot{S} = \dot{Q}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

Putting $T_1 - T_2 = \Delta T$ and $\sqrt{T_1 T_2} = T$, we get

$$\dot{S} = \dot{Q}\left(\frac{\Delta T}{T^2}\right) \qquad \ldots(7)$$

Thus the entropy gain is the product of two factors (i) $\dot{Q}$ which represents the flux $J_i$ which tends to attain equilibrium and (ii) $\dfrac{\Delta T}{T^2}$, which represents the driving force $(X_i)$ causing the flux, this is in agreement with equation (6) Substituting these values in (1), *i.e.*, $J_i = LX_i$

$$\dot{Q} = L\frac{\Delta T}{T^2} \qquad \ldots(8)$$

This is well known *Newton's Law of cooling*

## 12.9 Proof of Onsager Reciprocal Relations

For proof of these relations we shall utilise the statistical mechanical theory of fluctuations together with the concept of microscopic reversibility and assume that the rate of a macroscopic irreversible process is the same as the average rate of regression of statistical fluctuations in the state of the system. The procedure is as follows :

**(i) Fluctuations in an Isolated System :** Consider an isolated system which has been left isolated for a sufficiently long time to ensure equilibrium. Suppose that the state of the system is represented by a number of parameters $A_1, A_2 \ldots A_n$ (which may be the values of local pressure, temperature, volume, density etc). There are continuous variations in these parameters. The deviation of any parameter $A_i$ from its equilibrium value will be denoted by

$$\alpha_i = A_i - A_i^0$$

In equilibrium the entropy has maximum value, so the state variables $\alpha_i$ are zero, therefore the deviation $\Delta S$ of entropy from its equilibrium value due to fluctuation, $\alpha_i$ is given by quadratic equation

$$\Delta S = -\sum_{i>k=1}^{n}\left(\frac{\partial^2 \Delta S}{\partial \alpha_i \partial \alpha_k}\right)_0 \alpha_i \alpha_k$$

This may be expressed as

$$\Delta S = -\sum_{i>k=1}^{n} g_{ik}\,\alpha_i \alpha_k \qquad \ldots(9)$$

where $g_{ik} = \dfrac{\partial^2 (\Delta s)}{\partial \alpha_i}$ an mixed second order derivations appearing in a Taylor's series and is symmetric.

$$\therefore \qquad X_i = \frac{\partial (\Delta S)}{\partial \alpha_i} = -\sum_{k=1}^{n} g_{ik}\,\alpha_k.$$

Further

$$\therefore \qquad \dot{\Delta} S = -\sum_i g_{ik}\,\dot{\alpha}_i \alpha_k = \sum_i J_i X_i \qquad \ldots(11)$$

When $\qquad J_i = \sum_i \dot{\alpha}_i$

According to Einstein's fluctuation theory, the probability $P$ of fluctuations $d\alpha_i$'s is proportional to the exponential of the corresponding entropy deviation $\Delta S$ divided by $k$. Hence the probability of finding a state in which value of $\alpha_i$ lies between $\alpha_i + d\alpha_i$ is given by

$$P d\alpha_1\, d\alpha_2 \ldots d\alpha_n = \frac{\exp\left(\dfrac{\Delta S}{k}\right) d\alpha_1\, d\alpha_2 \ldots d\alpha_n}{\int\int \exp\left(\dfrac{\delta S}{k}\right) d\alpha_1\, d\alpha_2 \ldots d\alpha_k} \qquad \ldots(12)$$

The normalisation condition

$$\int \ldots \int \exp\left(\frac{\Delta S}{k}\right) d\alpha_1\, d\alpha_2 \ldots d\alpha_n = \int \ldots \int P\, d\alpha_1\, d\alpha_2 \ldots d\alpha_n = 1 \qquad \ldots(13)$$

∴ Average value of $\alpha_i X_j$ is given by

$$\overline{\alpha_i X_j} = \int \dots \int (\alpha_i X_j)\, P d\alpha_1\, d\alpha_2 \dots d\alpha_n \qquad \dots(14)$$

From (10) and (12), we have $X_j = \dfrac{\partial(\Delta_S)}{\partial \alpha_j} = \dfrac{\partial}{\partial \alpha_j}(k \log P)$

$$= k \frac{\partial(\log P)}{\partial \alpha_j}$$

$$\therefore \qquad \overline{\alpha_i X_j} = k \int \dots \int \alpha_i \frac{\partial(\log P)}{\partial \alpha_j} P\, d\alpha_1\, d\alpha_2 \dots d\alpha_n \int \alpha_i \frac{\partial(\log P)}{\partial \alpha_i} P d\alpha_j$$

$$= k \int \dots \int d\alpha_1\, d\alpha_2 \dots d\alpha_{(j-1)}\, d\alpha_{j+1} \dots d\alpha_n \int \alpha_i \frac{\partial P}{\partial \alpha_j} d\alpha_j \qquad \dots(15)$$

Integrating by parts the last erm of (15)

$$\int_{-\infty}^{+\infty} \alpha_i \frac{\partial P}{\partial \alpha_j} d\alpha_j = [\alpha_i P]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} P \frac{d\alpha_i}{d\alpha_j} d\alpha_j$$

But $P$ is zero at $\alpha_j = \pm \infty$; moreover $\alpha_i$ and $\alpha_j$ are independent variables,

$$\frac{\partial \alpha_i}{\partial \alpha_j} = \delta_{ij} = \begin{cases} 1 & \text{for } i = j \\ 0 & \text{if } i \neq j \end{cases}$$

Substituting these values in (15), we get

$$\overline{\alpha_i X_j} = -k \int \dots \int d\,\alpha_1\, d\alpha_2 \dots d\alpha_{j-1}\, d\alpha_{j+1} \int_{-\infty}^{+\infty} P\, \delta_{ij}\, d\alpha_j$$

Using normalisation condition (13), we get

$$\overline{\alpha_i X_j} = -k\, \delta_{ij} \; (i, j = 1, \dots n) \qquad \dots(16)$$

(ii) Now we shall use the principle of microscopic reversibility which implies the invariance of equations of motion of individual particles with respect to time reversal *i.e.*, $t \to (-t)$.

Now we consider the value of fluctuations of $\alpha_i$ at time $t$ and $\alpha_j$ alter a time interval $\tau$. Let these quantities be denoted by $\alpha_i(t)$ and $\alpha_j(t+\tau)$. The average of the product $\alpha_i(t)$ and $\alpha_j(t+\tau)$ after a long time is

$$\overline{\alpha_i(t)\, \alpha_j(t+\tau)} = \lim_{T \to \infty} \frac{1}{T} \int_0^T \alpha_i(t)\, \alpha_j(t+\tau)\, dt \qquad \dots(17)$$

From the general principle of statistical mechanics it can be shown that the time average (17) for a single system is equal to average over a microcanonical ensemble obtained by using the probability function (12)

Also if the consider the average value of the product $\alpha_j(t)\, \alpha_i(t+\tau)$, it differs from (17) merely by the substitution $t \to (-t)$, so we can express microscopic reversibility by the relation

$$\overline{\alpha_i(t)\, \alpha_j(t+\tau)} = \overline{\alpha_j(t)\, \alpha_i(t+\tau)} \qquad \dots(18)$$

Subtracting the same quantity $\overline{\alpha_i(t)\, \alpha_j(t)}$ from both sides and dividing by $\tau$, we get

$$\overline{\alpha_i(t) \left\{ \frac{\alpha_j(t+\tau) - \alpha_j(t)}{\tau} \right\}} = \overline{\alpha_j(t) \left\{ \frac{\alpha_i(t+\tau) - \alpha_i(t)}{\tau} \right\}}$$

In the limit $\tau \to 0$, we get

$$\overline{\alpha_i(t)\, \dot{\alpha}_j(t)} = \overline{\alpha_j(t)\, \dot{\alpha}_i(t)} \qquad \dots(19)$$

Onsager further assumed (a new hypothesis) that on the average the decay or regression of a fluctuation follows the ordinary phenomenological macroscopic **linear law** of the form (1) *i.e.*,

$$J_i = \dot{\alpha}_i = \sum_k L_{ik} X_k \qquad \dots(20)$$

Substituting equation (20) in equation (19), we get

$$\overline{\sum_k L_{jk}\, \alpha_i X_k} = \overline{\sum_k L_{ik}\, \alpha_j X_k} \qquad \dots(21)$$

Using equation (16), we get

$$-k \sum_k \delta_{ik} L_{jk} = -k \sum_k \delta_{jk} L_{ik}$$

$$\Rightarrow \qquad L_{ji} = L_{ij} \qquad \dots(22)$$

This is Onsager reciprocity relation

## 12.10 Applications of Onsager Relation

In order to develop the thermodynamical theory of irreversible phenomenon, it is necessary to calculate the entropy gain and then find the appropriate fluxes and forces.

We begin by considering an adiabatically insulated system composed of two chambers '1' and '2' maintained at temperatures $T$ and $T + \Delta T$. Now they are joined by making a hole This will result the heat flow and mass flow to attain equilibrium. Let the volume of the two chambers be $V$. In thermal equilibrium the vessels will have the same energy $U$, the same mass $M$ and the same entropy $S$. We choose $U$ and $M$ as state variables, because they obey the simple conservation laws. The variation $\Delta S_1$ of the entropy of chamber '1' is

$$\Delta S_1 = \left(\frac{\partial S}{\partial U}\right)_M \Delta U + \left(\frac{\partial S}{\partial M}\right)_U \Delta M + \frac{1}{2}\left(\frac{\partial^2 S}{\partial U^2}\right)_M (\Delta U)^2 + \left(\frac{\partial^2 S}{\partial U\, \partial M}\right) \Delta U\, \Delta M + \frac{1}{2}\left(\frac{\partial^2 S}{\delta M^2}\right)_U (\Delta M)^2 \dots(23)$$

Similarly for chamber '2' we have

$$\Delta S_2 = \left(\frac{\partial S}{\partial U}\right)_M \Delta U + \left(\frac{\partial S}{\partial M}\right)_U \Delta M + \frac{1}{2}\left(\frac{\partial^2 S}{\partial U^2}\right)(\Delta U)^2 + \left(\frac{\partial^2 S}{\partial U\, \partial M}\right) \Delta U\, \Delta M + \frac{1}{2}\left(\frac{\partial^2 S}{\partial M^2}\right)_U (\Delta M)^2 \dots(24)$$

From conservation law of $U$

$$\Delta U_1 + \Delta U_2 = 0 \Rightarrow \Delta U_1 = -\Delta U_2$$

Also $\qquad \Delta M_1 + \Delta M_2 = 0 \Rightarrow \Delta M_1 = -\Delta M_2$

∴ The net entropy variation of the entire system

$$2\Delta S = \Delta S_1 + \Delta S_2 = 2\left[\frac{1}{2}\left(\frac{\partial^2 S}{\partial U^2}\right)_M (\Delta U)^2 + \left(\frac{\partial^2 S}{\partial U\, \partial M}\right) + \frac{1}{2}\left(\frac{\partial^2 S}{\partial M^2}\right)_U (\Delta M)^2\right] \qquad \dots(25)$$

$$\Rightarrow \qquad \Delta S = \frac{1}{2}\left(\frac{\partial^2 S}{\partial U^2}\right)(\Delta U)^2 + \left(\frac{\partial^2 S}{\partial U\, \partial M}\right) \Delta U\, \Delta M + \frac{1}{2}\left(\frac{\partial^2 S}{\partial M^2}\right)_U (\Delta M)^2 \qquad \dots(25)$$

Taking its time derivative, we get

$$\dot{S} = \left[\frac{\partial^2 S}{\partial U^2}\right] \Delta U\, \Delta\dot{U} + \left[\frac{\partial^2 S}{\partial U\, \Delta M}\right] \Delta\dot{U}\, \Delta M + \left[\frac{\partial^2 S}{\partial U\, \partial M}\right] \Delta U\, \Delta\dot{M} + \left(\frac{\partial^2 S}{\partial M^2}\right)_U \Delta M\, \Delta\dot{M}$$

$$\Rightarrow \quad \dot{\Delta S} = \dot{\Delta U}\left[\left(\frac{\partial^2 S}{\partial U^2}\right)_M \Delta U + \left(\frac{\partial^2 S}{\partial U\,\partial M}\right)\Delta U\right] + \dot{\Delta M}\left[\left(\frac{\partial^2 S}{\partial M^2}\right)_V \Delta M + \left(\frac{\partial^2 S}{\partial U\,\partial M}\right)\Delta U\right] \quad \ldots(26)$$

We now specify the energy and mass fluxes,

$$\left.\begin{aligned} &\text{Energy flux } J_U = \dot{\Delta U} \\ &\text{mass flux } J_M = \dot{\Delta M} \end{aligned}\right\} \quad \ldots(27)$$

The corresponding generalised forces are given by

$$\left.\begin{aligned} X_U &= \Delta\left[\frac{\partial S}{\partial U}\right]_M = \left[\frac{\partial^2 S}{\partial U^2}\right]_M \Delta U + \left(\frac{\partial^2 S}{\partial U\,\partial M}\right)\Delta M \\ X_M &= \Delta\left(\frac{\partial S}{\partial M}\right)_U = \left(\frac{\partial^2 S}{\partial M^2}\right)_U \Delta M + \left(\frac{\partial^2 S}{\partial M\,\partial U}\right)\Delta U \end{aligned}\right\} \quad \ldots(28)$$

In view of these equations, equation (26) takes the form

$$\dot{\Delta S} = J_U X_U + J_M X_M \quad \ldots(29)$$

This is analogous to equation (6)

Further from linear relation (1), we have

$$\left.\begin{aligned} J_M &= L_{11} X_M + L_{12} X_U \ldots(a) \\ J_U &= L_{21} X_M + L_{22} X_U \ldots(b) \end{aligned}\right] \quad \ldots(30)$$

With reciprocaly relation $\quad L_{12} = L_{21} \quad \ldots(31)$

To find out the physical significance of (31), we must evaluate $X_U$ and $X_M$.

For a simple system at constant volume, we have from first and second laws of thermodynamics,

$$TdS = dU - \mu dM \quad \ldots(32)$$

where $\mu$ is chemical potential per unit mass

From (32), we have

$$\left(\frac{\partial S}{\partial U}\right)_M = \frac{1}{T} \text{ and } \left(\frac{\partial S}{\partial M}\right)_U = -\frac{\mu}{T} \quad \ldots(33)$$

Substituting these values in (28), we get

$$X_U = \Delta\left(\frac{\delta S}{\partial U}\right)_M = \Delta\left(\frac{1}{T}\right) = -\frac{\Delta T}{T^2} \quad \ldots(34\text{ (a)})$$

and
$$X_M = \Delta\left(\frac{\Delta S}{\Delta M}\right)_U = \Delta\left(-\frac{\mu}{T}\right) = -\Delta\left(\frac{\mu}{T}\right)$$

$$\Rightarrow \quad X_M = -\left(\frac{\Delta\mu}{T} - \frac{\mu}{T^2}\Delta T\right) \quad \ldots(34\text{ (b)})$$

As
$$\mu = u + pv - Ts$$

$$\Rightarrow \quad \Delta\mu = \Delta u + p\Delta v + v\Delta p - T\Delta s - s\Delta T$$
$$= v\Delta p - s\Delta T \text{ (since } \Delta u + p\Delta v = T\Delta s)$$

Substituting these values in (34 (b)) we get

$$X_M = -\left[\left(\frac{v\Delta p - s\Delta T}{T}\right) - \frac{(u + pv - Ts)\,\Delta T}{T^2}\right]$$
$$= -\frac{v\Delta p}{T} + \frac{\Delta T}{T}\left(\frac{u + pv}{T}\right)$$
$$\Rightarrow \quad X_M = -\frac{v\Delta p}{T} + \frac{h\Delta T}{T^2} \qquad \text{(Since } h = u + pv) \quad \ldots(35)$$

Substituting these values in equation (27), we get

$$J_M = -\frac{L_{11}v}{T}\Delta p + \frac{L_{11}h - L_{12}}{T^2}\Delta T \quad \ldots(36\text{ (a)})$$

and
$$J_U = -\frac{L_{21}V}{T}\Delta p + \frac{L_{21}h - L_{22}}{T^2}\Delta T \quad \ldots(36\text{ (b)})$$

In the stationary state, $J_M = 0$, so equation (36 a) gives the thermodynamic pressure difference

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_M=0} = \frac{L_{11}h - L_{12}}{L_{11}Tv} \quad \ldots(37)$$

If a pressure difference is maintained between the two chambers and uniform temperature throughout the system, the mass will flow from one vessel to the other and an associated flow of energy proportional to the flow of mass is observed. This effect is called the thermo mechanical effect and is given by [dividing 36 (b) with 36 (a) when $\Delta T = 0$]

$$\left(\frac{J_u}{J_m}\right)_{\Delta T=0} = \frac{L_{21}}{L_{11}} = Q^* \quad \ldots(38)$$

Hence from (37) using (31) and (36) we get

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_M=0} = \frac{h - Q^*}{Tv} \quad \ldots(39)$$

This equation connects the two cross-effects.

## EXERCISES

### SHORT ANSWER QUESTIONS

1. What do you mean by fluctuation ? How is it measured ?
2. Explain canonical ensemble is regarded as microcanonical ensemble.
3. State Fokker Planck equation.
4. State Wiener-Khintchine theorem.
5. Express ensemble average of the function $F^2(t)$, when $F(t)$ fluctuates randomly.
6. Explain correlation function.
7. State Nyguist's Theorem.
8. Distinguish between reversible and irreversible processes.
9. State two factors on which the thermodynamics of irreversible processes is based.
10. What an Onsager's reciprocal relations ?
11. What do you mean by electrical noise ?

## LONG ANSWER QUESTIONS

1. Name the quantities which suffer fluctuations in canonical and grand canonical ensembles. Find the fractional fluctuations among these quantities.
2. Find the probability of one dimensional random walk.
3. Derive Fokker Planck equation representing the motion due to a fluctuating force.
4. Discuss Fourier analysis of a random function. Hence derive Wiener-Khintchine theorem.
5. Define spectral density and correlation function of a random function. Derive Nyquist's theorem.
6. Distinguish between reversible and irreversible processes. Derive Onsanger relation and discuss its applications. *(Meerut 2006, 2001)*

## MULTIPLE CHOICE QUESTIONS : SELECT THE RIGHT CHOICE

1. The fluctuation in a parameter is measured by :
   (a) mean value (b) mean square value
   (c) mean square deviation (d) none of these
2. The probability of fractional deviation from most probable distribution is proportional to :
   (a) $e^{-s/n}$ (b) $e^{-s^2/n^2}$
   (c) $e^{-s^2/n}$ (d) $e^{-s/n^2}$
3. In canonical ensemble, to fluctuations occur in :
   (a) energy only (b) concentration only
   (c) energy and concentation both (d) neither energy nor concentation
4. In canonical ensemble the fractional fluctuation is proportional to ($N$ = number of particles) :
   (a) $N$ (b) $N^2$ (c) $N^{1/2}$ (d) $N^{-1/2}$
5. In grand canonical ensemble, the fluctuations occur in :
   (a) energy only (b) concentration only
   (c) energy and concentration both (d) neither energy nor concentration
6. In grand canonical ensemble the fluctuation is greater if :
   (a) volume is greater (b) volume is smaller
   (c) temperature is smaller (d) pressure is larger
7. The thermodynamics of irreversible processes is based on :
   (a) Linear law only (b) Reciprocal relations
   (c) both (a) and (b) (d) Neither (a) nor (b)
8. The reciprocity relation of irreversible processes was given by :
   (a) Onsager (b) Landau
   (c) Yang and Lee (d) Fokker and planck
9. The correlation function for harmonic variable $x(t)$ for small time interval $\tau$ is given by :
   (a) $\dfrac{x(t)}{x(t+\tau)}$ (b) $\overline{x(t)\,x(t+\tau)}$ (c) $\dfrac{\overline{x(t)+x(t+\tau)}}{2}$ (d) $x^2(t)\,x^2(t+\tau)$

10. The spectral density in terms of correlation function $C(\tau)$ is given by $[C(\tau) = ]$ :
    (a) $\int_{-\infty}^{+\infty} \omega^2 G(\omega)\, d\omega$ (b) $\int_0^{\infty} G(\omega) \cos \omega\tau\, d\omega$
    (c) $\int_0^{\infty} \omega G(\omega) \sin \omega\tau\, d\omega$ (d) $\int_0^{\omega_{max}} \omega G(\omega)\, e^{j\omega\tau}\, d\omega$

### ANSWERS

**1.** (c) **2.** (c) **3.** (a) **4.** (d) **5.** (c) **6.** (b) **7.** (c) **8.** (a)
**9.** (b) **10.** (b)

13

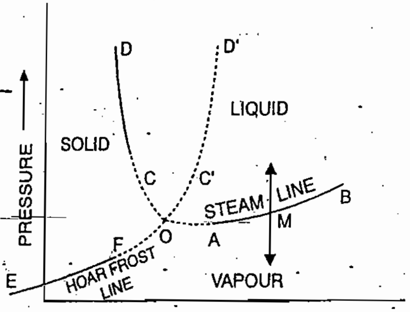
# PHASE TRANSITIONS

## 13.1 Triple Point

Normally there are three states of metter. One state may be changed to other state by suitably verying temperature and pressure. The two states sold and liquid are in equilibrium at melting point of solid, while liquid and vapour are in equilibrium at boiling point of liquid. At a particular temperature and pressure, the three states may be in equilibrium. This point is the *triple point*.

**Explanation**

(i) The boiling point of water increases with increase in pressure and vice versa. The curve $AB$ represents the relation between pressure and temperature and is called the *steam line* or *vaporization line* (fig 13.1). The liquid and vapour are in stable equilibrium together only along the line $AB$. At all points above $AB$ the substance is all liquid and below it there exists vapour only. If at a point $M$, pressure is raised keeping temperature constant, boiling point will consequently increase and all vapour will condense into liquid. Similarly if at $M$, pressure is decreased, all the liquid will vaporize and only vapour will remain.

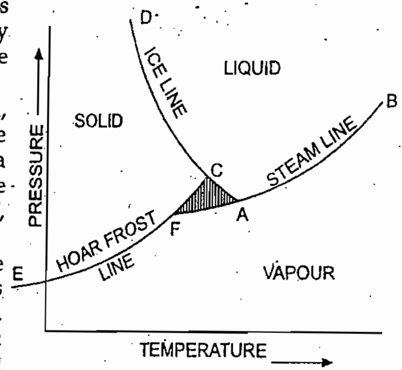


(Fig. 13.1)

(ii) The melting point of ice decreases with increase in pressure i.e., ice melts below 0°C at a pressure higher than the atmospheric pressure. The pressure temperature relationship can be represented by a curve $CD$ or $C'D'$ which is called the *ice line* or *fusion line.* The curve $CD$, which slopes to the left, is for ice type substances whose melting point is lowered with increase in pressure; while $C'D'$, which slopes to the right, is for wax type substances whose melting point is raised with increase in pressure. The substance is entirely solid on the left of the curve while entirely liquid on the right. The curve represents the equilibrium between the solid and liquid states.

(iii) When the pressure on ice is raised, evaporation from its surface slows down. The equilibrium between the solid and vapour states of a substance can be represented by a curve $EF$ called the *Hoar Forst line* or *sublimation line.* Above the curve $EF$, the substance is all solid and below it all vapour.

These three curves, when plotted on the same diagram, are found to meet in a single point $O$ as shown in Fig. 13.1. This point is called the **triple point.** *At the triple point, the pressure and temperature are such that the solid, liquid and vapour states of the substance can exist simultaneously in equilibrium.*



(Fig. 13.2)

**To show that there is only one triple point :** Suppose that the three curves do not meet at a point but intersect enclosing an area $ACF$ shown shaded in fig. 13.2. Then according to ice line $CD$, the substance must be entirely solid in the shaded area as it is to the left of $CD$. According to the steam line $AB$ the substance must be entirely liquid in the shaded portion as it is above $AB$ and according to hoar frost line $EF$ the substance in the shaded portion must be entirely vapour as it is below $EF$. But these three conclusions contradict one another and hence the shaded triangel $ACF$ cannot exist. Thus the three curves should meet in a single point $O$ called the triple point.

It should be noted that the triple point of water is not fixed but is different for different allotropic forms of ice.

## Solved Examples

**Example 1.** *The coordinates of the triple point of water are $t = 0{\cdot}0075$°C and $p = 0{\cdot}0060$ atmosphere. Calculate the slope of the ice line in atmos./°C*

*What is the physical significance of the negative sign, of the slope?*

**Solution.** Referring to fig. 13.2 of section 13.1, let $O$ be the triple point of water. Then the coordinages of point $O$ are

$$P = 0{\cdot}0060 \text{ atoms}, \; t = 0{\cdot}0075\text{°C}.$$

Now we know that the freezing point of water into ice at 1 atmosphere pressure is 0°C. Hence the coordinates of point $D$ on the ice line are

$$P' = 1 \text{ atmos.}, \; t' = 0\text{°C}$$

Hence for ice line $OD$

$$dP = P' - P = 1 - 0{\cdot}006 = 0{\cdot}994 \text{ atmos.}$$

and

$$dT = dt = t' - t = 0 - 0{\cdot}0075 = 0{\cdot}0075\text{°C}$$

Therefore, the slope of ice line is

$$\frac{dP}{dT} = \frac{dP}{dt} = -\frac{0{\cdot}994}{0{\cdot}0075} \text{ atmos./°C}.$$

Negative sign with the slope $dP/dT$ indicates that the melting point of ice decreases with an increase in pressure.

**Example 2.** *Calculate the pressure and temperature of the triple point of water. Given that the lowering of melting point of ice per atomsphere increase of pressure is 0·0072°C and the saturated vapour pressure at 0°C = 4·60 m.m. while at 1°C = 4·94 m.m.*

**Solution.** Let the triple point correspond to a temperature $t$°C and pressure $p$ mm of mercury.

Saturated vapour pressure at 0°C = 4·60 mm.

Saturated vapour pressure at 1°C = 4·94 mm.

∴ Increase in saturated vapour pressure for 1°C rise in temperature

$$= 4{\cdot}94 - 4{\cdot}60 = 0{\cdot}34 \text{ mm}.$$

Hence increase in vapour pressure for $t$°C = $0{\cdot}34t$

Therefore, saturated vapour pressure at triple point $t$°C is given by

$$p = (4{\cdot}60 + 0{\cdot}34t) \text{ mm}.$$

Now the melting point of ice at 760 mm (1 atmosphere) pressure is 0°C. But at the triple point the pressure is $(4{\cdot}60 + 0{\cdot}34t)$.

Hence Decrease in pressure $= 760 - (4{\cdot}60 + 0{\cdot}34t)$

$$= (755{\cdot}4 - 0{\cdot}34t) \text{ mm}.$$

It is given that a decrease in pressure of 760 mm. (1 atmos.) will increase the melting point of ice by 0·0072°C. Therefore by a decrease of $(755{\cdot}4 - 0{\cdot}34t)$ mm in pressure.

Increase in melting point $= \dfrac{0{\cdot}0072\times(755{\cdot}4-0{\cdot}34t)}{760}$

or Melting point $= \left[0+\dfrac{0{\cdot}0072\times(755{\cdot}4-0{\cdot}34t)}{760}\right]$

But this is the temperature $t$ at a triple point. Thus

$$t=\frac{0{\cdot}0072\times(755{\cdot}4-0{\cdot}34t)}{760}$$

or $$760t=5{\cdot}4388-0{\cdot}002448t$$

or $$760{\cdot}002448t=5{\cdot}4388$$

$$t=\frac{5{\cdot}4388}{760{\cdot}002448}$$

$$=\mathbf{0{\cdot}007156^\circ C}.$$

Substituting this value of $t$ in the expression for $p$, we get

$p=(4{\cdot}60-0{\cdot}34\times0{\cdot}007156)$

$$=\mathbf{4{\cdot}60243\ mm\ of\ Hg}.$$

**Example 3.** *The vapour pressure P (in mm. of mercury) of solid ammonia is given by*

$$\log_e P=23{\cdot}03-\frac{3754}{T}$$

*while that of liquid ammonia is given by*

$$\log_e P=19{\cdot}49-\frac{3063}{T}$$

*where T is in K.*

*Calculate the triple point of ammonia.* ***(Kanpur 2005; Rohilkhand 2004, 85S, 86S)***

**Solution.** At triple point, the vapour pressure of the substance in each of the three states is identical. Hence equating the vapour pressure of solid ammonia

$$\log_e P=23{\cdot}03-\frac{3754}{T} \qquad \ldots(1)$$

with that of liquid ammonia

$$\log_e P=19{\cdot}49-\frac{3063}{T} \qquad \ldots(2)$$

We have $23{\cdot}03-\dfrac{3754}{T}=19{\cdot}49-\dfrac{3063}{T}$

or $$\frac{1}{T}(3754-3063)=23{\cdot}03-19{\cdot}49$$

or $$\frac{691}{T}=3{\cdot}54$$

$\therefore$ $$\mathbf{T=195{\cdot}2\ K}$$

Substituting the value of $T$ in eq. (1), we get

$$\log_e P=23{\cdot}03-\frac{3754}{195{\cdot}2}$$

or $$\log_e P=3{\cdot}8$$

or $$2{\cdot}303\log_{10}P=3{\cdot}8$$

or $$\log_{10}P=\frac{3{\cdot}8}{2{\cdot}303}=1{\cdot}552$$

$\therefore$ $$\mathbf{P=44{\cdot}87\ mm\ Hg.}$$

*Thus the coordinates of triple point of ammonia are T = 195·2 K and P = 44·87 mm of Hg.*

## 13.2 Vander Waal's Equation and Phase Transition

**Vander-Wall's Equation of State**

The equation of state $PV=RT$ for an ideal gas is based on the assumption that molecules are infinitestimal in size and there are no inter-molecular forces. But this equation has been inadequate to describe the behaviour of real gases as none of them is perfect. Experiments over a wide range of temperature and pressure showed that actual gases deviated from the perfect gas equation and the *deviation was quite large at high pressures and low temperatures.* It indicates that these deviations are due to mutual attractions between the molecules and the finite size of the molecules. Joule Thomson experiment also established the existence of molecular attractions in gases. Actually at high pressures the size of the molecules of the gas becomes significant and can not be neglected. Also at high pressures, the molecules come nearer and the forces of inter-molecular attractions are appreciable. Vander Waal, therefore, corrected the perfect gas equation allowing for molecular attractions and the finite volume occupied by the molecules.

**Correction for the inter-molecular attractions**

A molecule in the interior of gas is attraced by other molecules in all directions and hence the net cohesive force on it is zero. But when a molecule strikes the walls of the container, it is pulled back by other molecules and hence the observed pressure of the gas at the walls of the container is less than the actual pressure within the body of the gas. This decrease in pressure $P$ is proportional to (i) the number of attracting molecules per unit volume, and (ii) the number of attracted molecules striking per unit area of the wall of the container per second. Both these factors depend upon the number of molecules per unit volume or the density $\rho$ of the gas.

$\therefore$ $$\text{Decrease in pressure } p\propto\rho^2\propto\frac{1}{V^2}$$

or $$p=\frac{a}{V^2}$$

where $a$ is a constant and $V$ is the volume of the gas.

Hence real pressure $=(P+p)=\left(P+\dfrac{a}{V^2}\right)$

where $P$ is the observed pressure.

Therefore, instead of $P$, we shall write in the equation of state the expression

$$\left(P+\frac{a}{V^2}\right)$$

**Correction for the finite size of the molecules**

As the molecules have finite size they occupy a space. Hence the actual space for their movement is less than the observed volume $V$ of the container. Therefore, the volume $V$ in the equation of state be written as $(V-b)$ where $b$ is a constant for unit mass of the gas.

Thus the Vander Waal's equation of state for a gas is

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \qquad \ldots(1)$$

where $a$ and $b$ are known as Vander Waal's constant and are different for different gases.

**Discussion**

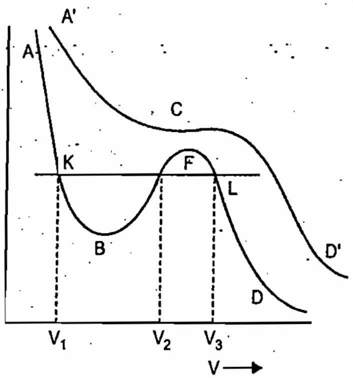
It should be appreciated that Vander Waal's equation of state includes qualitatively all features of actual gases. It is a convenient way to describe the behaviour of real gases and succeeds in explaining the deviations from the perfect gas equation. But *over very wide pressures and temperature ranges it fails.* It breaks down when applied to the differentiate between the various gases. The values of parameters $a$ and $b$ do not remain constant for a particular gas but vary considerably at different temperatures. Also their values obtained by different methods do not agree.

**Phase Transitions**

From Vander Waal's equation

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad \text{...(2)}$$

From this equation it can be shown that the substance can be separated into gaseous and liquid phases. Equation (2) is third degree in volume ($V$). It must have three real roots for certein values of $T$ and $P$. In other words the pressure versus volume curve at constant temperature (isotherm) is of the form $ABFD$ (fig). But the derivative $\left(\frac{\partial P}{\partial V}\right)_T$ is positive between points $B$ and $F$ and the state of the substance is unstable if $\left(\frac{\partial P}{\partial V}\right) > 0$. Hence in this region the substance can separate into two phases in this region.



(Fig. 13.3)

The portion of the curve $AB$ corresponds to liquid state (small volume). As the pressure is decreased, the liquid expands to a points $K$, after which change occurs along the straight line $KL$. The points $K$ and $L$ are uniquely defined by the equality condition of chemical potential $\mu_K(P, T) = \mu_L(P, T)$, the intermediate points corresponding to mixture of liquid and vapours phases. At point $K$, the substance is in liquid state and at point $L$, it is in vapour state. The position of point $K$ at a temperature corresponding to given isoterm is defined uniquely.

The portion $KB$ is not absolutely unstable because on this portion $\left(\frac{\partial P}{\partial V}\right)_T < 0$.

The states of this portion can be obtained without allowing the formation of vapour bubbles in the liquid (a superheated liquid). For this the liquid must be free from the agants which favour vaporisation. The portion $FL$ represents a super cooled vapour which can be obtained if the formation of the condersation centres is prevented. Such condensation centres easity arise from ions.

**Critical Point**

At sufficiently high temperature the first term in equation (2) predominates over the second term : The equation then becomes very similar to Clapeyron's equation for volume ($V - b$); but this equation has only one real root for each value of $P$. This corresponds to the known fact that at high temperatures a substance can not split into two phases at all.

How we attempt to find the temperature at which the separation into two phases ceases on the corresponding isotherm$A'CD'$ (fig), the points $B$ and $F$ where the derivative $\left(\frac{\partial P}{\partial V}\right)_T$ becomes zero, merge into the point $C$ and the region of unstable state disappears. All the three roots of the equation (2) merge at the point $C$, so $C$ corresponds to the triple root of this equation; but the expansion of the function ($P$) with respect to the difference ($V - V_C$) must begin with a third order term if $V_c$ is triple root. The linear and the quadratic terms in the expansion become zero if the first and the second pressure derivatives with respect to volume $V$ are equal to zero at point C. It is easy to locate the position of point C from Vander Waal's equation of state.

For first **derivative to become zero,** we have

$$\left(\frac{\partial P}{\partial V}\right)_{T_C} = -\frac{RT_C}{(V_C - b)^2} + \frac{2a}{V_C^3} = 0 \qquad (\text{at } V = V_C) \qquad \text{...(3)}$$

For second derivative to become zer, we have

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C} = -\frac{2RT_C}{(V_C - b)^3} - \frac{6a}{V_C^4} = 0 \qquad (\text{at } V = V_C) \qquad \text{...(4)}$$

From these equations, we get

$$(V_C - b) = \frac{V_C}{3} \text{ or } V_C = 3b \qquad \text{...(5a)}$$

Substituting this value in equation (3)

$$-\frac{RT_C}{4b^2} + \frac{2a}{(3b)^3} = 0$$

$$\Rightarrow \qquad T_C = \frac{8}{27}\frac{a}{Rb} \qquad \text{...(5b)}$$

the pressure $P$ at C is celculated by Vander Waal's equation (2)

$$P_C = \frac{RT_C}{V_C - b} - \frac{a}{V_C^3} = \frac{R\left(\frac{8}{27}\frac{a}{Rb}\right)}{(3b - b)} - \frac{a}{(3b)^2}$$

$$\Rightarrow \qquad P_C = \frac{1}{27}\frac{a}{b^2} \qquad \text{...(5c)}$$

Thus critical temperature, critical volume and critical pressures are

$$\boxed{T_C = \frac{8}{27}\frac{a}{Rb},\ V_C = 3b,\ P_C = \frac{1}{27}\frac{a}{b^2}} \qquad \text{...(6)}$$

If we represent the phase equilibrium curve in the plane ($P, T$), then the curve will end at point $P = P_C$ and $T = T_C$ where C is the critical point The separation into phases does not occur for $T > T_C$.

The critical point can exist only on the equilibrium curve between two such phases which has no feature that is incapable of varying continuously.

For example in crystals such a feature is regularity of crystal structure. The position of an atom in an ideal crystal defines to position of whole crystal. Similarly the position of a molecule in a liquid affects only the position of its closest neighbours. In such a case we can have a curve dividing the crystalline and liquid phases and so there can not be a critical point.

**Law of Corresponding States**

In terms of critical coordinates Vander Waal's equation taken the form

$$\left(\frac{P}{P_C} + \frac{3}{(V/V_C)^2}\right)\left(\frac{V}{V_C} - \frac{1}{3}\right) = \frac{8}{3}\left(\frac{T}{T_C}\right) \qquad \text{...(7)}$$

This equation may be written in terms of dimensionless variables

$$\frac{P}{P_C} = \hat{P};\ \frac{V}{V_C} = \hat{V} \text{ and } \frac{T}{T_C} = \hat{T} \text{ as}$$

$$\left(\hat{P} + \frac{3}{\hat{V}^3}\right)\left(\hat{V} - \frac{1}{3}\right) = \frac{8}{3}\hat{T} \quad \text{...(8)}$$

This result is called the law of corresponding states. In terms of $\hat{P}$, $\hat{V}$ and $\hat{T}$ all gases look alike provided they obey the Vander Waals equation of state. The values of *a* and *b* are usually obtained by filling the observed values of $P_C$ and $T_C$. The states of the substances at the same $\hat{P}$, $\hat{V}$ and $\hat{T}$ are called the corresponding state of the substances. The real gases do not obey this equation to high accuracy.

## 13.3 Matter Near the Critical Point

The investigations have been made by a number of physicists near the critical point. Some properties actually observed are

1. The densities of the liquid and the vapour gradually approach each other and become equal at the critical point.
2. At or very near the critical temperature, the boundary between the liquid and vapour states disappears and so they diffuse mutually and the surface tension disappears.
3. The entire mass presents a very flickering appearance which suggests that there might be the variation of density inside the mass.
4. The compressibility of vapour is infinite at the critical point and very large near this point.

These points were explained successfully by Andrew by assuming that just beyond the critical temperature the whole mass is converted into vapour consisting of a single constituent and it behaves like a gas near its point of liquefaction.

The experiment performed by Callender give clear concept about the state of matter near the critical point. He used pure water, without any trace of air, and found that the densities of liquid and vapour did become equal to 374°C (which is critical temperature of water), but there is difference of densities even beyond the critical temperature upto 380°C.

These observations were confirmed be Hein who stated that the disappearance of liquid meniscus is not only the criterion for the critical point. Under certain conditions some liquid may be present beyond this point. He defined *the critical point as the point at which the properties of two phases become equal.* This was further confirmed by Mass and his co-workers.

## 13.4 First and Second Order Phase Transitions

Several Substances undergo phase transitions under change of temperature and pressure. There are two types of phase transitions :

**1. First order Phase Transitions :** The changes of phase which take place at constant temperature and pressure and in which heat is either absorbed or evolved during change of phase are called first order phase transitions. In first order phase transitions the entropy and density (or volume) change. In first order phase transitions the Gibb's function *G* remains constant in both phases, while its first derivative with respect to temperature and pressure is discontinuous at transition point.

Example : When heat is given to water at 100°C and 1 atmospheric pressure, it changes from liquid to vapour state. The density of water is 1000 kg/m$^3$; while that of vapour is 0·6 kg/m$^3$. Therefore the *transformation of water into vapour at constant temperature and volume is first order* phase transition. Similarly, the *transformation of ice into water at 0°C and 1 atmospheric pressure is the example of first order phase transition.*

**2. Second Order Phase Transitions :** The second order phase transitions are those in which the density and entropy change slowly; and the first derivatives of Gibb's function with respect to temperature and pressure are continuous at transition point while the second order derivative of Gibb's function becomes discontinuous at the transition point.

**Example :** The *transformation of liquid helium I to liquid helium II* at λ point (2·19 K) is second order phase transition. In this transition these is no evolution or absorption of latent heat during change of states and the densities of liquid helium I and II are same. Similarly, *transformation of ferromagnetic substance into paramagnetic substance at curie temperature is a second order phase transition.*

## 13.5. Ehrenfest's Equations

These equations represent the condition of equilibrium between the two phases.

Let us consider a vapour-liquid mixture in equilibrium at vapour pressure *p* and temperature *T*. Both *p* and *T* remain constant throughout. Let $m_1$ and $m_2$ be the masses of liquid and vapour phases and $g_1$ and $g_2$ their specific Gibb's functions, then for the mixture the net Gibb's function

$$G = m_1 g_1 + m_2 g_2 \quad \text{...(1)}$$

where $G = G(p, T, m_1, m_2)$, $g_1 = g_1(p, T)$ and $g_2 = g_2(p, T)$

The condition for equilibrium requires

$$dG = g_1\, dm_1 + g_2\, dm_2 = 0 \quad \text{...(2)}$$

For a closed system the mass is conserved *i.e.*, $m_1 + m_2 = \text{constant}$

or $dm_1 + dm_2 = 0$ *i.e.*, $dm_2 = -dm_1$

Thus condition of equilibrium $dG = 0$ gives

$$g_1 = g_2 \quad \text{...(4)}$$

If *v* and *s* are specific volume and entropy, then we have

$$dg = v\, dp - s\, dT \quad \text{...(5)}$$

*i.e.*, $g = g(p, T)$

Taking its derivative

$$dg = \left\{\frac{\partial g}{\partial p}\right\}_T dp + \left\{\frac{\partial g}{\partial T}\right\}_p dT \quad \text{...(6)}$$

Comparing (5) and (6), we get

$$\left(\frac{\partial g}{\partial p}\right)_T = v \text{ and } \left(\frac{\partial g}{\partial T}\right)_p = -s \quad \text{...(7)}$$

As specific volumes (volumes per unit mass) of liquid and vapours are different, we find that the first derivatives of $g_1$ (for liquid) is different from that of $g_2$ (for vapour) at transition temperature *T* and pressure *p*,

$$\left(\frac{\partial g_2}{\partial T}\right)_p - \left(\frac{\partial g_1}{\partial T}\right)_p = -(s_2 - s_1) < 0 \quad \text{...(8)}$$

and

$$\left(\frac{\partial g_2}{\partial p}\right)_T - \left(\frac{\partial g_1}{\partial p}\right)_T = (v_2 - v_1) > 0 \quad \text{...(9)}$$

Obviously the slopes $\left(\frac{\partial g}{\partial T}\right)_T$ and $\left(\frac{\partial g}{\partial p}\right)_T$ are discontinuous

i.e.,
$$\left(\frac{\partial g_1}{\partial T}\right)_P \neq \left(\frac{\partial g_2}{\partial T}\right)_P \text{ and } \left(\frac{\partial g_1}{\partial p}\right)_T \neq \left(\frac{\partial g_2}{\partial p}\right)_T$$

From equation (4) the latent heat equation may be derived as follows :
Differentiating (4), we get

$$dg_1 = dg_2$$

i.e.,
$$v_1 dp - s_1\, dT = v_2\, dp - s_2 dT$$

This gives

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_2}$$

From second law of thermodynamics $dQ = TdS$, we have

$$L = Tds = T(s_2 - s_1) \quad i.e., \quad (s_2 - s_1) = \frac{L}{T}$$

$\therefore$
$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)} \qquad \text{...(10)}$$

This is famous Clausius Clapeyron's equation and holds for first order phase transitions.
Thus the first order transition can be characterised by either of the following statements :

1. The changes in entropy; volume and latent heat exist.
2. The density changes are discontinuous at transition temperature and pressure.
3. The first order derivatives of Gibb's function changes discontinuously.

**~~Condition of equilibrium for~~ second order ~~phase transitions.~~**

For second order phase transitions

$$\left.\begin{matrix} s_1 = s_2 \\ \text{and} \quad v_1 = v_2 \end{matrix}\right\} \qquad \text{...(11)}$$

Therefore from equations (8) and (9)

$$\left(\frac{\partial g_2}{\partial T}\right)_p - \left(\frac{\partial g_1}{\partial T}\right)_p = -(s_2 - s_1) = 0$$

or
$$\left(\frac{\partial g_1}{\partial T}\right)_p = \left(\frac{\partial g_2}{\partial T}\right)_p \qquad \text{...(12)}$$

and
$$\left(\frac{\partial g_2}{\partial p}\right)_p - \left(\frac{\partial g_1}{\partial p}\right)_T = (v_2 - v_1) = 0$$

or
$$\left(\frac{\partial g_1}{\partial p}\right)_T = \left(\frac{\partial g_2}{\partial p}\right)_T \qquad \text{...(13)}$$

If $k$ is isothermal compressibility and $\alpha$ coefficient of volume expansion at constant pressure, then

$$\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_p = \frac{\partial}{\partial T}\left[-\left(\frac{\partial g}{\partial T}\right)_p\right]_p = -\left(\frac{\partial^2 g}{\partial T^2}\right)_p$$

and
$$kv = -\left(\frac{\partial v}{\partial p}\right)_T = -\frac{\partial}{\partial p}\left[\left(\frac{\partial g}{\partial p}\right)_T\right]_T = \left(\frac{\partial^2 g}{\partial p^2}\right)_T \qquad \text{...(14)}$$

and
$$\alpha v = \left(\frac{\partial v}{\partial T}\right)_p = \frac{\partial}{\partial T}\left[\left(\frac{\partial g}{\partial p}\right)\right]_T = \frac{\partial^2 g}{\partial T\, \partial p}$$

$\therefore$
$$\left(\frac{\partial^2 g_2}{\partial T^2}\right)_p - \left(\frac{\partial^2 g_1}{\partial T^2}\right)_p = \frac{C_{P_1}}{T} - \frac{C_{P_2}}{T} \qquad \text{...(15)}$$

$$\left(\frac{\partial^2 g_2}{\partial p^2}\right)_T - \left(\frac{\partial^2 g_1}{\partial p^2}\right)_T = v(k_2 - k_1) \qquad \text{...(16)}$$

and
$$\frac{\partial^2 g_2}{\partial T\, \partial p} - \frac{\partial^2 g_1}{\partial T\, \partial p} = v(\alpha_2 - \alpha_1) \qquad \text{...(17)}$$

For second order phase transition

$$s_1 = s_2 \qquad \text{(at } T \text{ and } P\text{)}$$

But
$$ds = \left(\frac{\partial s}{\partial T}\right)_p dP + \left(\frac{\partial s}{\partial p}\right)_T dp$$

But $\left(\frac{\partial x}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$ (from Maxwell's relation)

$\therefore$
$$ds = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp = \frac{C_p}{T} dT - (\alpha v)\, dp$$

and
$$ds_1 = ds_2$$

$\therefore$
$$\frac{C_{p_1}}{T} dT - v\,\alpha_1\, dp = \frac{C_{p_2}}{T} dT - v\,\alpha_2\, dp \qquad (\text{since } v_1 = v_2)$$

$\therefore$
$$\frac{dp}{dT} = \frac{C_{p_2} - C_{p_1}}{Tv(\alpha_2 - \alpha_2)} \qquad \text{...(18)}$$

Similarly if we start with $v_1 = v_2$, then

$$dv_1 = dv_2$$

As
$$v = v(T, p)$$

$\therefore$
$$dv = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dv$$
$$= v\alpha\, dT - vk\, dp \text{ [from (14)]}$$

As $dv_1 = dv_2$, we have

$$v\alpha_1\, dT - vk_1\, dp = v\alpha_2\, dT - vk_2\, dp$$

$\therefore$
$$\frac{dp}{dT} = \frac{\alpha_2 - \alpha_1}{k_2 - k_1} \qquad \text{...(19)}$$

Equations (18) and (19) are known as Eherenfest's equations.

An important example of **second order Transition is the transition from non-ferromagnetic state to ferromagnetic state.** To explain this consider a ferromagnetic substance like iron and nickel. Some of the spins of atoms become spontaneously (without any external field) polarised in the same direction, below the Curie temperature $T_C$. This creats a macroscopic magnetic field. When temperature is raised, some of the regularly aligned spins flip over due to thermal agitation. This tends to destroy the initial ordered state. For $T > T_C$, the spins get oriented at random. The spontaneous magnetisation disappears. As $T_C$ is approached from both sides, the heat capacity of substance approaches infinity. Hence the transition from non-ferromagnetic to ferromagnetic state is of second order. It is associated with some kind of change of symmetry of the lattice. For example in ferromagnetism, the symmetry of spins is involved.

It may be noted that the phase transitions of second kind in contrast to ordinary first order phase transition is continuous in the sense that the state of the body changes continuously. Although the symmetry changes discontinuously at the transition point, at each instant, the body belongs to one of the two phases. At a phase transition point of the kind, the bodies in two different states are in equilibrium while at a phase transition point of the second kind, the states of the two phases are the same.

## 13.6 Critical Exponent

It is common experience that when the temperature of a substance is changed, the phase of substance changes. For example water freezes at 273 K and boils at 373 K, both at a fixed pressure of 1 atmosphere. If pressure is changed, these phase changes occur at different temperatures. We can find the pressure and temperature where the substance can exist in either of two phases. For example at $T = 373$ K and $P = 1$ atmosphere, water can exist as a high density liquid or a low density vapour. By the addition of latent heat at constant temperature and pressure, liquid is converted into vapour. If temperature is increased, we may get a remarkable new region where liquid and vapour coexist and the density difference between liquid and vapour goes to zero, so that water and steam become indistinguishable. The region where liquid vapour coexistence curve in $T - P$ diagram terminates is called the critical region. The critical phenomenon describe characteristic behaviour observed in this region surrounding the critical point at $(T_C, P_C)$. For water critical point occurs at $T = 647$ K and $P = 218$ atmosphere. The surface tension of water because zero at critical temperature.

Critical behaviour has been identified in many systems. In addition to the water-steam system, liquid gas systems generally show critical behaviour where the density difference between liquid and gas phase tends to zero. Other systems showing the critical behaviour are ferromagnets, ferroelectrics binary liquid mixtures, superfluids and super conductors. In many of these systems one phase is ordered and the other phase is disordered. It has become customary for convenience to introduce a parameter which vanishes at critical point and above it called order **parameter**. For example for a liquid-gas system, the order parameter is chosen as the density difference between the liquid and gas phases at given point $T, P$ on the co-existence curve, which approaches zero according to

$$\rho_L - \rho_v \approx (T_C - T)^{\beta}, T < T_C \qquad \ldots(1)$$

where $\beta$ is called the critical exponent.

Above the critical temperature the order parameter is zero. For a ferromagnetic system, the order parameter is the homogeneous magnetisation. The source of magnetisation is the spin related magnetism of electrons in the unfilled $d$ and $f$ shells of transition metals such as iron, cobalt and nickel. The interaction among electrons and the Pauli's exclusion principle keeps like spins separated. This results to lower energy for parallel spins. Below the critical temperature and in the absence of external magnetic field, the thermodynamically stable state is one in which a significant number of spins is aligned along a common direction, producing a net magnetisation. Above critical temperature the thermal agitations result no residual macroscopic magnetisation if external magnetic field $H = 0$. In the critical region above the critical point $T = T_C, H = 0$, the macroscopic magnetisation is either quite small or zero depending on whether $T$ is below or above $T_C$. The **common linkage between the behaviour of a liquid vapour critical system and a ferromagnetic critical system is the dominance of fluctuations in critical regions.**

In addition to critical exponent $\beta$, there are several other exponents given below : The critical exponent $\alpha$ gives a relation for specific heat in the vicinity of critical temperature.

$$c \sim | (T - T_C) |^{-\alpha} \qquad \ldots(2)$$

The critical exponent $\gamma$ is related to the critical behaviour of generalised susceptibility.

$$\chi \sim | (T - T_C) |^{-\gamma} \qquad \ldots(3)$$

The **critical exponent** $\delta$ occurs in following two relations :

(a) The relation between external magnetic field and magnetisation at critical temperature

$$H = M^{\delta}, T = T_C \qquad \ldots(4a)$$

(b) The relation between pressure and density at critical temperature

$$P - P_C \sim | (\rho - \rho_C |^{\delta}, T = T_C \qquad \ldots(4b)$$

These critical exponents are connected by scaling relations to reduce their independent numbers *e.g*,

$$\left.\begin{array}{ll} \alpha + 2\beta + \gamma = 2 & \text{Rushbrooke scaling law} \\ \gamma = \beta(\delta - 1) & \text{Widom scaling law} \end{array}\right\} \qquad \ldots(5)$$

These law were initially derived as inequalities and then were converted to equalities by scaling **hypothesis**. Several inequalities involving the critical exponents can be derived using thermodynamical stability considerations.

For example specific heat at constant magnetisation $C_M$ and specific heat at constant magnetic field $C_H$ for a magnetic system are related as

$$C_H - C_M = T\left(\frac{\partial H}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H^2 \qquad \ldots(6)$$

Thermodynamical stability requirements indicate that $C_M$ is non-negative

$$\therefore \qquad C_H \geq T\left(\frac{\partial H}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H^2$$

But susceptibility $\chi = \left(\frac{\partial M}{\partial H}\right)_T$

$$\therefore \qquad C_H \geq \frac{T}{\chi}\left(\frac{\partial M}{\partial T}\right)_H^2$$

For temperatures in the vicinity of critical temperature, we can make use of power law dependence of $C_H$, $\chi$ and $M$ on $(T_C - T)$, to obtain the inequility

$$(T_C - T)^{-\alpha} \geq A\,(T_C - T)^{2\beta + \gamma - 2}$$

where $A$ is *a* function independent of $T_C - T$ and $\alpha$ and $\gamma$ refer to critical exponents for $C_H$ and $\chi$ for $T < T_C$.

This gives $\qquad 2\beta + \gamma - 2 \geq -\alpha$

resulting in Rush boooke **inequality** $\alpha + 2\beta + \gamma \geq 2$

## 13.7 Ising Model

The Ising model was set up to investigate the behaviour of substances whose molecules posses a magnetic moment. The model assumes that the significant interaction exists between neighbouring molecules only.

Let there be $N$ particles arranged in the lattice and also the particles possess spin with a magnetic moment. The spins may be oriented in any of the two possible orientations either up $A$ or down $B$. Let their respective numbers be $N_+$ and $N_-$, so that

$$N_+ + N_- = N$$

Let the interaction energy (which is assumed between nearest neighbours only) of a pair of two adjacent +'s or of two adjacent –'s be equal to ε. The energy of an adjacent $A$ and $B$ is taken as zero. Then the energy levels of the system, assuming isotropic interaction, will be given by

$$E(\sigma_i) = -\varepsilon \sum_{<i,j>} \sigma_i \sigma_j - \mu_B H \sum_i \sigma_i \qquad \ldots(1)$$

where $\sigma_i$ is (up) $+1$ or (down) $-1$ and $\mu_B H$ is the interaction energy associated with external magnetic field $H$.

For $\varepsilon > 0$ the neighbouring spins tend to be parallel and ferromagnetism is possible. *For stable equilibrium the energy E, tends to be minimum. Hence the spontaneous configuration of least energy is the completely polarised (ordered) configuration in which all the Ising spins are oriented in the same direction.* The configuration results at absolute zero temperature (*i.e.*, $T = 0$) when there is no thermal agitation at all. For $\varepsilon < 0$, the neighbouring spins tend to be antiparallel and antiferromagnetism results.

In equation (1) no distinction is made between $i$ and $j$. The sum over $<i, j>$ has $\bar{z}\,(N/2)$ terms, where $\bar{z}$ is the number of nearest neighbours of a site *i.e.*, coordination number of the lattice and $N$ is the number of spins.

The partition function, which is essential for determination of thermodynamical quantities, is given by

$$\boxed{Z = \sum_{(\sigma_i)} e^{-\beta E_i(\sigma_i)}} \qquad \ldots(2)$$

where $\beta = (1/kT)$ and the sum is taken over $2^N$ possible combinations of $N$-spins.

It is rather difficult to calculate equation (2) exactly, Several approximation methods have been developed. Here we shall give Bragg Williams method which is the simplest.

Weiss theory of ferromagnetism

**Bragg-William's Approximation Method :** This approximation method assumes that the distribution of spins is **random**. Let $N_+$ and $N_-$ be the number of which $\sigma_i$ is up (or $+1$) and down or $(-1)$ respectively.

Then $\dfrac{N_+}{N}$ and $\dfrac{N_-}{N}$ represents the probability of finding a spin up $(+1)$ and down $(-1)$ on given lattice site.

Then equation (1) becomes

$$E = -\frac{1}{2} \bar{z} N \varepsilon \left[ \left( \frac{N_+}{N} \right)^2 + \left( \frac{N_-}{N} \right)^2 - \frac{2N_+N_-}{N^2} \right] - \mu_B H (N_+ - N_-) \qquad \ldots(3)$$

where we have assumed $N_+ > N_-$ in the last term.

The number $\dfrac{N_+}{N}$ is a measure of the **long-range order**, as it requires no co-relation between nearest neighbours. It only requires that in the entire lattice only a fraction $(N_+/N)$ of all the spins are up. If $(N_i/N)$ is known in the neighbourhood of a given spin, then the same average value is likely to occur everywhere on the entire lattice.

If $\mu_B$ is the magnetic moment associated with the spin, then the total magnetic moment is

$$N = \mu_B (N_+ - N_-) \qquad \ldots(4)$$

using

$$N = N_+ + N_-$$

$$\left. \begin{aligned} \frac{N_+}{N} &= \frac{1}{2}(1+m).\ N_- = \frac{1}{2}(1-m) \\ \text{where} \quad m &= \frac{M}{N\mu_B} \end{aligned} \right\} \qquad \ldots(5)$$

Then

$$E = -\frac{1}{2} \bar{z}\, \varepsilon N m^2 - \mu_B N m H \qquad \ldots(6)$$

Here $m$ is callod **long-range order parameter,**

$$m = \frac{N_+ - N_-}{N} = \frac{2N_+}{N} - 1,\ 1 \le m \le -1$$

The order parameter $m$ is chosen depending on the problem *e.g.* it may be magnetisation in a ferromagnetic system or fraction of superconducting electrons in a super conductor or amount of displacement in transitions where atoms are displaced from their positions, in symmetrical phase etc.

The number of arrangements of spins over the $N$ sites is given by the number of ways of choosing $N_+$ out of $N$ *i.e.*,

$$\Omega_{BW} = \frac{N!}{N_+!\,(N - N_+)!} \qquad \ldots(7)$$

From relation between entropy and probability

$$S = k \log \Omega_{BW}$$

$$= k \log \left\{ \frac{N!}{N_+!\,(N - N_+)!} \right\}$$

As $N_+ + N_- = N$ *i.e.*, $N - N_+ = N_-$, we have

$$S = k \log_e \left\{ \frac{N!}{N_+!\,N_-!} \right\}$$

$$= k\,\{\log_e N! - \log_e N_+ - \log_e N_-!\}$$

Using Stirling approximation $\log N! = N \log N - N$.

we get

$$\begin{aligned} S &= k\,[N \log_e N - N - N_+ \log_e N_+ + N_+ - N_- \log_e N_- + N_-] \\ &= k\,[(N_+ + N_-) \log_e N - N_+ \log_e N_+ - N_- \log_e N_-] \\ &= k\,[N_+ \log_e N + N_- \log_e N - N_+ \log_e N_+ - N_- \log_e N_-] \\ &= -k\,[N_+ (\log_e N_+ - \log_e N) + N_- [(\log_e N_- - \log_e N)] \\ &= -k \left[ N_+ \log_e \frac{N_+}{N} + N_- \log_e \frac{N_+}{N} \right] \end{aligned}$$

*i.e.*,

$$\begin{aligned} S &= -Nk \left[ \frac{N_+}{N} \log_e \frac{N_+}{N} + \frac{N_-}{N} \log_e \frac{N_-}{N} \right] \\ &= -Nk \left[ \frac{1}{2}(1+m) \log \left( \frac{1+m}{2} \right) + \frac{1}{2}(1-m) \log \left( \frac{1-m}{2} \right) \right] \end{aligned}$$

Helmholtz free energy

$$F = E - TS$$

$$\Rightarrow \quad F = -\frac{1}{2}\bar{z}\varepsilon Nm^2 - \mu_B Nm H - NkT - \log_e 2$$

$$\left[ +\frac{1}{2}(1+m)\log_e(1+m) + \frac{1}{2}(1-m)\log_e(1-m) \right] \qquad \ldots(9)$$

The equilibrium value of $m$ or $(N_A - N_B)$ is determined by

$$\frac{\partial F}{\partial m} = 0 \text{ i.e.,}$$

$$-\bar{z}\varepsilon Nm - \mu_B NH - NkT\left[\frac{1}{2}\log_e(1+m) + \frac{1}{2} - \frac{1}{2}\log_e(1+m) - \frac{1}{2}\right] = 0$$

or

$$\log_e \frac{1+m}{1-m} = 2\,\frac{\bar{z}\,\varepsilon m + \mu_B H}{kT} \qquad \ldots(10)$$

$$= 2x \text{ (say) where } x = \frac{\bar{z}\varepsilon m + \mu_B H}{kT}$$

It gives well known result of Weiss theory of ferromagnetism

$$\boxed{m = \frac{M}{N\mu_B} = \frac{e^{2x}-1}{e^{2x}+1} \approx \tanh x}$$

For $H = 0$, we get an expression for **spontaneous magnetic moment** as

$$m_S = \tanh(x)_{H=0} = \tanh \frac{\bar{z}\varepsilon m_S}{kT}$$

$$m_S = \tanh \frac{T_C m_S}{T} \qquad \ldots(12)$$

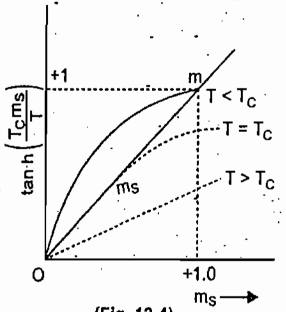
where

$$T_C = \frac{\bar{z}\varepsilon}{k} \text{ is critical temperature} \qquad \ldots(13)$$

and

$$m_S = \frac{M_S}{H\mu_B} \qquad \ldots(14)$$

Equation (12) can be solved graphically to obtain $m_S$ as a function of $T$ in Bragg-William approximations (fig. 13.4). For this the L.H.S. and R.H.S. are poltted separately as a function of $T$. The intercepts of two curves gives the value of $m$ at temperature of interest. It is clear tht the solution is $m_S = 0$ for $\frac{T_C}{T} < 1$ and $m_S = m, 0, -m$ for $\frac{T_C}{T} > 1$. But $m = 0$ is unacceptable because it corresponds to maximum of function $F$, instead of minimum. Thus $m_S = 0$ for $T > T_C$ and $m_S = \pm m$ for $T < T_C$. The solution $m_S = \pm m$ occurs because for $H = 0$, there is no difference of spin up and down.



(Fig. 13.4)

## 13.8 One Dimensional Ising Model

The one dimensional ising model consists of a chain of $N$-spin, each spin interacting only with its two nearest neighbours. In the absence of any external magnetic field, the energy of the configuration specified by $(\sigma_1, \sigma_2 \ldots \sigma_N)$ is given by

$$E_1 = -\varepsilon \sum_{i=1}^{N} \sigma_i \sigma_{i+1} \qquad \ldots(1)$$

It is convenient to arrange the chain of $N$-spins in the form of a ring (fig:), so that

$$\sigma_{N+1} = \sigma_1 \qquad \ldots(2)$$

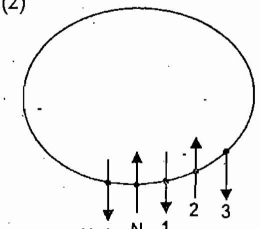
the partition function is

$$Z = \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} \exp\left[\beta\varepsilon\left(\sum_{i-1}^{N} \sigma_i \sigma_{i+1}\right)\right]$$

Now keeping in mind that $\sigma\sigma'$ can be $\pm 1$ and so using

$$\exp(c\,\sigma\sigma') = \begin{Bmatrix} e^{c} & (\sigma\sigma' = 1) \\ e^{-c} & (\sigma\sigma' = -1) \end{Bmatrix}$$

$$= \cosh c + \sigma\sigma' \sinh c$$



(Fig. 13.5)

we get

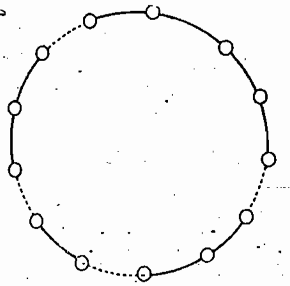
$$Z = \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} \Pi\,\{\cosh\beta\varepsilon + \sigma_i \sigma_{i+1} \sinh\beta\varepsilon\} \qquad \ldots(3)$$

the expansion of products in (3) gives the sum of terms, each of which is the product of the form

$$(\cosh\beta\varepsilon)^{N-s}(\sinh\beta\varepsilon)^{s}(\sigma_i\sigma_{i+1}\ldots\sigma_j\sigma_{j+1}) \qquad \ldots(4)$$

these terms, may be displayed graphically by continuous and dotted links forming the ring. The continuous links correspond to factor $\sigma\sigma'$ sinh $\beta\varepsilon$ (say) and dotted link to factor cosh $\beta\varepsilon$.

At a site when a continuous and a dotted link join, then its spin occurs only once and the sum of two values $\pm 1$ makes the product zero, while at the other site when two continuous links join its spin occurs squared and gives value $+1$ because $\sigma^2 = 1$. A non-zero contribution occurs when the chain of thick links, if present, has no ends. Thus the only non-zero terms are the first terms $(\cosh\beta\varepsilon)^N$ and the last $(\sinh\beta\varepsilon)^N$, so their, partition function



(Fig. 13.6)

$$Z = 2^N[(\cosh\beta\varepsilon)^N + (\sinh\beta\varepsilon)^N] \qquad \ldots(5)$$

for

$$T \neq 0,\ \beta\varepsilon = \frac{\epsilon}{kT} \neq \infty,$$

cosh $\beta\varepsilon$ > sinh $\beta\varepsilon$, so we have

$$Z = 2^N(\cosh\beta\varepsilon)^N = \left(2\cosh\frac{\varepsilon}{kT}\right)^N \qquad \ldots(6)$$

∴ Helmholtz free energy for the system is

$$F = -kT\log Z = -kT\log_e\left(2\cosh\frac{\varepsilon}{kT}\right)^N = -NkT\log_e\left(2\cosh\frac{\varepsilon}{kT}\right)$$

The energy of system

$$E = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right) = -T^2\frac{\partial}{\partial T}\left[-Nk\log_e\left(2\cosh\frac{\varepsilon}{kT}\right)\right]$$

$$= NkT^2 \times \frac{1}{\left(2\cosh\frac{\varepsilon}{kT}\right)} \times \left(2\cdot\sinh\frac{\varepsilon}{kT}\right) \times \left(-\frac{\varepsilon}{kT^2}\right)$$

$$= -N\varepsilon\tanh\frac{\varepsilon}{kT}$$

In this case there is no transition temperature.

So one dimensional Ising model can not be ferromagnetic

## 13.9. Yang and Lee Theory of Phase Transitions

The phase transition is basically the result of molecular interactions. Yang and Lee theory is a mathematical description of phase transition keeping in view that a phase transition is simply a singularity or discontinuity in the equation of state :

$$\left.\begin{aligned} P &= \frac{kT}{V}\log Z(z, V) \\ \text{and} \qquad \frac{1}{v} &= \frac{1}{V}\frac{\partial}{\partial z}\log Z(z, V) \end{aligned}\right\} \qquad \dots(1)$$

where $V$ is specific volume and $Z$ is the grand partition function, $z$ is the fugacity defined as

$$z = e^{\mu/kT}$$

Both $P$ and $V$ are analytic (or regular) functions of $z$ in complex $z$-plane and possess no real roots of the equation $Z(z, V) = 0$. This means the zeros of the function $Z(z, V)$ lie in complex $z$-plane, with no root on positive real axis.

When volume $V$ increases, the number of singularities increases and their positions may shift in the complex $Z$-plane. When $V$ is continuously increased and in the limit $V \to \infty$, some of the roots may converge towards the positive real-axis. In this limit the equation of state is given by

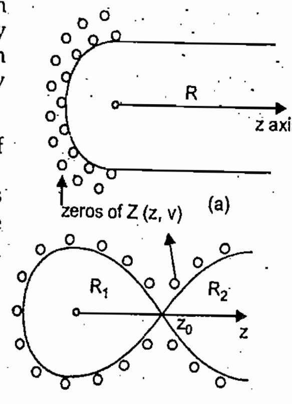
$$\left.\begin{aligned} P &= \lim_{V \to \infty}\left[\frac{kT}{V}\log Z(z, V)\right] \\ \text{and} \qquad \frac{1}{v} &= \lim_{V \to \infty}\left[\frac{1}{V}\frac{\partial}{\partial z}\{\log (z, V)\}\right] \end{aligned}\right\} \qquad \dots(2)$$

Now it is possible to find the possible signularities in the equation of state; these singularities will represent the phase transitions.

Consider a region $R$ in complex $Z$-plane, containing a segment of real positive $Z$-axis and no zero of $Z(z, v)$ for all values of $V$. It is reesonable to think that when $V \to \infty$, the condition $\frac{\partial p}{\partial V} \leq 0$ holds. In that case, the region under consideration represents single phase (i.e., no phase transition). If there exists a number of overlapping regions, each region will correspond to a phase of the system. Thus to study phase transitions, we have to investigate the behaviour of equation of state when $z$ goes from one region to another. For such a study the two theorems stated below have extreme importance :

**Theorem I :** $\lim\limits_{V \to \infty} \frac{1}{V}\log Z(z, V)$ exists for all values of $|z| > 0$. This limit is independent of shape of volume $V$ and is continuous non-decreasing function of $z$. It is assumed that in the limit $V \to \infty$, the surface area of volume considered, increases with increase of $V$ but no faster than $V^{2/3}$.

**Theorem II :** If $R$ is a region in the complex $z$-plane which contains a segment of positive real axis and contains no root of the equation $Z(z, V) = 0$ for any volume $V$, then for all values of $z$ in region $R$, the quantity $\frac{1}{V}\log Z(z, V)$ converges uniformly when $V \to \infty$. This imples that the function $Z(z, V)$ is an analytic function for all values of $z$ in region $R$.



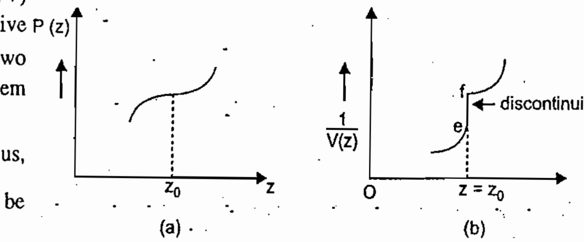
(b)

(Fig. 13.7)

In view of these theorems we study the possible behaviour of equation of state.

Suppose region $R$ contains entire positive $Z$-axis with no zeros; then the system is in single phase. On the other hand if a zero of $Z(z, V)$ approaches the point $z_0$ on real positive $z$-axis as $V \to \infty$, then there will be two regions $R_1$ and $R_2$ in which the theorem II holds.

At $z = z_0$, $P(z)$ must be continuous, though its first derivative $\frac{\partial P(z)}{\partial z}$ may be discontinuous.



(Fig. 13.8)

As an example consider the behaviour of system shown in fig. The system possess one phase for $z < z_0$ and other phase for $z > z_0$.

At $z = z_0$, $\frac{1}{V(z)}$ is discontinuous; thus we obtain the ***first order phase tranisition*** because at $z = z_0$, $P(z)$ is continuous but $\frac{dP(z)}{dz}$ is discontinuous.

On the other hand if first derivative $\frac{dP(z)}{dz}$ is continuous but second derivative $\frac{d^2P(z)}{dz^2}$ is discontinuous at $z = z_0$, then we have *second order phase transition.*

***Thus an equation of state is capable of exhibiting the phenomenon of phase transition. The phase transition occurs if a root z of equation Z (z, V) = 0 approaches a real positive z-axis in the limit V → ∞. The nature of phase transition is governed by the analytic behaviour of P (z) near such a root of z.***

## 13.10 Landau Theory of Phase Transitions

Landau gave a systematic theory of phase transitions applicable to a large variety of systems undergoing such transitions. Consider systems at constant volume and temperature, so that their Helmholtz free energy $F = U - \tau\sigma$ is minimum in equilibrium. Now question arises $F$ is minimum with respect to which variable. For simplicity Landau supposed that the system can be described by a single order parameter $x$ (say). The parameter may be the magnetisation of a feromagnetic system, the dielectric polarisation in a ferroelectric system, the fraction of superconducting electrons in a superconductor etc. In thermal equilibrium the order parameter has a certain value $x = x_0(\tau)$.

Landau assumed that $x$ can be specified independently and the Landau free energy function is

$$F_L(x, \tau) = U(x, \tau) - \tau\sigma(x, \tau) \qquad \dots(1)$$

where energy and entropy are taken when the parameter has specified value $x$ which is not necessarily $x_0$ The equilibrium value $x_0(\tau)$ is that value of $x$ at which the Landau function $F_L$ is minimum at a given temperature $\tau$ ($\tau = kT$). The actual Helmholtz free energy $F(\tau)$ of that system at temperature $\tau$ is equal to that minimum *i.e.*,

$$F(\tau) = F_L(x_0, \tau) \le F_L(x, \tau) \text{ if } x \ne x_0 \qquad \ldots(2)$$

If Landau free energy function $F_L$ at a given $\tau$, is plotted against $x$; then $F_L$ may have more than one minimum. The lowest of these determine the equilibrium state. In a first order transition the other minimum becomes the lowest minimum if temperature ($\tau$) is increased.

For most ferromagnetic and ferroelectric systems, the Landau function is an even function of $x$; we restrict ourselves to such systems. We also assume that the Landau function $F_L(x, \tau)$ is sufficiently well behaved function of $x$ and it can be expanded as a power series in $x$. For even function of $x$, $F_L$ may be expressed as

$$F_L(x, \tau) = f_0(\tau) + \frac{1}{2} f_2(\tau) x^2 + \frac{1}{4} f_4(\tau) x^4 + \qquad \ldots(3)$$

where $f_0(\tau), f_2(\tau), f_4(\tau) \ldots$ are expansion coefficients, the entire temperature dependence of $F_L(x, \tau)$ is contained in these coefficients. The simplest example of phase transition occurs when $f_2(\tau)$ changes sign at a temperature $\tau_0$, with $f_4$ positive and higher terms negligible. For simplicity we assume $f_2(\tau)$ linear in $\tau$ over specified temperature range in the form

$$f_2(\tau) = (\tau - \tau_0)\,\alpha \qquad \ldots(4)$$

and take $f_4$ as a constant in that temperature range. With these ideal limitations.

$$F_L(x, \tau) = f_0(\tau) + \frac{1}{2} \alpha (\tau - \tau_0) x^2 + \frac{1}{4} f_4 x^4 \qquad \ldots(5)$$

The assumed equation (4) can not be accurate over a very wide temperature range and it certainly fails at low temperatures because such a linear dependence is not consistent with the third law of thermodynamics.

For equilibrium value of $x$, $F_L$ should be minimum. For this we differentiate equation (5) with respect to $x$ at given $\tau$ and but equal to zero *i.e.*,

$$\left(\frac{dF_L}{dx}\right)_\tau = 0$$

$$\Rightarrow \qquad \left(\frac{\partial F_L}{\partial x}\right)_\tau = (\tau - \tau_0)\,\alpha x + f_4 x^3 = 0 \qquad \ldots(6)$$

This gives

$$x = 0 \quad \text{or} \quad x^2 = (\tau_0 - \tau)\left(\frac{\alpha}{f_4}\right)$$

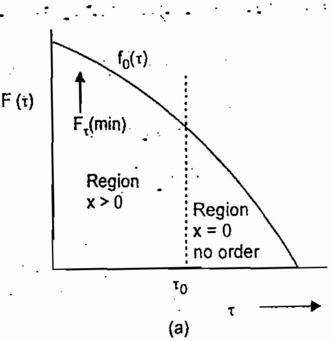
With $\alpha$ and $f_4$ positive, the root $x = 0$ corresponds to the minimum of the free energy function (5) at temperature above $\tau_0$; at this position Helmholtz free energy is

$$F(\tau) = f_0(\tau) \qquad \ldots(8)$$

The other root of $x$ given by $x^2 = \dfrac{(\tau_0 - \tau)\,\alpha}{f_4}$ corresponds to the minimum of the free energy function at temperatures below $\tau_0$; at this position the Helmholtz free energy is given by

$$F(\tau) = f_0(\tau) - \left(\frac{\alpha^2}{4f_4}\right)(\tau - \tau_0)^2 \qquad \ldots(9)$$

The temperature dependence of $F(\tau)$ for an idealised phase transition of second order is shown in Fig. (a), while the variation of Landau free energy with $x^2$ is shown in Fig. (b). From fig (b) it is clear that at a temperature below $\tau_0$, the equilibrium value of $x$ gradually increases.

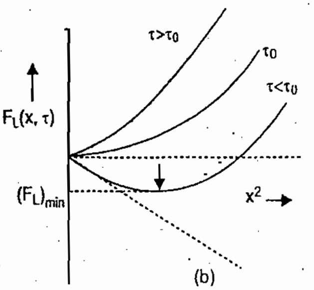


(Fig. 13.9 a)

This model describes a phase transition in which the value of order parameter approaching zero continuously as the temperature is increased to $\tau_0$. *The entropy* $\sigma = -\dfrac{\partial F}{\partial \tau}$ *is continuous at* $\tau = \tau_0$, so there is no latent heat at transition temperature $\tau_0$, such a transition is a second order transition

## Landau Theory of first order Transition

The transitions with a non-zero latent heat an called first order transitions. The liquid-gas transformation at constant pressure is a first order phase transition. The first order phase transitions are common in ferroelectric crystals and in metals. The Landau function describes a first order transition when the expansion coefficient $f_4$ is negative and $f_6$ is positive.



(Fig. 13.9 b)

Let $F_L(x, \tau) = f_0(\tau) + \frac{1}{2} \alpha (\tau - \tau_0) x^2 - \frac{1}{4} \mid f_4(\tau) \mid x^4 + \frac{1}{6} f_6 x^6 +$

$$\ldots(10)$$

The extremum of this function are given by $\dfrac{\partial F_L}{\partial x} = 0$

$$\Rightarrow \qquad \alpha(\tau - \tau_0) x - \mid f_4(\tau) \mid x^3 + f_6 x^5 = 0 \qquad \ldots 11\,(a)$$

This gives either $x = 0$

$$\text{or} \qquad \alpha(\tau - \tau_0) - \mid f_4(\tau) \mid x^2 + f_6 x^4 = 0$$

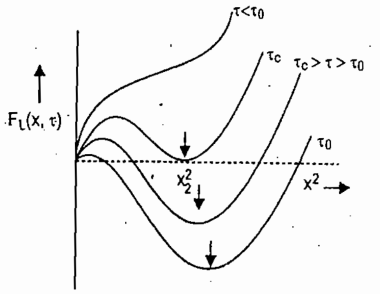
$$\Rightarrow \qquad x^2 = \frac{\mid f_4 \tau \mid \pm \sqrt{\mid f_4(\tau) \mid^2 - 4 f_6 \alpha (\tau - \tau_0)}}{2 f_6} \qquad \ldots 11(b)$$

The plot of Landau function versus $x^2$ for first order transition is shown in Fig.

At transition temperature $\tau_c$, the free energies will be equal for the phases for $x = 0$ and for $x$ given by 11 (b) (say $x = x_2$).

The value of transition temperature $\tau_c$ is not equal to $\tau_0$ and the first order parameter $x$ does not go to zero continuously at $\tau_c$.

For $\tau$ below $\tau_c$, the minimum is at larger value of $x$, but when $\tau > \tau_c$, there is a discontinuous change in the position of minimum.



(Fig. 13.10 b)

These results differ from second order transition when $x$ goes to zero continuously at $\tau_0 = \tau_c$ moreover a first order transition may show hysteresis as in supercooling or supersaturation but there is no hysteresis effect in second order phase transition.

## EXERCISES

### SHORT ANSWER QUESTIONS

1. What do you mean by triple point ? What is the value of triple point of water ?
2. Is triple factor of a substance unique ? Explain.
3. What are the two factors taken into account to derive the Vanderwaal's equation ? Write Vanderwaal's equation of state.
4. What are the conditions to obtain critical point in Vanderwaal's equation of state ? Express thermodynamic coordinates at critical point in Vanderwaal's equation.
5. Give four characteristics of matter near critical point.
6. What do you mean by first order and second order phase transitions ? Give examples.
7. Write Ehrenfest's equations for phase transitions.
8. What are critical exponents ? Give Rush broove inequality regarding critical exponents.
9. What is Landau function ? What is its value at equilibrium ?
10. Plot curves for Landau function versus variable parameter $x^2$ for first order transitions and state important characteristics.

### LONG ANSWER QUESTIONS

1. What do you mean by first order and second order phase transitions ? Give a clear distinction between them.
2. Derive Vanderwaal's equation of state and find the thermodynamic coordinates of critical point.
3. What do you mean by the triple point of a substance ? Show that the triple point of a substance is unique.
4. What do you mean by critical exponent ? Introduce various critical exponents known to you ? Are they quite independent ?
5. What are phase transitions of first and second kind? Discuss Ising model for phase transitions of second kind. ***(Meerut 2003)***
6. What do you mean by cooperative phenomenon ? Explain Ising model ? Use Bragg-Willium approximation method to obtain expressions for entropy and free energy under this model. ***(Meerut 2006, 2001)***
7. Give a brief account of one-dimensional Ising model.
8. What are phase transitions and critical indices ? How Yang and Lee theory may be used to explain phase transition. ***(Meerut 2005, 2002, 01)***
9. Give Landau theory of phase transitions. ***(Meerut Univ. 2005)***
10. Write short notes on :
    (a) Phase transitions of three matter states ***(Meerut 2006)***
    (b) Ising model ***(Meerut 2001)***
    (c) Yang and Lee theory ***(Meerut 2003)***
    (d) Landau theory ***(Meerut 2001)***

### MULTIPLE CHOICE QUESTIONS

Select the right choice

1. Triple point of a substance
   (a) is unique (b) has two values (c) has three values (d) does not exist
2. The correction term $\frac{a}{V^2}$ in Vanderwall's equation is due to :
   (a) finite size of molecules (b) intermolecular forces (c) surface tension effect (d) all of above
3. The Vanderwaal's gas obey perfect gas equation :
   (a) always (b) at high pressure and low temperatures
   (c) at high pressure and high temperature (d) at low pressure and low temperature
4. Vanderwaal's equation when solved for pressure $P$ has :
   (a) one root only (b) two roots only (c) three roots only (d) unique value
5. The critical temperature for Vanderwaal's is :
   (a) $\frac{a}{Rb}$ (b) $\frac{1}{9}\frac{a}{Rb}$ (c) $\frac{1}{27}\frac{a}{Rb}$ (d) $\frac{8}{27}\frac{a}{Rb}$
6. Conversion of boiling water at 1 atmosphere and 100°C in vapour is :
   (a) zero order phase transition (b) first order phase transition
   (c) second order phase transition (d) third order phase transition
7. Clausius Clapeyon's equation holds for :
   (a) first order phase transjition (b) Second order phase transition
   (c) both (a) and (b) (d) neither (a) nor (b)
8. The density and entropy changes suddenly .
   (a) in first order phase transition (b) in second order phase transition
   (c) both in first order and second order phase transitions
   (d) Neither in first order nor in second order phase transitions
9. The first derivative of Giib's function is continuous in :
   (a) first order phase transition (b) second order phase transition
   (c) both in first order and second order phase transitions
   (d) neither in first order not in second order phase transition
10. The Landau function in specified temperature range may be expressed as $F_L(x, \tau) =$
    (a) $f_0(\tau) + \alpha(\tau - \tau_0)^2 x^2$ (b) $f_0(\tau) + \alpha(\tau - \tau_0)\, x^4$
    (c) $f_0(\tau) + \alpha(\tau - \tau_0) + \beta(\tau - \tau_0)^2 + \ldots$ (d) $f_0(\tau) + \frac{1}{2}\alpha(\tau - \tau_0)^2 + \frac{1}{4} f_4 x^4$
11. The Landau function for parameter $x$ at given temperature usually has :
    (a) one root only (b) two roots (c) three roots (d) unique value
12. Landau curves for $F_L(x, \tau)$ against $x^2$ meet :
    (a) at $x = 0$ only (b) at $x \neq 0$ only (c) both (a) and (b) (d) neither (a) nor (b)

**ANSWERS**

1. (a) 2. (b) 3. (b) 4. (c) 5. (d) 6. (b) 7. (a) 8. (a)
9. (b) 10. (d) 11. (b) 12. (a)

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