B. Sc. II YEAR
Thermodynamics and Statistical Mechanics

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Thermodynamics and Statistical Mechanics

Contents

Course 5: Thermodynamics and Statistical Mechanics

Course code: BSCPH201   **Credit: 3**

UNIT-1   BASIC CONCEPT AND ZEROTH LAW OF THERMODYNAMICS

CONTENTS

1.1   INTRODUCTION

At the outset it is imperative to know about the course title- The Thermodynamics. Thermodynamics is a branch of physics which deals with the energy and work of a system. It was originated in 19th century as scientists were first discovering how to build and operate steam engines. Thermodynamics does not take into account the atomic constitution of matter i.e. its structure etc., but it deals only with the large scale response of a system which we can observe and measure in experiments. Small scale molecular interactions are described by the kinetic theory of gases. The methods complement each other; some principles are more easily understood in terms of thermodynamics and some principles are more easily explained by kinetic theory. Thermodynamics is a perfect mathematical science describing the inter-relationship between heat and any other form of energy viz., electrical, mechanical, chemical, magnetic etc. The basic concept is the transformation of heat into mechanical work through any bulk material. Thermodynamics has innumerable applications in physics, chemistry & engineering sciences. While studying thermodynamics, you will learn about some basic terms like temperature, thermodynamical system, internal energy, thermal equilibrium and about certain thermodynamical processes such as isothermal and adiabatic processes etc. You will also know here about the concept of a system and its surroundings. In our day to day life we often come across the examples of isothermal and adiabatic processes. The melting of ice at zero degree centigrade temperature and that of sudden burst of a tyre are the practical examples of isothermal and adiabatic processes respectively. The understanding of the different thermodynamic process will help you to know the physics behind many such practical examples. There are three principal laws of thermodynamics besides the one called the zeroth law. Each law leads to the definition of thermodynamic properties which help us to understand and predict the operation of a physical system. In the present unit you will become familiar with the zeroth law which introduces the concept of temperature and relates it to the thermal equilibrium.

1.2   OBJECTIVES

By the end of this unit, you should be able to-

- Get a clear picture of the system and its surrounding in thermodynamics
- Know about the macroscopic and microscopic properties of the system
- Explain the change of state of the system
- Explain the concept of heat and temperature
- Know the condition of thermal equilibrium
- Enunciate zeroth law of thermodynamics
- Interpret quasistatic, isothermal and adiabatic processes
- Solve simple numerical problems based on the above concepts

1.3   SYSTEM & SURROUNDINGS

A system may be defined as a definite quantity of matter (solid, liquid or gas) bounded by some closed surface. The simplest example of a system is a gas contained in a cylinder with a movable piston that can be heated by a burner. Here the system is the gas and the surroundings are piston and burner. When a system is completely uniform throughout such as a gas, mixture of gases, pure solid, a liquid or a solution you will say it is homogeneous system, but when it consists of two or more phases which are separated from one another by definite boundary surface it is said to be heterogeneous system e.g., a liquid and its vapor, two immiscible or partially miscible liquids.

Fig.1.1

Anything which is outside this system and can exchange energy with it and has a direct bearing on its behaviors called its surrounding. The complete system and its surrounding together is called universe. Further you can distinguish the system in three classes as discussed in the next article.
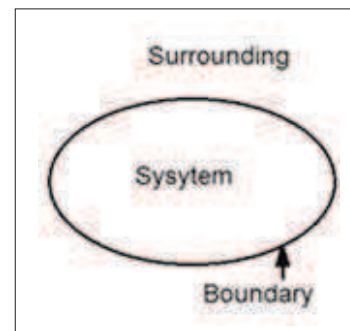
Boundary or wall is the surface that separates the system from the surroundings. This wall or boundary may or may not allow interaction between the system and surroundings.

1.3.1 THERMODYNAMIC SYSTEM

The thermodynamic state of a system is determined by four observable properties. These properties are its composition, pressure (P), volume (V) and temperature (T).
On the basis of the type of their boundaries, the systems can be categorized as follows:

    i.   **Open system:** A system which can exchange both energy and matter with its surrounding is called an open system e.g., air compressor: air at low pressure enters and air at high pressure leaves the system i.e., there is an exchange of matter & energy with the surrounding.

    ii.   **Close system:** A system which can exchange only energy (not matter) with the surrounding is called a closed system e.g., gas enclosed in a cylinder expands when heated and drives the piston outwards. The boundary of the system moves but the matter (gas) in the system remains constant.

    iii.   **Isolated system:** A system which is thermally isolated and has no exchange of heat or works with the surrounding is called isolated system e.g., a beverages or any other liquid contained in a thermos flask .

1.3.2 MACROSCOPIC AND MICROSCOPIC SYSTEMS

The behavior of the system can be described in two different ways namely macroscopic and microscopic. Macroscopic properties can usually be directly experienced by our senses. These properties describe the gross characteristics of the system and can directly be measured in the laboratory. Macroscopic properties are not concerned with the structure of the system (chemical composition). Pressure, temperature, volume, internal energy, entropy etc. are few examples of these properties. A macroscopic system is one whose state can completely be described in terms of its macroscopic properties or coordinates.

Microscopic properties cannot be directly experienced by our sense of perception. These properties describe the internal structure (atoms & molecules) of the system and cannot be measured directly in the laboratory.

In fact the macroscopic & microscopic properties are simply the different ways of describing the same system so they are related to each other e.g., the pressure of a gas is related to the average rate of change of momentum due to all the molecular collisions taking place on a unit area. Higher is the rate of change of momentum, higher will be the pressure. Here the pressure is a macroscopic property, whereas the rate of change of momentum due to molecular collisions is a microscopic property. Similarly the temperature of a gas (macroscopic property) is related to the average kinetic energy of translational motion of its molecules which is microscopic.

1.3.3 TEMPERATURE AND HEAT

The temperature of a body is a measure of its hotness or coldness . In fact we distinguish hot bodies or cold bodies by our sense of touch. That is by touching we can roughly distinguish between a hot and a cold body.

 Let us consider two bodies A and B kept in contact such that A is at higher temperature. After some time they both acquire the same temperature which is approximately in between the two temperatures. It means there is something which has been transferred from A to B. This something is called Heat. Thus heat is that physical entity which is transferred from one body to other because of a temperature difference between them. In fact, heat is a form of energy which is transferred from one body to other because of a temperature difference between them.

We can explain it with a simple example of water level. If two vessels are filled with water up to the levels of different height and are inter connected, the water will always flow from the higher level to the lower level side. Similarly, heat will flow from a body at higher temperature to a body at lower temperature when they are brought in contact with one another.

There is a distinction between temperature of a body and the heat that it contains. In fact the heat that a body contains depends upon its mass as well as upon its temperature. For example the sparks from a blacksmith's hammer are white hot (at very high temperature) but they do

not burn the hand since their mass is very small, therefore contain little heat. On the other hand a jug of hot water (at a much lower temperature than the spark) causes a severe burn because it contains more heat.

Hence, the flow of heat depends only on the temperature difference but the quantity of heat flown does not depend only on temperature difference but also depends on mass and specific heat of the body. For example, if a hot body and a cold body are put in mutual contact, heat flows from hot to a cold body until they attain a common temperature. It means the temperature of a hot body falls and that of cold body rises. But these temperature- changes are not necessarily equal because the masses (and also the specific heats) of the two bodies may be different.

1.3.4 INTERNAL ENERGY

The energy content of a system is called its internal energy. The internal energy of a system is the energy contained within the system, excluding the kinetic energy of motion of the system as a whole and the potential energy of the system as a whole due to external force fields. It keeps account of the gains and losses of energy of the system that are due to changes in its internal state. It is the sum of following forms of energy of the system-

(i)   Kinetic energy due to translational, rotational and vibrational motion of molecules, all of which depend only on the temperature

(ii)   Potential energy due to intermolecular forces, which depends on the nature and separation between the molecules and

(iii)   The energy of electrons & nuclei
        In practice, it is not possible to measure the total internal energy of a system in any given state rather only change in its value can be measured.

Let us formulate the expression for internal energy. Consider a thermodynamic system interact with its surrounding and passes from an initial equilibrium state i to a final equilibrium state f through a certain process (path) Let Q be the heat absorbed by the system and W the work done by the system. W is taken positive when work is done by the system during this process. Q is considered positive when heat is taken by the system. The Quantity (Q-W) can be calculated here. It is experimentally found that if the system be carried from the state i to f through different paths, the quantity (Q-W) is found to be the same although Q and W individually are different for different paths. Thus when a "thermodynamic system passes from state i to f the Quantity (Q-W) depends only upon the initial and final (equilibrium) states and not on the path taken by the system between these states". The quantity (Q-W) is defined as the "change in the internal energy" of the system.

U_f_U_i = ΔU = Q -W
        (1.1)

Here U (internal energy) is a function of thermodynamical co-ordinates i.e.

U = f (p, v, t)
        (1.2)

Eq. 1.1 can be used to measure the change in internal energy of the system, if some arbitrary value is assumed as the value of the initial state, its value in any other state can be computed from the above equation. However in practice the change in internal energy is only important. Experimentally it has been observed that the internal energy of a system is a function of states only and does not depend upon the path by which the state has been achieved.

Self Assessment Questions (SAQ) 1

Explain the followings:
1. Thermodynamics
2. Thermodynamic system
3. Microscopic properties
4. Macroscopic properties
5. Temperature
6. Internal Energy

1.4. THERMAL EQUILIBRIUM

If a system 1 with temperature T1 and system 2 with temperature T2 are in thermal contact, there will be exchange of heat between the two systems if there is a temperature gradient (i.e. when T1 is not equal to T2). The process of heat exchange will continue until both the temperature become equal. i.e. T1 = T2. Then the two systems are said to be in thermal equilibrium.   Hence two systems in thermal contact or a system in thermal contact with the surrounding attain thermal equilibrium by attaining the same temperature (Fig. 1.2)
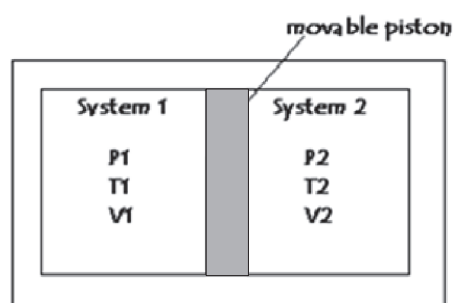
Fig.1.2

1.5 EQUATION OF STATE

An equation of state is a thermodynamic equation relating state variables which describes the state of matter under a given set of physical conditions. In other words the equation of state is the known relationship between the thermodynamic variables or properties. It is an equation

which provides a mathematical relationship between two or more state functions associated with matter such as its temperature, pressure, volume and internal energy.

With the above description of equation of state the Boyle's laws, Charles' law, Dalton's law of partial pressures are all regarded as examples of equation of state. Some other examples of equation of state are given below.

1.5.1 THE IDEAL GAS EQUATION OF STATE

The equation of state for an ideal gas is $PV = nRT$
$$(1.3)$$
where P is the pressure, V is the volume, R is the universal gas constant (R=8.314 JK^{-1}mol^{-1}), T is temperature in Kelvin, and n is the number of moles of the gas.

1.5.2 VAN DER WAALS EQUATION OF STATE

The equation of state for real gases, can be expressed by van der Waals Equation which is

$$\left(P + \frac{a}{V}\right)(V - b) = RT$$
$$(1.4)$$

where quantities *a* and *b* are constants for a particular gas but differ for different gases. There are many more equations of state that you may come across besides these two given above.

1.6   ZEROTH LAW OF THERMODYNAMICS: CONCEPT OF TEMPERATURE

Let us analyse a situation in which two systems are separated by a diathermic (good conductor of heat) and adiabatic (bad conductor of heat) walls. Now Let us consider the systems A, B, C in which A and B are isolated from each other through an adiabatic wall and both are in contact with C through diathermic wall as is shown in fig.1.3. As time passes A and B will separately attain equilibrium with C. Now if the diathermic and adiabatic walls are interchanged, no further   change in states of any of the three systems will occur. This indicates that system A and B themselves are in thermal equilibrium before the walls are interchanged. This experimental observation was first developed by R.H Fowler in 1931 and was named as Zeroth law of thermodynamics which can be stated as follows:
"If two systems are separately in thermal equilibrium with a third one, then they themselves are in thermal equilibrium with each other."
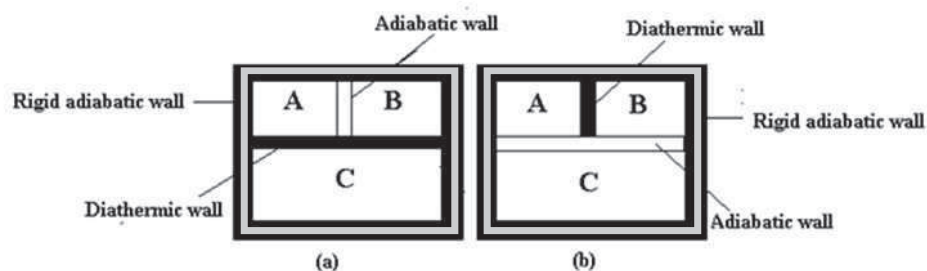
Fig. 1.3

This law in a more general form, can be expressed as:

"If a system A is in thermal equilibrium with each of the several other systems B,C,D,E etc., separately then any pair among B,C,D,E etc., will be in mutual thermal equilibrium i.e., D and C or B and D or B and C are always in equilibrium."

Zeroth law permits us to assert that *all systems* in thermal equilibrium with each other have a common property. We call this common property as *temperature*. The temperature is a property of a system that determines whether or not a system is in thermal equilibrium with other systems. Equal temperatures imply thermal equilibrium; unequal temperatures imply its absence. Thus the zeroth law gives the concept of temperature.

Let us analyse the concept of temperature in mathematical terms. Let two systems A and B with coordinates (x_A, y_A) and (x_B, y_B) respectively, be in equilibrium as shown in Fig.1.3 (b). Now if we remove A from contact of B and change its state so that the new variables become (x_A', y_A') and again make contact with B to find that A is still in equilibrium with B, zeroth law tells us that the two states of A viz., (x_A, y_A) and (x_A', y_A') are in equilibrium. In this way we can find a number of states of A as (x_A, y_A), (x_A', y_A'), (x_A'', y_A'') etc., all of which are in thermal equilibrium with the same state (x_B, y_B) of B so that all these states of A are in thermal equilibrium with each other and thus, have the same temperature. Now if all these states of A are plotted on a x – y graph they will form a curve as shown in Fig. 1.4, the locus of all those points which represent states at same temperature is called an *isotherm*. All the points on an isotherm represent states in equilibrium with each

Fig.1.4 Isotherm of system A

other. A similar isotherm of *B*, all points of which are in thermal equilibrium with any of the states of isotherm A will be called a corresponding isotherm. A process in which all thermodynamic coordinates but the temperature are changed is called an isothermal process i.e., in an isothermal process the pressure or volume of the system may change but the temperature of the system does not change.

Let us now give the mathematical presentation of the concept of temperature. Suppose two systems A and B are in thermal equilibrium. At equilibrium both the systems assume fixed

coordinates. Any change in the state of one system will change the state of the second in a restricted way. Hence equations of constraint for the two systems A and B in thermal equilibrium is based on the fact that coordinates of the one depend upon those of the other and thus is written in a combined way as:

$f_{AB}(x_A, y_A, x_B, y_B) = 0$

(1.5)

Similarly, when A is in thermal equilibrium with B and C separately, we may write

$f_{AB}(x_A, y_A, x_B, y_B) = 0$ and

(1.6)

$f_{AC}(x_A, y_A, x_C, y_C) = 0$

(1.7)

Functions f_{AB} and f_{AC} may be quite different from each other. However, from both these equations the common value of x_A can be obtained as.

$x_A = f'_{AB}(y_A, x_B, y_B)$ and

$x_A = f'_{AC}(y_A, x_C, y_C)$

which give

$f'_{AB}(y_A, x_A, y_A) - f'_{AC}(y_A, x_C, y_C) = 0$

(1.8)

But, from zeroth law, B and C should be in equilibrium. Thus we must have

$f_{BC}(x_B, y_B, x_C, y_C) = 0$

(1.9)

Eqs. (1.8) and (1.9) represent the same equilibrium conditions and thus they must agree with each other. Comparing with eq. (1.9) we must therefore, drop the variable y_A from eq. (1.8). (In a physical example the co-ordinate y_A will cancel out from two sides of equation). Thus eq. (1.8) takes the form

$f'_{AB}(x_B, y_B) - f'_{AC}(x_C, y_C) = 0$ or

$f'_B(x_B, y_B) = f'_C(x_C, y_C) = T$ (say)

(1.10)

subscripts A are also dropped as f' are functions of B and C only. Eqs. (1.9) and (1.10) show that if B and C are in equilibrium, there exists a function f' of the variables x and y for each one, having a common value T and we may write that for any system A in equilibrium with a reference system

$f'(x, y) = T$

(1.11)

This common value T of all these functions is the empirical temperature. The next step is to define the difference of temperatures. Let a contact between two systems A and B result in a net transfer of energy from A to B. Then A will be said to be at a higher temperature than B at their initial states. Thus, the order of temperature may be given by this definition. However, it does not give a scale of temperature which may enable us to define some unit for

temperature by which different temperatures may be measured. Developing a proper scale of the temperature measurements is out of scope of the present unit. For further description on temperature measurements you may consult the book mentioned at serial number three in the list of suggested reading given in the last section of the unit.

Self Assessment Questions (SAQ) 2

(i)   What do you mean by thermal equilibrium? Explain.
(ii)   What is equation of state? Give some examples.

1.7   *THERMODYNAMIC PROCESSES*

A system is said to be undergone a thermodynamic process when there is some sort of energy change within the system, generally associated with changes in pressure, volume, internal energy, temperature, or any sort of heat transfer.

There are several specific types of thermodynamic processes that often take place (and in practical situations) in thermodynamics. Each has a unique trait that identifies it, and which is useful in analyzing the energy and work change related to the process. Some important thermodynamic processes are explained below.

Adiabatic process: This is a thermodynamic process in which there is no heat transfer into or out of the system. For this process, change in quantity of heat is zero.

$$\text{i.e., during this process } \Delta Q = 0$$

Isochoric process: This is a thermodynamic process that occurs at constant volume This implies that during this process no work is done on or by the system.

$$\text{i.e., during this process } \Delta V = 0$$

Isobaric process: This is a thermodynamic process that occurs at constant pressure.
$$\text{i.e., during this process } \Delta P = 0$$

Isothermal process: This is a thermodynamic process that takes place at constant temperature. It is possible to have multiple processes within a single process. A good example would be a case where volume and pressure change during a process, resulting in no change in temperature and no heat transfer.
$$\text{i.e., during this process } \Delta T = 0$$

Cyclic processes: These are series of processes in which after certain interchanges of heat and work, the system is restored to its initial state.
For a cyclic process change in internal energy $\Delta U = 0$,
and if this is put into the first law of thermodynamics which states $\Delta U = \Delta Q - \Delta W$,
$$\text{then for cyclic process } Q = W$$

This implies that the net work done during this process must be exactly equal to the net amount of energy transferred as heat; the stored internal energy of the system remains unchanged.

Reversible process: A reversible process can be defined as one in which direction can be reversed by an infinitesimal change in some properties of the system.

Irreversible process: An irreversible process can be defined as one in which direction cannot be reversed by an infinitesimal change in some properties of the system.

Quasi-static process: This is a process that is carried out in such a way that at every instant, the system departs only infinitesimal from an equilibrium state (i.e. almost static). Thus a quasi-static process closely approximates a succession of equilibrium states. A process taking place at an extremely slow rate can be treated as a Quasi-static process.

Non-quasi-static process: This is a process that is carried out in such a way that at every instant, there is finite departure of the system from an equilibrium state. Usually a fast process is a non-quasi static in nature.

Let us learn about the adiabatic, isothermal and quasistatic processes in detail:

1.7.1 QUASISTATIC PROCESS

A finite unbalanced force may cause the system to pass through non- equilibrium states. A quasistatic process is defined as the process in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through which the system passes can be considered as equilibrium states.

A quasistatic process is an ideal concept which can never be satisfied rigorously in practice. However in actual practice many processes closely approach a quasistatic process with no significant error.

1.7.2 ISOTHERMAL PROCESS

When a thermodynamic system undergoes a process under the condition that its temperature remains constant then the process is said to be isothermal.

The essential condition for an isothermal process is that the system must be placed in a perfectly conduction chamber so that the heat produced or absorbed during the process at once goes out or comes in from outside. In this way the temperature will remain constant. But in practice we do not find a perfect conductor. Therefore, a perfect isothermal process cannot be obtained.

We can, however, obtain approximate isothermal process if the process is extremely slow. For example if a gas filled in a brass cylinder(good conductor of heat) is compressed very slowly with the help of a piston. The heat produced by compression gets enough time to go outside the cylinder through its walls. Hence temperature of the gas remains constant i.e., change in temperature is zero during the process($\Delta T = 0$). Similarly if the gas is slowly expanded it loses energy in doing work against the piston but an equal amount of heat comes in from outside. Again the temperature remains constant.

Graphically Isothermal Process can be represented by the curve as shown in Fig.1.5

If a system is perfectly conducting to the surrounding and the temperature remains constant throughout the process, it is called an isothermal process. Consider a working substance at a certain pressure and temperature and having volume represented by the point A, fig.1.5. Now the gas expands and its volume attains point B on the curve.
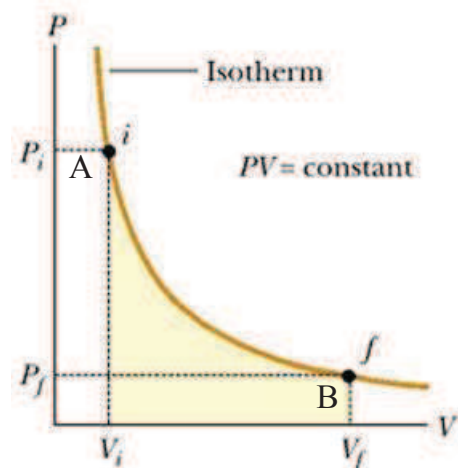
Pressure is decreased and work is done by the working substance at the cost of its internal energy and suffers a fall in temperature. But the system is perfectly conducing to the surrounding, it absorbs heat from the surrounding and maintains a constant temperature.

Fig.1.5

Thus from *i* to *f* the temperature remains constant. The curve *i.f* is called the isothermal curve or isotherm. In going from *f* to *i* and the system gives out extra heat to the surrounding and maintains the temperature constant.

Thus during isothermal process the temperature of the working substance remains constant as it can absorb heat or give heat to the surroundings. The equation of isothermal process is

$\qquad$ PV = constant $\hfill$ (1.12)

For an ideal gas undergoing isothermal process the change in internal is zero, i.e.,

$(U_2 - U_1) = 0$ $\hfill$ (1.13)

1.7.3 ADIABATIC PROCESS

When a thermodynamic system undergoes a process under the condition that no transfer of heat takes place in or out of the system then the process is said to be adiabatic.

Such a process can occur only when the system is perfectly insulated. But such a system is not possible and hence a perfect adiabatic change is impossible. We can however obtain
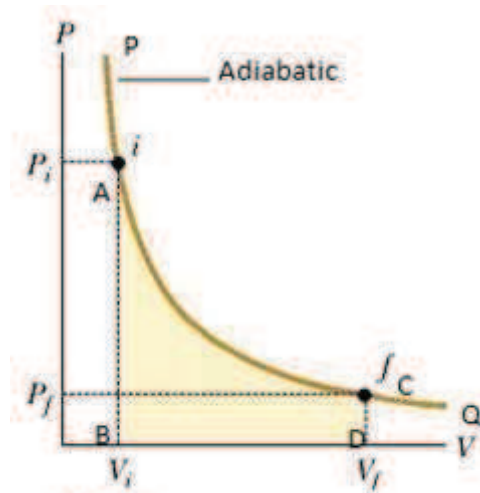
Fig.1.6

approximate adiabatic process in a way that if the process is extremely rapid so that there is very little time for the heat to escape as it is suddenly compressed. The heat produced due to compression is added to its internal energy and its temperature rises. That is why the bicycle pump is heated when the air in it is suddenly compressed. Conversely if a gas is suddenly expanded the external work done by it is drawn from its internal energy and its temperature falls. When a motor-car tyre bursts the sudden expansion of its air into the atmosphere is adiabatic and the tyre is cooled.

Other examples of adiabatic process are the expansion of steam in the cylinder of a steam engine and the compression of air in a diesel engine. The compression is so rapid that the behavior of the air is adiabatic.

Graphically adiabatic process can be represented as shown in Fig.1.6.

As you know that in adiabatic process when a system undergoes from an initial state i to final state f in such a way that no heat leaves or enters the system hence you can write
$$\Delta Q = 0$$
Thus when a system expands adiabatically then W (work done) is positive and   its internal energy decreases eq.(1.14), if the system is compressed adiabatically then W is negative. Thus in case of compression, internal energy increases eq.(1.15).

$U_2 - U_1 = $ -W   (1.14)

$U_2 - U_1 = $ - (-W) = W   (1.15)

The equation of adiabatic process is
P V^γ = constant   (1.16)

where γ is the ratio of the specific heats of the gas at constant pressure (C_p) to that at constant volume (C_v). You will revisit these processes in more detail when you will learn about the first law of thermodynamics in next unit.

Self Assessment Questions (SAQ) 3

Explain the following:

             i.   Open and closed systems
          ii.   Isolated system
       iii.   Isochoric process
       iv.   Isobaric process
        v.   Quasi-static process

1.8   SUMMARY

In this unit you have learnt some basics for understanding thermodynamics. The initial part of the unit is devoted to the understanding of the thermodynamic system and its surroundings. Important features of the unit can be summarized in the following points.

- A thermodynamic system can be represented by the four properties which are its composition, temperature, pressure and volume. Further the systems can be categorized into three types that is open system, closed system and isolated system on the basis of the type of their boundaries.
- Depending upon the parameters used to describe the state of the system completely the system may be macroscopic or microscopic.
- The temperature of a body is a measure of its hotness or coldness. Heat is a form of energy whose flow from one body to another solely depends upon the temperatures difference of the bodies.
- The internal energy of a system is the energy contained within the system, excluding the kinetic energy of motion of the system as a whole and the potential energy of the system as a whole due to external force fields. It keeps account of the gains and losses of energy of the system that are due to changes in its internal state.
- Two systems in contact are in thermal equilibrium when there is no exchange of heat between them or they maintain the same temperature between them.
- The equation of state of a system is the known relationship between the thermodynamic variables or properties. It is an equation which provides a mathematical relationship between two or more state functions associated with matter such as its temperature, pressure, volume and internal energy.
- Zeroth law states that if two systems are separately in thermal equilibrium with a third one, then they themselves are in thermal equilibrium with each other. The concept of temperature is derived from it.
- Any change in any one of thermodynamical coordinates (i.e., pressure, volume, internal energy / temperature, or any sort of heat transfer) of a system while others remaining invariable with time leads to different types of thermodynamical processes to happen viz., Isobaric process, Isochoric process, Isothermal process and Adiabatic process.

- A quasistatic process is defined as the process in which the deviation from thermodynamic equilibrium is infinitesimally, small and all the states through which the system passes can be considered as equilibrium states.

These concepts will further help you in understanding the succeeding topics.

1.9 GLOSSARY

1   Miscible liquids- A distinct layer between two liquids will not form when you have a solution that is labeled miscible. When a distinct layer does form in a mixed solution this is called immiscibility. For example, a type of immiscible liquid is oil and water.

2   Conservation-the principal by which the total value of a physical quantity remains constant in a system

3   Impose - force on someone

4   Compressed - pressed into a smaller space

5   Expansion - the action of becoming larger or more extensive

6   Limitation - a restriction

7   Surrounding - environment area around a thing or person

8   Microscopic - as small as to be visible only with a microscope or sometime even smaller like molecules.

9   Macroscopic - visible to naked eye or relating to large scale

10   Undergo – suffer

11   System - a set of things working together as part of a mechanism

12   Equilibrium - the conditions of system in which all competing influences are balanced

1.10 REFERENCES

1.   Heat, thermodynamics and statistical physics, BrijLal and Subrahmanyam, S. Chand Pub., N. Delhi
2.   Thermodynamic and statistical physics, Sharma and Sarkar, Himalaya Publishing House, Delhi
3.   Thermal Physics, B.K.Aggarwal, Lokbharti Publications, Allahabad
4.   Thermal Physics, Kumar, A. and Taneja S.P., R. Chand & Co. Pub. New Delhi.

1.11 SUGGESTED READING

1.   Kirkwood, J.G. and Oppenheim, I. (1961) Chemical Thermodynamics (McGraw-Hill: New York).
2.   Callen, H.B. (1960) Thermodynamics (Wiley: New York).
3.   Schooley, J.F., ed. in chief. (1982) Temperature, Vol. 5, Parts 1 and 2 (American Institute of   Physics: New York).

1.12 TERMINAL QUESTIONS

1.12.1 SHORT ANSWER TYPE

1. Explain the term 'heat and temperature'.

2. Distinguish between isothermal and adiabatic process.

3. Draw P-V diagram representing isothermal and adiabatic processes.

4. Show that change in the internal energy of a non-isolated system is zero.

1.12.2 LONG ANSWER TYPE

1. Explain thermodynamic system and thermodynamic variables.
2. Explain the terms:
    i.   Open system
    ii.   Closed system
    iii.   Isolated system
3. State and explain zeroth law of thermodynamics. What is its importance? On the basis of this deduce the concept of temperature?
4. What do you mean by quasi-static process? Can it be achieved in practice? State its importance.
5. What is internal energy of a system? "Internal energy is state function and not a path function", discuss.

UNIT-2   FIRST LAW OF THERMODYNAMICS

CONTENTS

2.1   INTRODUCTION

In previous unit we learnt about the basics of thermodynamics and the Zeroth law of thermodynamics.In this unit we will study the first law of thermodynamics which places work and heat as the only way, the internal energy of a system of a body can be altered. It is a version of the law of conservation of energy which states that the total energy of an isolated system remains constant. However, a perfectly isolated system does not exist in practice. All systems exchange energy with their surroundings through one or other process no matter how well insulated they are. For example, hot tea or water in a thermos flask will only stay hot for a few hours and will reach to room temperature with the passage of time.

2.2 OBJECTIVES

After studying this unit, you will be able to

- Define first law of thermodynamics
- Explain different types of specific heat capacity and relationship between them
- Relate heat, work done and internal energy for different types of processes
- Explain heat transfer into or out of the system.
- *K*now the insufficiency of first law of thermodynamics

2.3 FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is simply the principle of conservation of energy applied to a thermodynamic system. This law can be explained as follows:-

If a quantity of heat dQ is supplied to a body, then in general it is used in three ways.

(i)   Partially, it is used in raising the temperature of the body *i.e.*, increasing its internal kinetic energy dU_K.

(ii)   Partially, it is used in doing internal work against molecular attraction, *i.e.*, increasing the internal potential energy dUp.

(iii)   And rest is used in expanding the body against the external pressure *i.e.*, in doing external work dW.

So, above statement can be written as,

$$dQ = dU_K + dU_P + dW \tag{2.1}$$

This is the differential form of the first law of thermodynamics.

But,

$$dU_K + dU_P = dU \qquad \text{(where } dU \text{ is the increase in total internal energy of the body)}$$

$\therefore \quad dQ = dU + dW \text{ or}$ \hfill (2.2)

$\Delta Q = \Delta U + \Delta W$ \hfill (2.3)

Therefore, in all transformations, the energy due to heat units supplied must be balanced by the sum of external work done and increase in its internal energy.

In equation (2.3) we should note that,

Equation (2.2) represents the differential form whereas eq. (2.3) stands for change in respective quantities.

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

(ii)   If the heat is taken by the body then ΔQ is positive and if it is given by the body ΔQ is negative.

(iii)   Similarly, if the work is done by the system then ΔW is positive and if the work is done on the system then ΔW is negative.

Important features of first law of thermodynamics

The mathematical form of the first law contains three important features:

(i)   Heat is a form of energy.

(ii)   Energy is conserved in a thermodynamic system process.

(iii)   Every thermodynamic system in equilibrium state possesses internal energy and this internal energy is a function of its state i.e. temperature only.

(iv)   It is applicable to any process by which a system undergoes a physical or chemical change.

2.4 SPECIFIC HEAT CAPACITY OF A SUBSTANCE

The specific heat capacity of a substance is defined as the amount of heat supplied per unit mass of the substance for per unit rise in its temperature. If an amount ΔQ of heat is given to a mass m of the substance and its temperature rises by ΔT, the specific heat capacity C is given by the equation

$$C = \frac{\Delta Q}{m \Delta T} \qquad (2.4)$$

The same is true when temperature is lowered by taking heat from the substance.

This definition applies to any form of the substance, solid, liquid or gas. Mathematically the specific heat capacity of a material is defined as the quantity of heat required to raise the temperature of unit mass of the material through 1 degree. For pure water 1 calorie heat is required to raie its temperature by 1°C

$$\text{Thus, Sp. heat capacity of water} = 1 \text{ cal/gm°C}$$
$$= 1 \text{ kilo cal/kg°C}$$
$$= 4.18 \times 10^3 \text{ joule / kg°C} \quad (\because 1 \text{ cal} = 4.18 \text{ J})$$

This definition is sufficient for solids and liquids. Since the gases are compressible the specific heat of a gas may vary from zero to infinity. For example, if a gas is compressed, its temperature rises without supplying any heat to it (i.e., $Q = 0$). Hence specific heat

$$C = \frac{Q}{m \, \Delta T} = 0 \tag{2.5}$$

On the contrary, if the gas is allowed to expand freely, without any rise in temperature (i. e., when $\Delta T = 0$) then

$$C = \frac{Q}{m \times 0} = \infty \tag{2.6}$$

Hence the specific heat of a gas is defined by considering any of the two (pressure or volume) as constant. Thus, a gas has two specific heats

(i) C_p , the specific heat at constant pressure which is defined as the amount of heat required to raise the temperature a unit mass of a gas through 1°C when to pressure is kept constant. It is expressed as $C_p = \left(\dfrac{\Delta Q}{\Delta T}\right)_p$ \hspace{1cm} (2.7)

(ii) C_v, the specific heat at constant volume which is defined as the amount of heat required to raise the temperature of unit mass of a gas through 1°C, when its volume is kept constant. It is represented as:

$$C_v = \left(\frac{\Delta Q}{\Delta T}\right)_v \tag{2.7a}$$

C_p is always greater than Cv. Let us see how?

Heat capacity of a gas is different under these two conditions. Suppose the heat is supplied to a gas and is allowed to expand at constant pressure. Then the supplied heat is used up in doing two things:

(i)   It raises the temperature of the gas (i.e., increase in its internal energy) and

(ii)   It does work in expanding the gas against the external pressure .

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

or $\Delta Q = \Delta U + pdV$ (2.8)

On the other hand, when gas is heated at constant volume, no work is done ($\Delta W = PdV = 0$) and the entire amount of heat supplied is used to raise its temperature. Thus, more heat is required for raising the temperature of the gas through 1°C at constant pressure than at constant volume. Hence specific heat of a gas at constant pressure (C_p) is greater than the specific heat at constant volume (C_v) i.e., $C_p > C_v$.

2.4.1. THERMODYNAMIC PROOF OF MAYER'S RELATION

Let us consider one gram-molecule (mole) of an ideal gas at pressure p, Kelvin temperature T and volume V. Let C_V and C_p be the molecular specific heats at constant volume and at constant pressure respectively.

Let the gas be heated at constant volume so that its temperature is raised by an infinitesimal amount dT. The heat supplied will be $C_v\, dT$. As the volume remains constant, the external work done is zero. The differential form of the first law of thermodynamics is written as equation (2.2)

$dQ = dU + dW,$

where dQ is the heat supplied, dU the increase in internal energy and dW the work done (all expressed in same units). Here $dQ = C_v\, dT$ and $dW = 0$, so that

$C_V\, dT = dU$ (2.9)

Let the same gas be now heated at constant pressure p until the temperature is raised by the same amount of dT. The heat supplied will be $C_P\, dT$. Now, the gas would expand and external work against the pressure p would be done. If dV be the change in volume of the gas, the external work would be $p\, dV$. Thus, for this process, $dQ = C_p\, dT$ and $dW = p\, dV$. Hence, from the first law of thermodynamics, we have

$C_P\, dT = dU + p\, dV.$ (2.10)

The temperature change is the same in both the cases. Since internal energy U depends only on the temperature for an ideal gas (Joule's law), the internal energy-change dU is same in both processes. Then, eliminating dU from eq. (2.9) and (2.10) we get

$(C_P – C_V) \, dT = p \, dV.$ (2.11)

Now, the equation of state for one mole of an ideal gas is

$pV = RT,$

where R is the universal gas constant.

Differentiating it, keeping p constant, we get

$p \, dV = R \, dT$

Putting this value of $p \, dV$ in eq. (2.11), we obtain

$(C_P – C_V) \, dT = R \, dT$

or, $C_P – C_V = R$ (2.12)

This relation was first obtained by Mayer in 1842 and is therefore called "Mayer's relation".

It is perfectly true for an ideal gas and very nearly true for real gases at moderate pressures.

In Mayer's relation, R must be expressed in the same unit as C_P and C_V. Usually C_P and C_V are expressed in cal/(mole-K). Hence R must also be in calorie/(mole-K).

Since $R = 8.31$ joule/(mole-K) and 4.18 joule = 1 calorie, we have

$R = \dfrac{8.31}{4.18} = 1.99$ calorie / (mole - K).

∴ $C_P – C_V = 1.99$ calorie/(mole-K) $\simeq 2$ calorie/(mole-K).

2.5 THERMODYNAMICAL EQUILIBRIUM

Generally a system is said to be in equilibrium when its properties or state variable do not change appreciably with time over the interval of interest that is observation time or we can say that:

Any state of homogeneous system in which any two of the three variables P, V, T remain constant with time as long as the external conditions remain unchanged is said to be in thermodynamic equilibrium.

A system is said to be in thermodynamical equilibrium when it satisfies the following requirements :

2.5.1 MECHANICAL EQUILIBRIUM

For a system to be in mechanical equilibrium there should be no macroscopic movement within the interior of the system (no unbalance forces acting) and also none between the system and surrounding or with another system.

2.5.2 CHEMICAL EQUILIBRIUM

For a system to be in chemical equilibrium there should be no chemical reaction within the system and also no movement of any chemical constituents from one part of the system to the

other i.e. the internal structure and the chemical composition of the system should remain unchanged.

2.5.3 THERMAL EQUILIBRIUM

This occurs when two systems in thermal contact or a system that is in thermal contact with the surrounding do not exchange any heat. This is attained when the two systems or one system and its surrounding area are at the same temperature.

2.6 APPLICATION OF FIRST LAW OF THERMODYNAMICS

In this section we will apply first law of thermodynamics to certain basic processes to get simple relations involving the internal energy, work done and heat.

2.6.1. ISOCHORIC PROCESS

The process in which the volume of the system remains constant is called isochoric process. If volume remains constant then the work done $\Delta W (= pdV)$ by the system   will   be zero ($dV = 0$). But by the first law of thermodynamics we have,

$$\Delta U = \Delta Q - \Delta W$$

Putting ΔW =0, we get,

$$\Delta U = \Delta Q$$

Hence, in an isochoric process, the heat taken or lost by the system is entirely used in increasing or decreasing the internal energy of the system.

2.6.2. ISOBARIC PROCESS

The process, in which pressure of the system remains constant, is known as isobaric process. The boiling of water to steam or the freezing of water to ice are the examples of isobaric process.

Let *m* gm of water is converted into steam at constant pressure and temperature also. If V_l is the volume of the water in liquid state and V_v is the volume of water in vapour state, then work done by the system (in expanding from V_l to V_V against the constant pressure p) will be,

$$W = \int_{V_l}^{V_v} pdV = p\int_{V_l}^{V_v} dV$$

$$= p \ (V_V - V_l)$$

and heat absorbed by the mass m during the change of state is,

$$Q = m\ L_v$$

where L_v is latent heat of vaporization.

If ΔU be the change in its internal energy, then from the first law of thermodynamics,

$$\Delta U = Q - W$$

$\therefore \qquad \Delta U = mL - p(\mathrm{V}_v - \mathrm{V}_l)$

It is the expression for change in internal energy of the system during vaporization (isobaric process).

Similarly, we can determine the expression for the change in the internal energy of the system during freezing (isobaric process),

$$\Delta U = mL - p(V_{ice} - V_l)$$

Here L_i is the latent heat of fusion of ice.

2.6.3. ISOTHERMAL PROCESS

The process in which temperature of the system remains constant is known as isothermal process. The temperature remains constant only in the change of state *i.e.,* liquid to vapour or liquid to ice as in the case of isobaric process. So we may write

$$\Delta U = m\ L_v - p(V_V - V_l)$$

and $\quad \Delta U = m\ L_i - p(V_{ice} - V_l)$

2.6.4. ADIABATIC PROCESS

The process in which the total heat of the system remains constant i.e. no heat flows into or out f the system, is called an adiabatic process. The system is thermally insulated from the surroundings and heat can neither enter into the system nor can leave it. So for such a process heat $Q = 0$, and from the first law of thermodynamics, we have

$$\Delta U = Q - W$$
$$\Delta U = -W$$

Thus, in an adiabatic process the change in internal energy of a system, is equal to the amount of work done. If work is done by the system i.e., work done is positive, the internal energy is decreased. On the other hand if work is done on the system i.e., work done is negative, the

internal energy is increased. When a gas is suddenly compressed (adiabatic process), the work done on the gas is added to its internal energy so that its temperature rises. That is why a bicycle pump becomes hot when air in it is compressed to fill in cycle tube. Similarly, when a gas is suddenly expanded, the work against the surroundings is done by drawing heat from its internal energy. A decrease in its internal energy decreases the temperature of the gas. That is why when a motor car tyre bursts, the tyre gets cooled because of sudden expansion of air adiabatically.

2.6.5. FREE EXPANSION

If a system expands in such a way that no heat enters or leaves the system (adiabatic process) and also no work is done by the system or on the system, then this expansion is known as free expansion.

Let us consider a well insulated vessel (adiabatic) with rigid walls and divided into two parts, one containing a gas and the other evacuated. When the partition is suddenly removed, the gas rushes into the vacuum and expands freely. If U_i and U_f be the initial and final internal energies of the gas, then by the first law of thermodynamics,

$$\Delta U = Q - W$$

But, $Q = 0, W = 0$

So, $\Delta\ U = 0$

i.e., $U_i - U_f = 0$

or $U_i = U_f$

Thus, in the free expansion, the initial and final internal energies remain the same.

2.6.6. CYCLIC PROCESS

In a cyclic process, the system after passing from initial state to final state comes back to its initial state. So, in this process the net change in the internal energy of the system is zero ($\Delta U = 0$). Hence, by the first law of thermodynamics, $\Delta U = Q - W$, we have

$\Delta U = 0$ so, $Q - W = 0$ or $Q = W$

It means, in the cyclic process the heat taken by the system is equal to the work done by the system. In differential form, we may write

$$\oint dQ = \oint dW$$

Thus, for a closed system undergoing a cycle of processes, the cyclic integral of heat is equal to the cyclic integral of work.

2.6.7. ADIABATIC EQUATION OF A PERFECT GAS

Let us consider one mole of an ideal gas having a volume V at a pressure p and *K*elvin temperature T. Suppose it undergoes a small adiabatic expansion. In doing so, it does the necessary external work at the cost of its own internal energy which therefore decreases and hence its temperature falls.

Let dV be the infinitesimally small change in the volume of the gas at pressure p. Then the external work done by the gas in its expansion will be

$dW = p \, dV$

(2.13)

If dT be the fall in temperature of the gas, the heat lost by it will be $C_V dT$ where C_v is the gram-molecular specific heat at constant volume. Now, in an ideal gas the molecules do not attract each other, so that its internal energy is entirely the kinetic energy of the molecules which depends only on the temperature of the gas. Therefore, the decrease in the internal energy of the gas by dU is equal to the heat lost by it. Thus,

$dU = C_V \, dT$

(2.14)

Now, the first law of thermodynamics for an adiabatic process ($dQ = 0$) becomes

$dU + dW = 0$

Substituting the values of dU and dW from eq. (2.14) and eq. (2.13) we get

$C_v dT + pdV = 0$

(2.15)

Now, the equation of state for one mole of an ideal gas is

$pV = RT$

where, R is the universal gas constant. This on differentiation gives

$p \, dV + V \, dp = R \, dT$

or $dT = \dfrac{p\ dV + V\ dp}{R}$

Substituting for dT in eq. (2.15), we get

$$C_V \left(\dfrac{p\ dV + V\ dp}{R} \right) + p\ dV = 0$$

or $C_V\ (p\ dV + V\ dp) + R\ p\ dV = 0.$

But $R = C_P - C_V$ (Mayer's relation).

$\therefore$ $C_V\ (p\ dV + V\ dp) + (C_P - C_V)\ p\ dV = 0$

or $C_V\ V\ dp + C_p\ p\ dV = 0$

Dividing by $C_V\ p\ V,$ we obtain

$$\dfrac{dp}{p} + \dfrac{C_p}{C_V} \dfrac{dV}{V} = 0$$

or $\dfrac{dp}{p} + \gamma\ \dfrac{dV}{V} = 0$

where γ is the ratio of the gram-molecular specific heats of the gas ($\gamma = C_p/C_V$). Integrating the last expression, we have

$$\log p + \gamma \log V = \text{a constant}$$

or $p\ V^{\gamma} = \text{constant.}$
        (2.16)

This relation is known as Poisson's law.

If p_i, V_i be the initial and p_f, V_f the final pressures and volumes of the gas respectively, then

$$p_i\ V_i^{\gamma} = p_f\ V_f^{\gamma}$$

Relation between Temperature and Volume : Let us put $p = RT/V$ in eq. (2.16) which gives

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

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

    (2.17)

or $T_i V_i^{r-1} \;=\; T_f\, V_f^{r-1}$

Relation between Temperature and Pressure: Let us put V = RT/p in eq. (2.16). This gives

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

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

or $$T\, p^{(1-\gamma)/\gamma} = \text{constant.}$$

    (2.18)

Example 1: Calculate the change in internal energy when 0.004 kg of air is heated from 0°C to 2°C, the specific heat of air at constant volume being 0.172 kilo cal/kg °C.

Solution: From first law of thermodynamics

$$dQ = dU + dW$$

Since air is heated at constant volume

∴ $dW = PdV = 0$

The heat taken by the air is

$$dQ = mC_V dT$$

Therefore, $dU = dQ - dW$

$$= mC_V dT - 0$$

$$= 0.004 \times 0.172 \times 2$$

$$= 1.376 \times 10^{-3} \text{ kcal.}$$

Example 2: What is the change in energy per gm of air if 15gm of air is heated from 0°C to 5°C at constant volume by adding 150 cals of heat.

Solution: We know that

$$dU = dQ - dW$$

Since the air is heated at constant volume

$$dW = PdV = 0$$

Therefore, $dU = dQ - dW$

$$= 150 - 0$$

$$= 150 \text{ cals}$$

The change in internal energy per gm of air is $\dfrac{150 \text{ cal}}{15 \text{ gm}} = 10$ cal/gm

Self Assessment *Question* (SA*Q*) 1

Can heat be given to a substance without rise in temperature?

Self Assessment *Question* (SA*Q*) 2

A thermos bottle containing coffee is vigorously shaken and thereby the temperature of coffee rises. Consider coffee as the system. (i) Has heat been transferred to coffee? (ii) Has work been done on coffee? (iii) What is the sign of ΔU?

Example 3: Calculate the value of J from the following data : specific heat of oxygen at constant volume C_V = 5.03 cal/(mole-K), γ = 1.4, R = 8.31J/(mol-K). Why the value of J so obtained differ from the standard value of 4.18 joule/calorie?

Solution: C_V = 5.03 calorie / (mole - K) $\gamma = \dfrac{C_p}{C_V} = 1.4$

$\therefore$ $C_p = \gamma C_V = 1.4 \times 5.03 = 7.04$ calorie /(mole - K)

From Mayer's relation:

$$C_p - C_V = R \text{ (all in same units)}$$

$\therefore$ $R = 7.04 - 5.03 = 2.01$ calorie/(mole-K)

$$= (2.01 \text{ calorie}) J/(\text{mole-}K)$$

where, J is the number of joule/calorie. But we are given that R = 8.31 joule/(mole-K).

$$\therefore \quad (2.01 \text{ calorie}) \, J \, / \, (\text{mole-}K) = 8.31 \text{ joule} \, / \, (\text{mole-}K)$$

or
$$J = \frac{8.31 \text{ joule}}{2.01 \text{ calorie}} = 4.31 \text{ joule} \, / \, \text{calorie}$$

This value differs from the standard value because the formula used above holds only approximately for a real gas.

Example 4: The height of the Niagara falls is 50 meter. Calculate the difference between the temperature of water at the top and at the bottom of the fall; if J = 4.2 joule/calorie.

Solution: Suppose m kg of water falls in one second. The potential energy lost in one second is

$$W = m \, g \, h = (m \times 9.8 \times 50) \text{ joule.}$$

This lost energy is converted into heat. If Q be the heat produced, then

$$Q = \frac{W}{J} = \frac{(m \times 9.8 \times 50) \text{joule}}{4.2 \text{ joule/calorie}}$$

This heat causes a temp-rise, $\Delta T = \dfrac{(0.117m) kcal}{m \; kg \times 1.0 \; kcal/(kg- \, C)} = 0.117°C.$

Example 5: A 2.0 gm bullet moving with a velocity of 200 meter/second is brought to a sudden stoppage by an obstacle. Assuming the total heat produced is acquired by the bullet, calculate the rise in temperature of the bullet. Sp. heat of bullet material is 0.03 kcal/(kg - °C). Given : J = 4.2 joule / calorie.

Solution: The kinetic energy of the moving bullet is

$$W = \frac{1}{2} m \, v^2 = \frac{1}{2} \times 0.002 \text{kg} \times (200 \text{ m/s})^2 = 40 \text{ joule}$$

By sudden stoppage of the bullet, the whole of the energy is converted into heat. The heat equivalent of this energy is

$$Q = \frac{W}{J} = \frac{40 \text{ joule}}{4.2 \text{ joule/cal}} = 9.52 \text{ cal} = 9.52 \times 10^{-3} \text{ kcal.}$$

If ΔT be the rise in temperature of the bullet due to this heat, then

$$Q = mc \, \Delta T. \hspace{3cm} \text{(c being sp. heat)}$$

$\therefore\ 9.52 \times 10^{-3}$ kcal $= 0.002$kg $\times 0.03$kcal/(kg-°C) $\times \Delta T$

or
$$\Delta T = \frac{9.52 \times 10^{-3}}{0.002 \times (0.03/℃)} = 159°C$$

Example 6: Two samples of air having same composition and initially at the same temperature and pressure are compressed from a volume V to a volume $V/2$, one isothermally, the other adiabatically. In which sample is the final pressure greater? What will be the result in case of expansion, instead of compression?

Solution: For the isothermal compression, we have

$$p\ V = \text{constant.}$$

If V is changed to V/2, the pressure p is changed to 2 p.

For the adiabatic compression, we have

$$p\ V^{\gamma} = \text{constant.}$$

If V is changed to V/2, the pressure p is changed to $(2)^{\gamma}\ p$.

Thus, the final pressure in isothermal compression is $2\ p$, and in adiabatic compression is $(2)^{\gamma}\ p$. Since γ is greater than 1, we have

$$(2)^{\gamma}\ p > 2p$$

that is, the final pressure is greater in case of adiabatic compression.

The result will be otherwise i.e., the final pressure would be greater in case of isothermal expansion.

Example 7: A motor car tyre has a pressure of 2 atm at the room temperature of 27°C. If the tyre suddenly bursts, find the resulting temperature.

Solution: Given, $P_1 = 2$ atm

$$T_1 = 273 + 27 = 300\ K$$

$$P_2 = 1 \text{ atm.,} \quad T_2 =?, \quad \gamma = 1.4$$

$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma}} \quad \text{or,} \quad \left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$\left(\tfrac{1}{2}\right)^{0.4} = \left(\tfrac{T_2}{300}\right)^{1.4}$$

or, $2.304 \times 0.4 \log_{10}(0.5) = 1.4 [\log_{10} T_2 - \log_{10} 300] \times 2.304$

or $-0.1204 = 1.4 \log_{10} T_2 - 3.4608$

or $1.4 \log_{10} T_2 = 3.4680 - 0.1204 = 3.3476$

or $\log_{10} T_2 = \tfrac{3.3476}{1.4} = 2.3911$

∴ $T_2 = \text{Antilog} (2.3911) = 246.1K$

or $T_2 = -26.9°C$

Example 8: A certain quantity of air at 27°C and 1 atm pressure is suddenly compressed to half its original volume. Find the final (i) pressure and (ii) temperature of the air. (Given $\gamma = 1.4δ, 2^{1.4} = 2.64$)

Solution:

(i) $P_1 = 1$ atm; $P_2 = ?$, $\gamma = 1.4$

$V_1 = V$ $V_2 = \tfrac{V}{2}$

During sudden compression, the process is adiabatic.

∴ $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

or, $P_2 = P_1 \left[\tfrac{V_1}{V_2}\right]^{\gamma}$

$= 1 [2]^{1.4} = \text{Antilog} [1.4 \log 2] = \text{Antilog} [1.4 \times 0.30]$

∴ $P_2 = 2.636$ atm

(ii) $V_1 = V$, $V_2 = \tfrac{V}{2}$, $T_1 = 300K$; $T_2 = ?$, $\gamma = 1.4$

$T_1(V_1)^{\gamma - 1} = T_2 (V_2)^{\gamma - 1}$

$T_2 = T_1 [\, 2\,]^{1.4 - 1}$

$= 300 [\, 2\,]^{0.4}$

$$= 395.9 \; K$$

T = 395.9 K

2.7   INSUFFICIENCY AND LIMITATIONS OF THE FIRST LAW OF THERMODYNAMICS

Limitations of the first law of thermodynamics are discussed below:

1. No restriction on the direction of the flow of the heat: the first law establishes definite relationship between the heat absorbed and the work performed by a system. However, it does not indicate whether heat can flow from a cold end to a hot end or not. For example: we cannot extract heat from the ice by cooling it to a low temperature. Some external work need to be done.

2. Does not specify the feasibility of the reaction: first law does not specify that process is feasible or not. For example, when a rod is heated at one end then equilibrium has to be obtained which is possible only by some expenditure of energy.

3. Practically it is not possible to convert the entire heat energy into an equivalent amount of work.

    To overcome these limitations, another law is needed which is known as second law of thermodynamics.

The second law of thermodynamics helps us to predict whether the reaction is feasible or not and determines direction of the flow of heat. The second law also tells that certain amount of heat energy cannot be completely converted into equivalent amount of work.

2.8 SUMMARY

This unit introduces the first law of thermodynamics and some other important terms associated with it. These are summarized below -

- The first law of thermodynamics is a form of law of conservation of energy which relates change in internal energy, heat and work done as : $\Delta Q = \Delta U + \Delta W$

- The specific heat capacity of a substance is defined as the heat supplied per unit mass of the substance per unit rise in the temperature and is given by the relation

$$C = \frac{\Delta Q}{m\Delta T}$$

- The relation between specific heat at constant pressure(C_P) and specific heat at constant volume(C_V) is given by the Mayer's relation, $C_P - C_V = R$
- The modified form of the first law can be obtained for each of the known thermodynamic processes.
- The first law of thermodynamics neither puts any restrictions on the direction of flow of heat nor specifies the feasibility of the reaction, hence is insufficient.

2.9 GLOSSARY

1.   Conservation-the principal by which the total value of a physical quantity remains constant in a system
2.   Impose - force on someone
3.   Compressed - pressed into a smaller space
4.   Expansion - the action of becoming larger or more extensive
5.   Limitations - a restriction
6.   Surrounding - environment area around a thing or system
7.   Microscopic - as small as to visible only with a microscope
8.   Macroscopic - visible to naked eye or relating to large scale
9.   Undergo - suffer
10.   System - a set of things working together as part of a mechanism
11.   Equilibrium - the conditions of system in which all competing influences are balanced

2.10 REFERENCES

1.   Heat, thermodynamics and statistical physics, BrijLal and Subrahmanyam, S. Chand Pub., New Delhi
2.   Thermodynamic and statistical physics, Sharma and Sarkar, Himalaya Publishing House.
3.   Thermal Physics, B.*K*. Agarwal, Lokbharti Publications. Allahabad.
4.   Thermal Physics, Kumar, A. and Taneja, S.P., R. Chand & Co., New Delhi.

2.11 SUGGESTED READINGS

1. Fundamentals of thermodynamics, Richard S.
2. Heat and Thermodynamics – Zamansky & Dittman. 7th Ed., Mc Graw Hill.

2.12 TERMINAL QUESTIONS

2.12.1 SHORT ANSWER TYPE

1. Explain how the first law of thermodynamics leads to the concept of Internal energy.

2. What are the limitations of first law?

3. Give applications of first law to-   a) isobaric   b) isothermal process

4. Show that first law is a particular form of general law of conservation of energy.

2.12.2 LONG ANSWER TYPE

1. Distinguish between Isothermal and Adiabatic changes. Show that for an adiabatic change in a perfect gas PV^r = constant

2. Explain why the specific heat at constant pressure C_P is greater than that the specific heat at constant volume C_v. Prove $C_P - C_V = R$.

2.12.3 NUMERICAL ANSWER TYPE

1. The temperature of 5gm of air is raised from 10^0C to 12^0C at constant volume. Compute the increase in its internal energy. Specific heat of air at constant volume is 0.172 cal/gm °C and $J = 4.18$ joule / cal.

2. Calculate the change in internal energy when 5gm of air is heated from 0°C to 2°C, the specific heat of air at constant volume being 0.172 cal/gm $°C^{-1}$. ($J = 4.18 \times 10^7$ erg/cal.)

3. A system absorbs 250 cal. of heat and at the same time does 83.6 joule of external work. (i) Find the change in the internal energy of the system (ii) Find the change in the internal energy or the system when it absorbs 250 cal. of heat and at the same time 83.6 joule of work is done on it. (iii) What will be the change in the internal energy of the gas from which 40 calorie of heat is removed at constant volume?

2.12.4 OBJECTIVE ANSWER TYPE

1. Work done in a free expansion process is:

(a) + ve

(b) – ve

(c) Zero

(d) Maximum

(e) Minimum

2. Energy can neither be created nor destroyed but can be converted from

one form to other is inferred from

(a) Zeroth law of thermodynamics

(b) First law of thermodynamics

(c) Second law to thermodynamics

(d) Basic law of thermodynamics

(e) Claussius statement.

3. In an isothermal process, the internal energy

(a) Increases

(b) Decreases

(c) Remains constant

(d) First increases and then decreases

(e) First decreases and then increases

2.13 ANSWERS

2.13.1. SELF ASSESSMENT *Q*UESTIONS (SA*Q*S)

1.   When a condensed system like ice is put in contact with flame then heat from the flame will flow into the ice due to the temperature difference. But the temperature of ice does not rise, instead of it, the ice changes from condensed state to liquid state at constant temperature. Thus, the addition of heat without rise in temperature is possible.

2.   (i) No, heat will not be transferred to coffee which is thermally insulated.

(ii) Yes, by shaking, work has been done on coffee against the viscous forces in it.

(iii) From first law of thermodynamic

$$\Delta\ U = Q -\ W$$

Here $Q = 0$ and W is negative, so

$$\Delta U = 0 - (-W) = W$$

This mean that ΔU is positive. Hence the internal energy of coffee increases.

2.13.2. TERMINAL *Q*UESTIONS: NUMERICAL ANSWER TYPE

1. We know that

$$dU = dQ - dW$$

Since the air is heated at constant volume, therefore

$$dW = PdV = 0$$

and $dQ = mC_V dT$

$$= 5 \times 0.172 \times (12 - 10)$$

$$= 1.72 \text{ cal}$$

$\therefore$ $dU = dQ - 0$

$$= 1.72 \text{ cal.}$$

2. From first law of thermodynamics

$$dQ = dU + dW$$

Since air is heated at constant volume, hence no external work is done *i.e.,*

$$dW = 0$$

The heat supplied is

$$dQ = mC_V dT \text{ cal}$$

$$= mC_V dT \times J \text{ erg}$$

Therefore, $dU = dQ - dW$

$$= mC_V dT \times J - 0$$

$$= 5 \times 0.172 \times 2 \times 4.18 \times 10^7$$

$$= 7.19 \times 10^7 \text{ erg.}$$

3. We know that

$$dU = dQ - dW$$

(i) Here, dQ = 250 cal., dW = -83.6 joule.

∴ $dW = -\dfrac{83.6}{4.18}$ cal

$= -20$ cal.   [∵ J = 4.18 joule]

∴ $dU = 250 - (-20)$

$= 270$ cal.

(ii) Here dQ = 250 cal. dW = 83.6 joule = 20 cal.

∴ $dU = 250 - 20 = 230$ cal.

(iii) Since the volume of the gas is constant, so $dW = 0$

∴ $dU = dQ = -40$ cal.

Negatives sign shows that heat is extracted from the gas.

2.13.3. OBJECTIVE QUESTION ANSWERS

1. (c)   2. (b)   3. (c)

UNIT 3   SECOND LAW OF THERMODYNAMICS

CONTENTS

3.1 INTRODUCTION

The first law of thermodynamics is based on the law of conservation of energy. Though it helps us in determining the change in different entities such as heat, internal energy, work done etc., it however fails to give the practical feasibility of a reaction to proceed spontaneously. There are many examples of processes which are perfectly allowed by the first law but are not possible in practice. For example, water kept in bucket cannot freeze by itself. If we follow first law of thermodynamics it is possible as a part of water may absorb heat energy from the rest of water and evaporate. The rest of water will freeze due to loss of some heat energy. However, this is not possible practically. This leads us to the conclusion that some more rules are need to be laid to completely understand the spontaneity of the process. The second law of thermodynamics puts some restrictions to the efficiency of processes and thus helps us in determining the feasibility of the process. This law is very important while understanding the working of heat engines and refrigerators. After going through the present unit you will find that the second law of thermodynamics implies to the fact that the efficiency of heat engine cannot be unity and the coefficient of performance of a refrigerator cannot be infinite. The contribution of the French Engineer-Carnot in developing the theoretical reversible engine and his theorem forms the last part of this chapter.

3.2 OBJECTIVES

By the end of this unit, you will be able to -
- Explain work and heat as path function
- Differentiate between reversible and irreversible processes
- Write expression for work done for different types of processes
- Enunciate different statements of the second law of thermodynamics and their equivalence
- Explain heat engine and its various parts
- Learn about Carnot cycle and Carnot engine
- State and prove Carnot theorem
- Solve simple numerical problems based on these concepts

3.3 HEAT

Heat is a form of energy which is transferred from one part of the body to another or from one body to another by virtue of difference of temperature. This transfer of heat can only be by one or more of the three processes namely: conduction, convection and radiation, also the amount of heat (thermal energy) produced is always proportional to the amount of work done. Both are the transient phenomena and have same unit. The heat Q is taken as positive, when it is transferred from the surroundings to the system and Q is negative when heat is transferred from system to the surroundings.

3.3.1 HEAT - A PATH FUNCTION

Heat is a path function. This implies that when a system changes from state 1 to 2, the quantity of heat (Q) transferred will depend upon the intermediate stages through which the system passes i.e. its path.

Hence heat is an inexact differential and is written as δQ

On integrating, we get

$$\int_{1A}^{2A} \delta Q = Q_{1A}^{2A} \tag{3.1}$$

Here, Q_1^2 represents the heat transferred during the given process between the states 1 and 2 along a particular path A.

3.4   WORK

The work can be done by system or it can be done on the system. When the work is done by the system it is taken positive but if work is done on the system then it is taken negative.

3.4.1 WORK - A PATH FUNCTION

Suppose a system is taken from an initial equilibrium state 1 to a final equilibrium state 2 by two different paths A and B shown in Fig. (3.1). The processes are quasi-static.

The area under P-V plot gives the work done in that process. In the above plot we can see that the areas under these curves are different and hence the quantities of work done are also different.
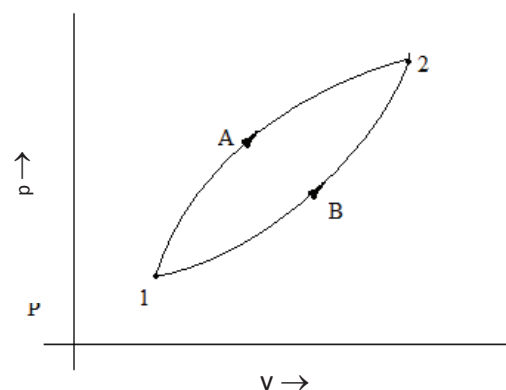
Fig. (3.1)

For path A

$$W_A = \int_{1A}^{2A} \delta W = \int_{1A}^{2A} P dV$$
$$\tag{3.2}$$

For path B

$$W_B = \int_{1B}^{2B} \delta Q = \int_{1B}^{2B} P dV$$
$$\tag{3.3}$$

The values of W_A and W_B are not equal. Therefore work cannot be expressed as a difference between the values of some property of the system in the two states. Therefore, it is not correct to represent

$$W = \int_{W1}^{W2} \delta W = W_2 - W_1$$
$$(3.4)$$

It may be pointed out that it is meaningless to say "Work in a system or work of a system". Work cannot be interpreted similar to temperature or pressure of a system.

It terms of calculus δW is an inexact differential. It means that W is not a property of the system and δW cannot be expressed as the difference between two quantities that depend entirely on the initial and the final states.

Hence, heat and work are path functions and they depend only on the process. They are not point functions such as pressure or temperature. Work done in taking the system from state 1 to state 2 will be different for different paths.

3.4.2 COMPARISON OF HEAT AND WORK

There are many similarities between heat and work. These are:

1. Heat and work are both transient phenomena. Systems do not possess heat or work. Unit of work is same as the unit of heat.
2. When a system undergoes a change, heat transfer or work done may occur.
3. Heat and work are boundary phenomena. They are observed at the boundary of the system.
4. Heat and work represent the energy crossing the boundary of the system.
5. Heat and work are path functions and hence they are inexact differentials. They are written as δQ and δW repsectively.
6. (a) Heat is defined as the form of energy that is transferred across a boundary, by virtue
       of difference of temperature or temperature gradient.
7. (b) Work is said to be done by a system if the sole effect on things external to the system
       could be the raising of a weight.
8. From thermodynamic sign convention heat transferred to a system is positive and heat transferred from a system is negative, while work transferred to a system is negative and work transferred out of a system is positive with respect to that system.

3.5 QUASISTATIC PROCESS

A quasistatic process is defined as the process in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through
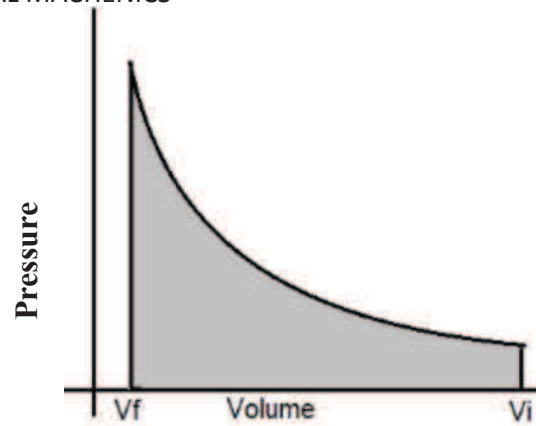
Fig (3.2)

which the system passes during the process can be considered as equilibrium states. The given diagram(Fig. 3.2)shows the P-V plot when pressure is not constant and changes in infinite steps (quasistatic conditions) duringcompression from initial volume, V_i to final volume, V_f. Work done on the gas **is** represented by the shaded area. In actual practice, many processes closely approach to a quasistatic process and may be treated as such with no significant error.

Consider the expansion of a gas in a closed cylinder fitted with a frictionless piston. Initially weights are on the piston and the pressure of the gas inside the cylinder is higher than the atmospheric pressure. If the weights are small and are taken off slowly one by one, the gas inside the cylinder will very slowly expand and the process can be considered quasistatic. If, however, all the weights are removed at once, expansion takes place suddenly and it will be a non- equilibrium process. The system will not be in equilibrium at any time during this process.

A quasistatic process is an ideal concept that is applicable to all thermodynamic systems including electric and magnetic systems. It should be noted that conditions for such a process require extremely slow rate and can never be satisfied rigorously in practice.

3.6 INDICATOR DIAGRAMS

The work done in a quasi-static thermodynamic process (e.g., a slow change in volume of a gaseous system) can be easily obtained with the help of pressure P and volume V graph. Such plots are called Indicator diagrams. These diagrams can be drawn with the help of a device called the indicator which directly records the changes in the volume and pressure.

3.6.1 THERMODYNAMIC PROCESSES

A change in the thermodynamic coordinates (pressure, volume, temperature etc.) of a thermodynamic system brings about a change in the state of the system and is called a thermodynamic process or simply a process.

3.6.2 WORK DONE DURING AN ISOTHERMAL PROCESS

If the change in pressure and volume of a gas (system) takes place in such a manner that its temperature remains the same throughout, it is called an isothermal process.

Let a gas be filled in a cylinder with a piston at room temperature under atmospheric pressure. If the piston be pushed down a little to compress the gas (i.e., the work is done on the gas) its internal energy will increase and its temperature will rise a little. If the temperature is to be maintained constant, the extra heat must at once be conducted to the surroundings. Similarly, if the gas is allowed to expand (push the piston up a little) i.e., work is done by the gas, its internal energy decreases and its temperature falls a little. Again to maintain its temperature constant, heat must at once be conducted to it from the surroundings.
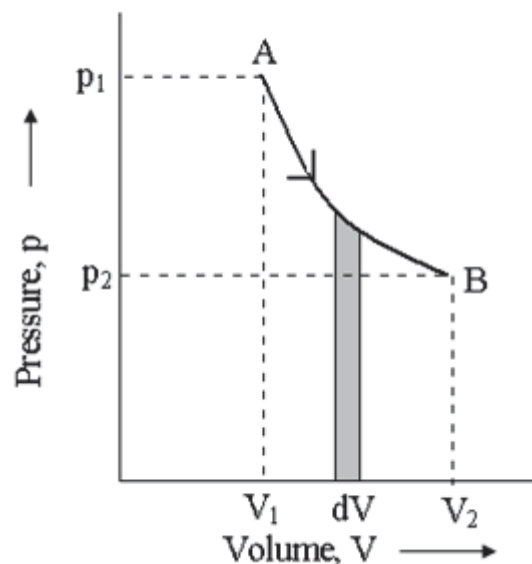
Fig (3.3)

Let 1 gm mole of a perfect gas is allowed to expand under isothermal conditions. Let its initial volume V_1 and pressure P_1 be represented by point A and its final volume V_2 and pressure P_2 by the point B on P-V indicator diagram (Fig. 3.3) keeping its temperature constant.

Let us consider a small increase dV in the volume of the gas at pressure P. Then, the work done by the gas,

dW= p dV   (shaded strip in the figure)   (3.4)

Therefore, the total work done by the gas during the whole expansion from volume V_1 at A to volume V_2 at *B* will be

$$W = \sum dW = \int_{V1}^{V2} pdV = \text{Area under the curve AB}$$ (3.5)

Since, for a perfect gas $pV = RT$, where R is the gas constant for 1gm mole of the gas, then
$$p = R\frac{T}{V}$$ (3.6)

Putting the value of P in equation (3.5), we get
$$W = RT \int_{V1}^{V2} \frac{dV}{V} = RT \log_e \{\frac{V2}{V1}\}$$ (3.7)
$$W = 2.3026 \, RT \log_{10} \{\frac{V2}{V1}\}$$ (3.8)

Since, the temperature remains constant and Boyle's law is obeyed, therefore

$P_1V_1 = P_2V_2$ or $\frac{V_2}{V_1} = \frac{P_1}{P_2}$ (3.9)

Hence, equation (3.8) become

$W = 2.3026 \, RT \log_{10} \frac{P1}{P2}$ (3.10)

If we take 1 gm of the gas in place of 1 gm mole then the gas constant will be r and equation (3.8) and (3.10) then become,

$W = 2.306 rT \log_{10}(V_2/V_1)$ and (3.11)

$W = 2.306 rT \log_{10}(p_1/p_2)$ (3.12)

3.6.3 WORK DONE DURING AN ADIABATIC PROCESS

Adiabatic means heat does not go out or come in the system. So adiabatic process implies a process in which heat is neither allowed to enter nor leave the system. Thus, it is a process which takes place in complete thermal isolation from the surroundings.

Let, a gas be filled in a cylinder with a piston at the room temperature and atmospheric pressure. Also the cylinder and piston are perfectly insulated. If the piston be pushed a little to compress the gas i.e., the work is done on the gas, its internal energy will increase and its temperature will rise a little as the heat developed cannot possibly escape out to the surroundings. Similarly, if the gas be allowed to expand i.e., work is done by the gas, its internal energy decreases and its temperature falls a little. Again no heat can possibly enter the cylinder from outside.
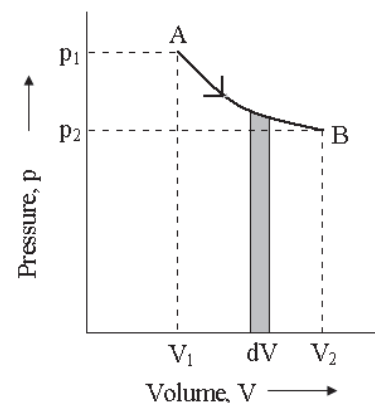
Fig (3.4)

Let 1 gm mole of a perfect gas be allowed to expand adiabatically from an initial volume V_1 to a final volume V_2, the pressure changing from P_1 to P_2 (P-V diagram shown in Fig. 3.4). Then, work done by the gas,

$W = \int_{V1}^{V2} p\,dV$ (3.13)

Since, for a perfect gas, in an adiabatic process,

$pv^{\gamma} = K$ (constant)   or (3.14)

$p = \frac{K}{V^{\gamma}}$ (3.15)

Putting the value of p in equation (3.13), we get

$W = \int_{V_1}^{V_2} \frac{K}{V^{\gamma}} dV$ (3.16)

$$= K \int_{V_1}^{V_2} \frac{dV}{V^\gamma}$$

$$= \left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V1}^{V2}$$

$$= \frac{K}{1-r} \left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$$

$$W = \frac{K}{\gamma-1} \left[\frac{K}{V_1^{1-\gamma}} - \frac{K}{V_2^{1-\gamma}}\right] \tag{3.17}$$

Also in adiabatic expansion, we have
$$P_1 V_1^\gamma = K = P_2 V_2^\gamma$$

Putting the value of K in equation (3.17), we have

$$W = \frac{1}{(\gamma-1)} \left[\frac{P_1 V_1^\gamma}{V_1^{1-\gamma}} - \frac{P_2 V_2^\gamma}{V_2^{1-\gamma}}\right]$$

or, $$W = \frac{1}{(\gamma-1)} \left[p_1 V_1 - p_2 V_2\right] \tag{3.18}$$

It can be shown that the work done by the gas during adiabatic expansion from volume V_1 at pressure p_1 to volume V_2 at pressure p_2 given by the area under the p-V curve for the gas i.e.,

$$W = \int_{V1}^{V2} pdV = \frac{1}{(\gamma-1)} (p_1 V_1 - p_2 V_2)$$

$$= \text{area under the curve AB}$$

Again, we have
$$p_1 V_1^\gamma = p_2 V_2^\gamma = K, \text{ so,}$$
$$V_1 = (K/p_1)^{1/\gamma} \text{ and } V_2 = (K/p_2)^{1/\gamma} \tag{3.19}$$

Thus,

$$W = \frac{1}{(\gamma-1)} \left[p_1 \left(\frac{K}{p_1}\right)^{1/\gamma} - p_2 \left(\frac{K}{p_2}\right)^{1/\gamma}\right]$$

or $$W = \frac{(K)^{1/\gamma}}{(\gamma-1)} \left[(p_1)^{\gamma-1/\gamma} - (p_2)^{\gamma-1/\gamma}\right] \tag{3.20}$$

As the temperature of the gas changes from T_1 to T_2 and also we have $p_1 V_1 = RT_1$ and $p_2 V_2 = RT_2$ (where R is gas constant for 1 gm mole gas), substitution of these values in equation (3.18) results

$$W = \frac{R}{(\gamma-1)}(T_1 - T_2) \tag{3.21}$$

If we take 1gm of the gas in place of 1 gm mole then the gas constant will be r and eq.(3.21) becomes,

$$W = \frac{r}{(r-1)}(T_1 - T_2) \tag{3.22}$$

Since, in an adiabatic process, heat is not allowed to enter or leave the system, the external work W is done by the gas at the expense of its own internal energy and the work done becomes equal to decrease in internal energy of the gas.

Self Assessment Question (SAQ) 1

What is an indicator diagram? What information does it give? Draw p-V diagram for an isothermal and an adiabatic process.

Example 1: Calculate the work done when one gram molecule of a gas expands isothermally at 27°C to double its original volume. (Given that, R =8.3 joule/°C mol).

Solution: The work done during an isothermal process,

$W = R\,T\,\log_e \frac{V2}{V1} = 2.3026\ R\ T\ \log_{10} \frac{V2}{V1}$

Here, T=27 °C =273+27=300K

V_1=V, V_2=2V and R=8.3 J/°C mole.

Putting the values, we have

$W = 2.3026 \times 8.3 \times 300 \log_{10} \frac{2V}{V}$

$= 2.3026 \times 8.3 \times 300 \log_{10} 2$

$= 5733.47 \times 0.3010 = 1725$ joule

Example 2: Air is compressed adiabatically to half its volume. Calculate the change in its temperature.

Solution: Since process is adiabatic, so

$T_1 V_1{}^{\gamma-1} = T_2 V_2{}^{\gamma-1}$ or $\left(\frac{V1}{V2}\right)^{\gamma-1} = \left(\frac{T2}{T1}\right)$

Here, V_1 = V and V_2 = V/2   and for air γ = 1.4

$\left(\frac{V}{V/2}\right)^{1.4\text{-}1} = \left(\frac{T2}{T1}\right)$

or $T_2 = T_1(2)^{0.4}$

$= 1.319 T_1$

Change in temperature, $T_2 - T_1 = 1.319 T_1 - T_1 = 0.319\ T_1 K$

Example 3: 1 gram of molecule of a monoatomic perfect gas at 27 ^{0}C is adiabatically compressed in a reversible process from an initial pressure of 1 atmospheric unit (atm) to a final pressure of 50 atm. Calculate the change in temperature.

Solution: For an adiabatic process,

$$(P_1 / P_2)^{\gamma-1} = (T_1 / T_2)^{\gamma}$$

Here, $p_1 = 1$ atm, $p_2 = 50$ atm

$T_1 = 27°C = 300\ K$ and for monoatomic gas $\gamma = 5/3$

Putting the values, we get

$$(\frac{1}{50})^{5/3-1} = (\frac{300}{T2})^{5/3}$$

or $(50)^{2/3} = (\frac{T2}{300})^{5/3}$

or $(2/3) \log 50 = (5/3) \log T_2 - \log 300] = (5/3)[\log T_2 - 2.4771]$

or $(2/3)\ 1.6990 = (5/3) \log T_2 - (5/3)\ 2.4771$

$(2/3) \log T_2 = 1.1327 + 4.1285$

$\log T_2 = 3.1567$

$T_2 = 1434K$

or $T_2 - T_1 = 1434 - 300 = 1134°C$

3.7 REVERSIBLE PROCESS

A reversible process is one which can be reversed in such a way that all changes taking place in the direct process are exactly repeated in the inverse order and opposite sense, and no changes are left in any of the bodies taking part in the process or in the surroundings. For example, if an amount of heat is supplied to a system and an amount of work is obtained from it in the direct process; the same amount of heat should be obtainable by doing the same amount of work on the system in the reverse process.

Conditions of Reversibility

 A process can be reversible only when it satisfies two conditions:

(i)   Dissipative forces such as friction, viscosity, inelasticity, electrical resistance, magnetic hysteresis etc. must be completely absent. Suppose a gas is contained in a cylinder fitted with a piston and placed in contact with a constant-temperature source. The piston is loaded so that the pressure exerted by the piston on the gas exactly balances the pressure of the gas on the piston. If the load on the piston is now decreased, the gas will expand, doing external work in pushing up the piston and also in overcoming the friction between the piston and the walls of the cylinder. The heat necessary for this work is taken from the source. If now the load on the piston is increased, the gas will be compressed. The work used in pushing up the piston during

the expansion is now recovered. On the contrary, more work has to be done against the friction. The expansion is therefore irreversible. Similarly, other dissipative effects like inelasticity, electrical resistance, etc. make the process irreversible.

(ii)   The process must be quasi-static. When the gas expands, an amount of work is done by the gas to give kinetic energy to the piston. This work cannot be recovered during the reverse process, but on the contrary, more work is to be done to give kinetic energy to the piston. Hence in order to make the expansion of the gas reversible, the pressure of the gas on the piston should be only infinitesimally different from the pressure exerted by the piston on the gas. Under the condition the expansion or compression will take place infinitely slowly so that no kinetic energy will be produced. These conditions are never realized in practice. Hence a reversible process is only an ideal conception.

3.8 IRREVERSIBLE PROCESSES

Any process which is not exactly reversible is an irreversible process. All practical processes such as free expansion, Joule-Thomson expansion, electrical heating of a wire, diffusion of liquids and gases etc., are irreversible processes. All natural processes such as conduction, radiation, radioactive decay etc., are also examples of irreversible process.

Self Assessment Question (SAQ) 2

Classify the reversible and irreversible processes from the following and give reasons:
(i)   Isothermal expansion of a gas
(ii)   Adiabatic compression of a gas
(iii)   Diffusion of gases
(iv)   Transfer of heat from a hot body to a cold body
(v)   Joule expansion of a perfect gas
(vi)   Joule-Thomson effect
(vii)   Transfer of heat by radiation
(viii)   Electrical heating of a wire
(ix)   A very slow extension or contraction of a spring
(x)   Production of heat by friction

Self Assessment Question (SAQ) 3

Can a given amount of mechanical energy (work) be converted into heat completely? If so, give an example. Is the reverse possible?

3.9 HEAT ENGINE

Any cyclic device that continuously converts into mechanical work is called a heat engine. There are three main parts in a heat engine: a hot body called hot reservoir or source, working substance, and a cold reservoir or 'sink'. The working substance takes certain amount of heat from the source, converts a part of it into useful work and gives out the rest to the sink. This series of processes is called a 'cycle' because the working substance returns to its original state. This is shown schematically in Fig.3.5. By repeating the same cycle over and over again, work can be continuously obtained at the expense of heat energy.
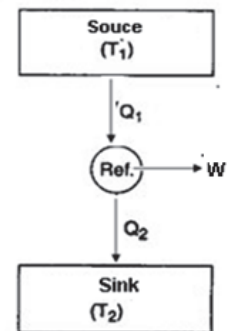
Suppose the working substance takes in an amount of heat Q_1 from the source and gives out an amount Q_2 to the sink. Suppose W is the amount of work obtained. The net amount of heat absorbed by the substance is $Q1-Q_2$, which has been actually converted into work because there is no change in its internal energy as the system returns back to its original state. Applying the first law of thermodynamics to one complete cycle we get,

$$Q_1 - Q_2 = W \qquad\qquad (3.23)$$

Thermal Efficiency: The 'thermal efficiency η of an engine is defined as the ratio of the work obtained to the heat taken from the source, that is

$$\eta = \frac{W}{Q1} = \frac{Q1-Q2}{Q1} \quad \text{or}$$
$$(3.24)$$

$$\eta = 1 - \frac{Q2}{Q1}$$

Often the efficiency is expressed in percentage and then

$$\eta_{\%} = \left[1 - \frac{Q_2}{Q_1}\right] \times 100 \qquad\qquad (3.25)$$

This equation indicates that the efficiency of the heat engine will be unity when $Q_2 = 0$ (no heat is given out to the sink). This is however not possible in practice. This means that the engine cannot convert all the heat taken in from the source into work.

We cannot define the efficiency as W/Q_2, because in that case we shall have

$$\eta = \frac{W}{Q2} = \frac{Q1-Q2}{Q2} = \frac{Q1}{Q2} - 1 \qquad\qquad (3.26)$$

so that the condition for the ideal value of efficiency (i.e., η =1) would be $Q_1=2Q_2$ which is absurd.

3.9.1   *REVERSIBLE ENGINE*

In an engine the working substance undergoes a cyclic process. It takes in heat from a hot body, converts a part of it into work and gives out the rest to a cold body, returning to its initial state. During this cycle the conditions of the hot and cold bodies and of the surrounding change. If this cycle can be traversed in the reverse order such that all the parts of the engine completely recover their original conditions and no changes left in the surroundings, the cycle is a 'reversible cycle', and the engine is a 'reversible engine'. Such an engine can be realized (i) the working parts of the engine are free from friction, (ii) the pressure and temperature of the working substance never differ appreciably from its surroundings at any stage of the cycle, so that all the processes involved in the cycle are quasi-static.

These conditions can never be realized in practice. Hence a reversible engine is an ideal conception (Carnot had presented an imaginary picture of such an engine).

Self Assessment Question (SAQ) 4

What do you understand by a heat engine and its efficiency? What is meant by a reversible engine?

3.10 SECOND LAW OF THERMODYNAMICS

The first law of thermodynamics states the equivalence of mechanical work and heat, when one is completely converted into other (W=Q). Thus, it is the principle of conservation of energy applied to a thermodynamic system.

If, however, we propose to extract a certain quantity of heat from a body and convert it completely into work, the first law would not be violated. But, in actual practice this is found to be impossible. If this were possible, we could drive ships across an ocean by extracting heat from the water of the ocean. Thus the first law simply tells that if a process takes place, energy will remain conserved. It does not tell us whether the process is possible or not. Similarly, of a hot body and a cold body are brought in contact, the first law is not violated whether the heat flows from the hot to the cold body or vice-versa. By experience we know that heat never flows from cold to hot body. The purpose of the second law is to incorporate such experimental facts into thermodynamics.

There are statements of the second law of thermodynamics proposed by different scientists-

(i)   Kelvin-Planck statement

(ii)   Claussius statement

3.10.1 KELVIN-PLANCK'S STATEMENT

In a heat engine, a working substance takes in heat from a hot body, converts a part of it into mechanical work, and gives out the rest to a cold body, No engine has ever been designed

which can operate in a cycle by taking heat from a body and converting all of it into work; some heat must always be given to a colder body. This experience led Kelvin and Planck to state the following:

It is impossible to construct a device which operating in a cycle, will take heat from a body and convert it completely into work, without leaving any change anywhere:

3.10.2 CLAUSSIUS STATEMENT

In a refrigerator, a working substance takes in heat from a cold body, has a net amount of work done on it by an external agent (electric supply), and gives out a larger amount of heat to a hot body. It thus transfers heat from a cold body to a hot body with the aid of external work or energy. No refrigerator has ever been designed which can run without supply of external energy. This experience led Clausius to state that:

"It is impossible to construct a device which operating in a cycle, will take heat from a cold body and reject it to a hot body without expenditure of work by an external energy source". In other words-heat cannot flow spontaneously from a colder body to a hotter body.

3.10.3 EQUIVALENCE OF KELVIN-PLANCK AND CLAUSSIUS STATEMENTS

We can show that these two statements of the second law are equivalent

Let us suppose that there is a refrigerator R (Fig.3.6) which transfers an amount of heat Q_2 from a cold body to a hot body without having any supply of external energy. It is thus against the Clausius statement. Now, suppose an

Fig (3.6)

engine E working between the same hot and cold bodies takes in heat Q_1 from the hot body, converts a part $(W = Q_1 - Q_2)$ into work, and gives up the remaining heat Q_2 to the cold body. The engine E alone does not violate the law. But if the refrigerator R and the engine E are combined together, they form a device that takes in heat $Q_1 - Q_2$ from the hot body and converts all into work without giving up any amount to the cold body. This is clearly against the Kelvin-Planck statement.

Similarly, let us suppose that there is an engine E (Fig.3.7) which takes in an amount of heat Q_1 from a hot body and converts it completely into work $W(=Q_1)$, without giving any
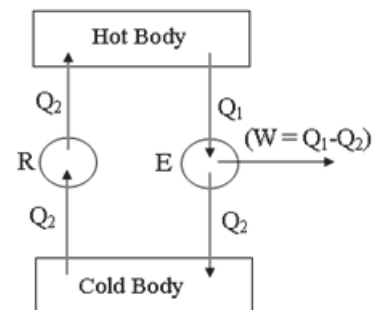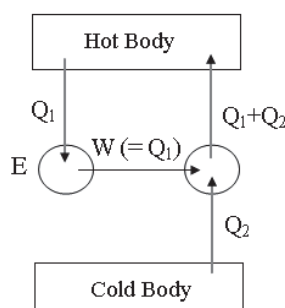
Fig:3.7

heat to the cold body. It is against the Kelvin-Planck statement. Now, suppose a refrigerator R working between the same hot and cold bodies takes in heat Q_2 from the cold body, has work $W(=Q_1)$ done upon it by an external agent, and gives out heat Q_1+Q_2 to the hot body. The refrigerator R alone does not violate the law. But both E and R together form a device which transfers an amount of heat Q_2 from a cold body to a hot body with no external energy source. This is clearly against the Clausius statement.

The second law of thermodynamics supplements the first law. The first law simply tells us that any device cannot deliver more energy than it receives. It does not speak regarding any limitation, or any condition necessary for the delivery of energy. The second law, however, does it. For example, heat taken in by a substance cannot be all delivered as work, or heat cannot flow spontaneously from a colder to a hotter body. These phenomena are not disallowed by the first law, but they are disallowed by the second law.

3.11 CARNOT CYCLE AND CARNOT ENGINE

Sadi Carnot, a French engineer, developed a theoretical reversible engine such that it operates between two reservoirs and operates with maximum possible efficiency . The cycle of processes adopted by this engine is called Carnot cycle. The Carnot cycle is a reversible cycle, this means that all the processes involved in it are reversible.

The Carnot cycle consists of two isothermal processes and two adiabatic processes. Fig.3.8
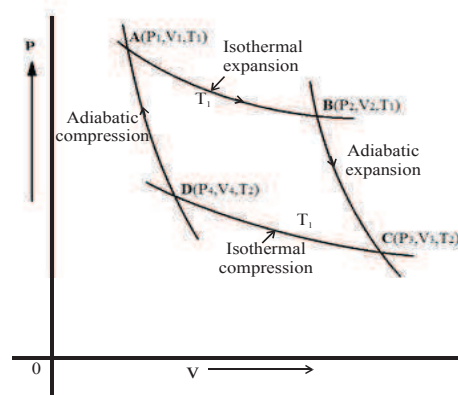
Figure 3.8

shows the Carnot cycle for a heat engine with ideal gas as its working substance.

The Carnot cycle has the following sequence of operations:

- Step 1→2 : Reversible isothermal expansion of gas $(P_1,V_1,T_1→P_2,V_2,T_1)$
  In this step, the gas absorbs heat (Q_1) from the reservoir at temperature T_1. Since the process is isothermal, there is no change in internal energy and so the temperature of the system.
  From the first law of thermodynamics,
  $\delta Q = \delta U + \delta W$
  Putting $\delta U = 0$, we get,
  $\delta Q = \delta W + 0$ or
  $\delta W = \delta Q$
  $W_{1→2} = Q_1 = \mu RT_1 \ln\left(\frac{V_2}{V_1}\right)$ (3.27)

- Step 2→3 : Reversible adiabatic expansion of gas $(P_2,V_2,T_1→P_3,V_3,T_2)$
  In this step, the work is done by the gas adiabatically at the expense of internal energy which causes drop in temperature of system. From the first law of thermodynamics,
  $\delta Q = \delta U + \delta W$
  Putting $\delta Q = 0$, we get,
  $\delta U + \delta W = 0$ or
  $\delta W = -\delta U$
  $W_{2→3} = \frac{\mu R(T_1-T_2)}{\gamma-1}$ (3.28)

- Step 3→4 : Reversible isothermal compression of gas $(P_3,V_3,T_2→P_4,V_4,T_2)$
  In this step, the gas releases heat (Q_2) to the reservoir at temperature T_2. There is no change in internal energy and temperature of system as the process is isothermal. From the first law of thermodynamics.
  $\delta Q = \delta U + \delta W$
  Putting $\delta U = 0$, we get,
  $\delta Q = \delta W + 0$ or
  $\delta W = \delta Q$
  $W_{3→4} = Q_2 = \mu RT_2 \ln\left(\frac{V_4}{V_3}\right)$
  $= -\mu RT_2 \ln\left(\frac{V_3}{v_4}\right)$ (3.29)

- Step 4→1 : Reversible adiabatic compression of gas $(P_4,V_4,T_2→P_1,V_1,T_1)$
  In this step, the work is done on the gas adiabatically. This leads to increase in internal energy of the system causing increase in temperature of system. From the first law of thermodynamics,
  $\delta Q = \delta U + \delta W$
  Putting $\delta Q = 0$, we get,
  $\delta U + \delta W = 0$ or

$$\delta W = -\delta U$$

$$W_{4 \to 1} = \mu R \left(\frac{T_1 - T_2}{\gamma - 1}\right) \tag{3.30}$$

3.11.1 EFFICIENCY OF CARNOT ENGINE

The efficiency of heat engine is defined as ratio of net work done to the heat absorbed in one complete cycle. If the heat engine receives heat Q_1 and rejects heat Q_2 then efficiency is given by-

$$\eta = \frac{Wnet}{Q1} = \frac{Q1 - Q2}{Q1} = 1 - \frac{Q2}{Q1} \tag{3.31}$$

Now, the total work done

W $= W_{1 \to 2} + W_{2 \to 3} - W_{3 \to 4} - W_{4 \to 1}$

   $= W_{1 \to 2} + W_{3 \to 4}$ ($\because$ $W_{2 \to 3}$ and $W_{4 \to 1}$ are equal and opposite and hence they cancel each other).

$$= \mu RT_1 \ln \left(\frac{V_2}{V_1}\right) - \mu RT_2 \ln \left(\frac{V_3}{V_4}\right) \tag{3.32}$$

Therefore,

$$\eta = 1 - \left(\frac{T_2}{T_1}\right) \frac{\ln\left(\frac{V_3}{V_4}\right)}{\ln\left(\frac{V_2}{V_1}\right)} \tag{3.33}$$

Now Since 2→3 is an adiabatic process,

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \tag{3.34}$$

i.e., $$\frac{V_2}{V_3} = \left[\frac{T_2}{T_1}\right]^{1/(\gamma-1)} \tag{3.35}$$

Similarly, since step 4→ 1 is an adiabatic process

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

i.e., $$\frac{V_1}{V_4} = \left[\frac{T_2}{T_1}\right]^{1/(\gamma-1)} \tag{3.36}$$

From eqs. (3.35) and (3.36)

$$\frac{V_3}{V_4} = \frac{V_2}{V_1} \tag{3.37}$$

Using Eq. (3.33) in Eq. (3.37), we get

$$\eta = 1 - \frac{T_2}{T_1} \qquad\qquad (3.38)$$

From relations (3.31) and (3.38), we have

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

i.e. in a Carnot cycle, the ratio of the amount of heat rejected to the sink to the heat received from the source is equal to the ratio of their respective temperatures.

In other words the efficiency of Carnot engine depends only upon the temperature of the source and te sink and is independent of the nature of the working substance.

Graphically the efficiency of a Carnot engine is measured by the area covered by the Carnot cycle in the indicator diagram ($p - V$ diagram).

3.11.2 CARNOT THEOREM

The second law of thermodynamics gives two important conclusions which can be taken together in the form of a theorem called Carnot's theorem. According to this theorem "The efficiency of a Carnot reversible engine is maximum and is independent of the nature of the working substance".

or

"The efficiency of all reversible heat engines operating between the same two temperatures is the same and no irreversible heat engine working between the same two temperatures can have greater efficiency than Carnot's reversible heat engine".

To prove it, let us consider two heat engines E_A and E_R operating between a source at temperature T_1 and sink at temperature T_2 (Fig. 3.9). Let E_A be any heat engine and E_R be a reversible heat engine. Let us assume efficiency η_A of E_A is greater than efficiency η_R of E_R. In order to prove the Carnot theorem we have to contradict our assumption.

Fig. (3.9)

Let the rates of working of the engine E_A be Q_{1A} and that of E_R be Q_{1R} such that-

$Q_{1A} = Q_{1R} = Q_1$

As assumed, $\eta_A > \eta_R$
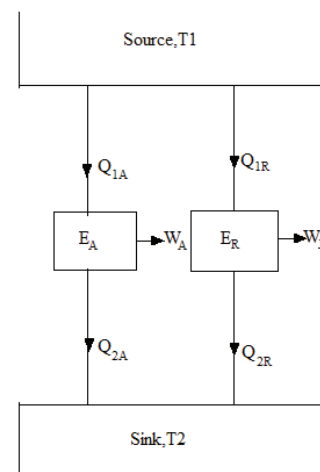
As we know that, $\eta = \frac{Wnet}{Q1}$

So we can write, $\frac{W_A}{Q_{1A}} > \frac{W_R}{Q_{1R}}$

Therefore, $W_A > W_R$ ($\because QA = Q_R$)A

Let us reverse E_R. Since E_R is a reversible heat engine, therefore, the magnitude of heat transferred and work done will remain the same but their directions will reverse (Fig. 3.10).

Since $W_A > W_R$ some part of W_A which is equal to W_R in magnitude can be fed to drive the reversed heat engine E_R. Since, $Q_{1A}=Q_{1R}=Q_1$, the heat discharged by E_R may be supplied to E_A thus the source may be eliminated. The net result is that E_A and E_R together constitute a heat engine which operating in a cycle produces a net work done W_A-W_R (Fig. 3.11) while exchanging heat with a single reservoir at temperature T_2, thus violating the Kelvin-Planck statement. Hence our assumption is wrong.
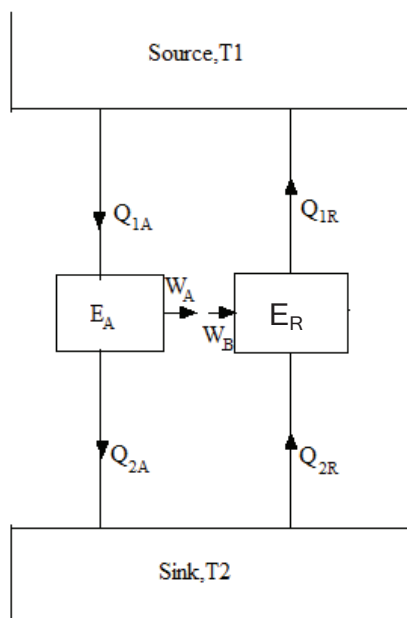
Fig. (3.10)
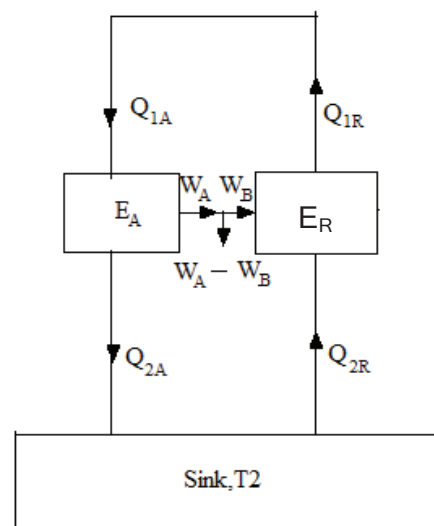
Fig. (3.11)

Therefore, $\eta_A < \eta_R$ and this proves the Carnot theorem.

3.11.3 CARNOT ENGINE AS A REFRIGERATOR

When a Carnot engine works in the reverse direction i.e., when it absorbs Q_2 amount of heat from the sink and work W is done on the working substance and finally Q_1 amount of heat is rejected to the source at higher temperature, the arrangement acts like a refrigerator.

The efficiency of a refrigerator is measured in terms of coefficient of performance.

The coefficient of performance k is defined as the ratio of the heat absorbed from the sink to the work done on the working substance by the external agent. i.e.,

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

Hence, the value of k may be greater than unity.

Self Assessment Question (SAQ) 5

(i) Can the efficiency of any heat engine be unity?

(ii) Do all reversible heat engines have the same efficiency?

3.12 SUMMARY

In this unit, you have studied about the concept of heat and work. The unit also explains the insufficiency of the first law of thermodynamics and hence the necessity of the formulation of second law of thermodynamics. The unit also explains other important aspects which are summarized below:

- Work and heat are path functions as they depend on the type of process and not just on initial and final states.
- If heat is added to the system, $Q > 0$
  If heat is removed from the system, $Q < 0$
  If work is done by the system, $W > 0$
  If work is done on the system, $W < 0$
- A quasistatic process is the process in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through which the system passes during the process can be considered as equilibrium states. Practically, quasistatic process cannot be realized but an extremely slow process can be considered as close to quasistatic process.
- Indicator diagrams are the p-V plots of various processes. They indicate the change in pressure with volume at any stage of the process. The area under these diagrams gives the work done during the process.
- Work done is given by-
    for adiabatic process, $W = \frac{R}{(\gamma - 1)}(T_1 - T_2)$

    for isothermal process, $W = 2.3026 \, RT \log_{10} \frac{P_1}{P_2}$

- A reversible process is one which can be reversed in such a way that all changes taking place in the direct process are exactly repeated in an inverse order and opposite sense, and no changes are left in any of the bodies taking part in the process or in the surroundings.
- Any process other than reversible process is called irreversible process.
- Any cyclic device by which heat is converted into mechanical work is called a heat engine. It has parts: source, working substance and sink.

- A reversible engine is one which the parts of engine namely working substance, source and sink acquire their original state completely if the cycle is traversed in reverse order. The reversible engine is an ideal engine and cannot be realized in practice.
- The second law of thermodynamics disallows some processes consistent with the first law of thermodynamics. It states
    - Kelvin-Planck statement: No process is possible whose sole result is the absorption of heat from a reservoir and its complete conversion into work.
    - Claussius statement: No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.
    - Putting simple, the Second law implies that no heat engine can have efficiency η equal to 1 or no refrigerator can have co-efficient of performance k equal to infinity.

- The Carnot cycle consists of following processes-reversible isothermal expansion, reversible adiabatic expansion, reversible isothermal compression and reversible adiabatic compression of working substance. The heat engine that operates on Carnot cycle is called Carnot Engine.
- The efficiency of Carnot Engine is given by $\eta = 1 - \dfrac{T_2}{T_1}$, where T_2 is temperature of sink and T_1 is the temperature of source.
- The Carnot Theorem states - "All heat engines operating between a given constant temperature source and a given constant temperature sink, none has a higher efficiency than a reversible engine."

3.13 GLOSSARY

1. Conservation- the principle by which the total value of a physical quantity remains constant in a system
2. Impose - force on someone
3. Compressed - pressed into a smaller space
4. Transient – lasting for a short period of time
5. Expansion - the action of becoming larger or more extensive
6. Surrounding - environment area around a thing or system or person.
7. Undergo - suffer
8. System - a set of things working together as part of a mechanism
9. Equilibrium - the conditions of system in which all competing influences are balanced

3.14 REFERENCES

1. Heat, Thermodynamics and Statistical Physics, Brij Lal and Subrahmanyam, S.Chand Pub., New Delhi.
2. Thermodynamic and statistical physics, Sharma and Sarkar, Himalaya Publishing House.

3   Basic and applied thermodynamics, Nagg PK, Tata McGraw-Hill, N.Delhi

3.15   SUGGESTED READINGS

- Fundamentals of thermodynamics, Richard Sonntag Clans Borgnakke.
- Thermodynamic Kinetic theory and statistical thermodynamics, F.W.Sears and G.L.Salinger.
- Heat and Thermodynamics, Zemansky and Dittnon.

3.16 TERMINAL QUESTIONS

3.16.1 SHORT ANSWER TYPE

1.   (a) The temperature of the surface of the sun is approximately 6000 K. If we take a big lens and focus the sun-rays, can we produce a temperature of 8000 K?

(b) Ocean contains enormous amount of heat energy. Can we drive a ship across the ocean by utilizing this energy?

(c) Show that the heat transfer through a finite temperature difference is irreversible.

2.   An ideal gas expands to double its volume isobarically, isothermally or adiabatically. For   which expansion are -

(i) largest and smallest changes in temperature

(ii) largest and smallest amount of work done

(iii) largest and smallest heat absorption by the gas

3.   A gas is filled in a box whose opposite walls are maintained at different temperatures. Explain heat conduction through the gas.

4.   If the door of a refrigerator remains open, then why a room cannot be cooled? Explain your answer.

5.   Explain why the islands and coastal areas of continents have a moderate temperature variation.

3.16.2 LONG ANSWER TYPE

1.   Give Kelvin-Planck and Clausius statements of the second law and show their equivalence.

2.   What do you understand by a heat engine and its efficiency?

3.   What is the purpose of the second law of thermodynamics?

3.17 ANSWERS

3.17.1 SELF ASSESSMENT QUESTIONS (SAQS)

2.

a)   Isothermal expansion of a gas: Let us imagine a gas contained in a cylinder having perfectly insulating walls but a perfectly conducting base, and fitted with a frictionless piston. The cylinder is placed on a heat-reservoir maintained at a constant temperature, which is the same as the temperature of the gas. The piston is loaded, so that the pressure exerted by the piston on the gas exactly balances the pressure of the gas on the piston. Suppose the load on the piston is decreased by an infinitesimally small amount. The gas will expand, doing external work in pushing up the piston and its temperature will tend to fall. It will thus very slightly deviate from equilibrium, but an amount of heat equivalent to the work done will immediately flow from the heat-reservoir to the gas which will again be at the temperature of the reservoir and attain equilibrium. Thus the infinitely slow isothermal expansion of a gas in the absence of any friction is an example of a reversible process. The conditions described above are however ideal. In practice, a very slow isothermal expansion is approximately reversible.

b)   Adiabatic compression of a gas: Again, if the cylinder containing the gas is a perfect insulator (including its base) and the gas is compressed infinitesimally slowly, the compression is reversible. In practice, it can be made only approximately reversible.

c)   Diffusion of gases: When two or more gases diffuse into one another, there is a change in chemical composition and the process is irreversible.

d)   Transfer of heat from hot to cold body: This process is irreversible, because heat cannot be transferred back from the cold to the hot body without leaving any change elsewhere.

e)   Joule expansion (or free expansion) of a Perfect gas: In this process, the (perfect) gas changes from a volume V_i to a larger volume V_f without any change in temperature. To revert the gas to its initial state, it would have to be compressed to V_i by some external device. The external work so done would be converted into heat. To ensure that the gas retains its initial temperature and no changes are left in the surroundings, the heat produced would have to be extracted from the gas

and converted completely into work. Since this last step is impossible, the process is irreversible.

f) Joule-Thomson effect: The Joule-Thomson expansion of a gas is an irreversible process. The reason is same as for free expansion. (any heat cannot be completely converted into work)

g) Transfer of heat by radiation: Heat coming from a hot body by radiation cannot be radiated back to the hot body without leaving any change elsewhere. Hence the process is irreversible.

h) Electrical heating of a wire: The electrical energy dissipated as heat in the wire cannot be fully converted into electrical energy and so the process is irreversible.

i) Very slow extension or contraction of a spring: In this process, if carried out extremely slowly, the spring passes through states of thermodynamic equilibrium, which may be traversed just as well in one direction as in the opposite direction. The process is therefore approximately reversible.

j) Dissipation of mechanical energy to heat through friction: Suppose a body moves on a surface from an initial position, spends its mechanical energy to overcome friction between itself and the surface, and again returns to its initial position. The energy spent is dissipated as heat. Now, if the body be allowed to go round its path in the reverse direction, its energy spent previously cannot be recovered. On the contrary, the body will have to further spend its energy against the friction in the reverse path. Hence the process is irreversible.

3.

Complete conversion of work into heat: We can convert a given quantity of work 'completely' into heat. For example, when we rub two stones together under water, the work done against friction is converted into heat which is communicated to the surrounding water. Since the state of the stone is the same at the end of the process as at the beginning, the net result of the process is merely the conversion of mechanical work into heat with 100 percent efficiency (W=Q). This conversion can be continued indefinitely.

The reverse process is, however, not possible. We cannot make a device by which a given amount of heat can be 'completely' converted into work. At first thought, the isothermal expansion of an ideal gas can be considered as a process in which heat is converted completely into work. In this case $\Delta U=0$ (since the temperature remains constant) and so the heat absorbed by the gas is equal to the work done by the gas during the expansion (Q=W). But here the state of the gas changes. Its volume increases and pressure decreases until atmospheric pressure is reached at which the process stops. Thus the conversion of heat into work cannot be continued indefinitely.

5.

(i) No

(ii) No. This is because efficiency of reversible engine depends upon temperature of sink and source. Therefore, the temperature of sink and source needs to be same otherwise they will have different efficiencies.

3.17.2 TERMINAL QUESTIONS: SHORT ANSWER TYPE

1.

(a) Production of 8000K temperature by sun-rays: It is not possible to produce a temperature of 8000K by focusing sun-rays. The reason that the creation of a temperature of 8000K by transferring heat from a colder body (sun at 6000K) by means of lens is a violation of the second law of thermodynamics.

(b) Driving a ship by extracting heat form ocean: It is an attractive idea to drive ship on the energy drawn from the internal energy of water. At the start of its cycle the engine of the ship will draw some heat Q_1 from the water, convert a part of it into work, but where it would reject the rest? By the second law, it must reject some heat into a colder reservoir but none is available at hand. Theoretically, it is possible if we can arrange some conveyance to the cold upper atmosphere but practical difficulties would make it almost impossible.

From Carnot's cycle also, we see that the efficiency is

$$\eta = 1 - \frac{T2}{T1}$$

Thus, η = 0, if, T2 = T1, that is, without a temperature-difference the conversion of thermal energy into mechanical work is impossible.

(c) Heat Conduction is irreversible: Suppose there are two bodies 1 and 2 at temperatures T_1 and T_2 where $T_1 > T_2$. When they are brought into contact, heat flows by conduction from 1 to 2 till they reach a common temperature. Heat cannot flow in the reverse direction, from 2 to 1, because heat-flow by itself from cold to hot body is not allowed by the second law of thermodynamics. Thus heat- conduction is an irreversible phenomenon.

3.

Fig. (3.8) shows isobaric, isothermal and adiabatic expansions.

(i) In isobaric process pressure is constant, then temperature will rise, in isothermal expansion temperature will remain unchanged and in adiabatic expansion the temperature falls. So, rise in temperature is larger in isobaric expansion than the temperature drop in adiabatic expansion.

Fig (3.12)

(ii) The work done by the gas is largest in isobaric expansion and smallest in adiabatic expansion.

(iii) According to the first law of thermodynamics,
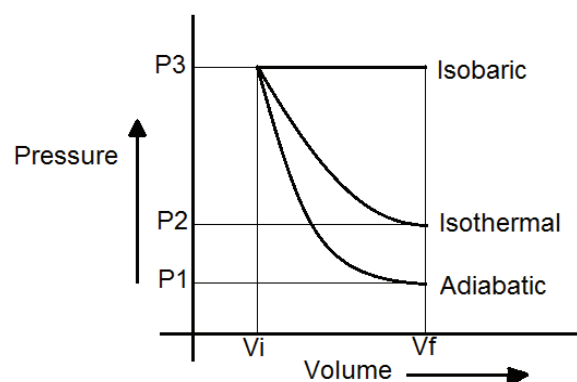
Q = W+ ΔU

For isobaric expansion temperature rises, it means internal energy ΔU increases. Also work done is large, so heat absorption is largest. For isothermal expansion,

ΔU = 0

Q = W

For adiabatic expansion, Q=0, i.e. heat absorbed by the gas is smallest.

4.

The gas molecules rebounding from the hotter wall have a greater energy than those rebounding from the colder walls. On account of random kinetic motion, there is a transfer of higher energy molecules towards the colder wall, and of lower energy molecules towards the hotter wall. Consequently heat conduction takes place from hotter to colder wall through the gas.

5.

The refrigerator removes heat from its interior and gives it out into the surrounding air, thus warming the air. For doing this, additional energy is supplied to the refrigerator by an electric motor. The heat given out into the air is the sum of the energy from the motor and that removed from the interior of the refrigerator. So, we can say that the refrigerator adds more heat into the room than it removes from its interior. On opening its door it will run continuously and hence add even more heat to the room than when its door is closed.

6.

The specific heat of water is about five times higher than that of clay or sand. Therefore, if same quantity of heat be given to (or taken from) the same mass of water and earth, the water will have a much smaller rise (or fall) in temperature than the earth. This gives a very important effect on the climate of islands and coastal areas. During a hot day the temperature of the sea rises more slowly than that of the land, and during night the temperature of sea falls more slowly than the heat radiated by that of the land, and during night temperature of sea falls more slowly than the heat radiated by the land. Therefore, during the day the cooler sea keeps the land (near it) cool, while during the night it tends to keep the land warm. This transfer of heat takes place through the movement of air. Thus, the land near the sea undergoes a smaller day and night temperature variation than the land elsewhere. Similarly, the land near the sea remains cooler during the summer and warmer during the winter than the land far from the sea.

UNIT 4   ENTROPY

CONTENTS

4.1 INTRODUCTION

In the previous unit, you have studied about reversible and irreversible processes, heat engines, Carnot cycle, Carnot theorem, second law of thermodynamics etc.. In this unit, we shall study an important physical quantity in thermodynamics called entropy. We shall also study the entropy change in reversible and irreversible processes. In the present unit, we shall learn about Clausius theorem, temperature entropy diagram, Kelvin scale of temperature, absolute zero temperature and Nernst heat theorem.

4.2 OBJECTIVES

After studying this unit, you should be able to-

- Understand entropy, Clausius theorem and third law of thermodynamics.
- Solve problems based on entropy
- Apply Clausius theorem, Nernst theorem
- Understand absolute zero temperature
- Understand zero point energy

4.3 ENTROPY

Initially the thermodynamic state of a system was represented by only three variables named pressure, volume and temperature. In 1854, Rudolf Clausius while studying the thermodynamic systems realized that to represent the thermodynamic state of a system, in addition to these three variables we must have at least one more thermodynamical variable. This added quantity was named "Entropy". It was proved successfully that like pressure, volume and temperature the entropy is also a function of the state of the system.

 The concept of entropy was introduced for many reasons. The changes in the state of a system can be represented in different ways e.g. the isothermal change (in which the temperature remains unchanged), the isobaric change (in which the pressure remains constant) and the isochoric change (in which the volume of the system remains constant). Now the real question arises that which quantity remains constant during an adiabatic change. It was established that the entropy remains constant in an adiabatic change in the system. The systems have a tendency to change from a more ordered state to a more disordered state. The perception of entropy expresses this in a better physical and mathematical form. The entropy of a substance is a real quantity, just like pressure, volume and temperature. Despite being an very important quantity, it can't be represented in some physical form. It, therefore, becomes very difficult to visualize it and to understand its exact nature. Entropy can be conveniently understood by studying its effect, properties and other aspects.

4.3.1 GENERAL CONCEPT OF ENTROPY

Let us consider a number of isothermals I_1, I, I_3,.... at temperatures T_1, T_2, T_3... respectively as represented in the P-V diagram (Fig. 4.1). let A_1 and A_2 are two adiabatic curves which cut

the isothermal at points (a, b), (c, d), (e, f), ... respectively. We can now imagine abdca to be a Carnot cycle, so that it works between temperatures T_1 and T_2, extracting heat Q_1 from the source and rejecting Q_2 to the sink, so that the efficiency of a Carnot engine completing the cycle abdca can be given by

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

or $\quad 1 - \dfrac{Q_2}{Q_1} = 1 - \dfrac{T_2}{T_1}$

or $\quad \dfrac{Q_2}{Q_1} = \dfrac{T_2}{T_1}$

or $\quad \dfrac{Q_1}{T_1} = \dfrac{Q_2}{T_2}$ $\hspace{4cm}$ (4.1)

 Similarly, for Carnot cycle cdfe, extracting heat Q_2 from the source at temperature T_2 and rejecting Q_3 to sink at T_3, then we have

$$\frac{Q_2}{T_2} = \frac{Q_3}{T_3}$$ $\hspace{4cm}$ (4.2)
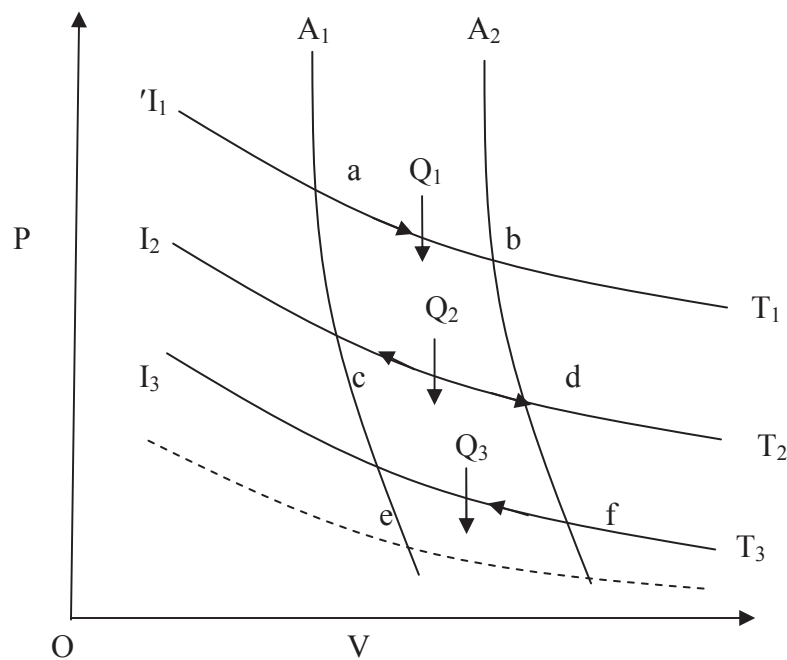
Fig. (4.1)

Similar relations can be obtained for other mini Carnot cycles bound by adiabatics A_1 and A_2. Obviously, for all these Carnot cycles

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = ... = \text{constant} \hspace{2cm} .....(4.3)$$

In going from one adiabatic to the other the system either absorbs heat or rejects it. If the exchange of heat is Q at temperature T, then generalizing relation (4.3), we can write-

$$\frac{Q}{T} = \text{constant} \qquad\qquad\qquad\qquad .....(4.4)$$

This ratio is determined by two adiabatics, it can be regarded as some measure of the process. This constant ratio $\frac{Q}{T}$ is given the name entropy of the system.

If S_1 and S_2 are the entropies corresponding to the adiabatic curves A_1 and A_2 respectively, then we can write

$$S_2 - S_1 = \frac{Q}{T} = \text{constant} \qquad\qquad\qquad .....(4.5)$$

If the adiabatics 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 can be written as

$$dS = \frac{dQ}{T} \qquad\qquad\qquad\qquad .....(4.6)$$

In the above discussion, the changes from adiabatic A_1 to A_2 were considered isothermal but this is not necessary. The only necessary condition is that the change should be reversible.

In general, the change in entropy in passing from one adiabatic to another can be expressed as

$$\int_{S_1}^{S_2} dS = \Delta S = S_2 - S_1 = \int_A^B \frac{dQ}{T} \qquad\qquad .....(4.7)$$

The expression $\int_A^B \frac{dQ}{T} = \int_{S_1}^{S_2} dS$ is a function of the thermodynamic coordinates of a system and refers to the value of the function 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 thermo-dynamical coordinates defining the state of the system viz., the pressure, temperature, volume or internal energy and its change between the two states is equal to the integral of the quantity $\frac{dQ}{T}$ between the states along any reversible path joining them. dS is an exact differential as it is differential of an actual function.

Since in an adiabatic change, no heat energy is given to or removed from the system i.e. there is no exchange of heat, dQ = 0, therefore, the change in entropy is

$$dS = \frac{dQ}{T} = \frac{0}{T} = 0$$

Thus, in an adiabatic process, the change in entropy of a system is zero or in other words, in the adiabatic processes, the entropy of a system remains constant. Due to this reason the adiabatic curves on the P-V diagram are called isentropics or constant entropy curves also.

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

$$\text{change in entropy} = \frac{\text{Heat given or taken by the system}}{\text{Absolute temperature of the system}}$$

We conclude that dimensions of entropy are the same as the ratio of heat (or energy) and temperature. Its unit is joule/Kelvin (J/K).

4.3.2 PHYSICAL SIGNIFICANCE OF ENTROPY

The change in the entropy of a substance defined by the relation $dS = \frac{dQ}{T}$ shows that the heat energy has the same dimensions as the product of entropy and absolute temperature. In earth's gravitational field the potential energy of a body is proportional to the product of its mass and the height above some zero level. A comparison indicates that if we regard height as corresponding to temperature, then mass corresponds to entropy. Thus, entropy of a system is a quantity which bears to heat motion a similar relation as mass bears to linear motion.

4.4 ENTROPY CHANGE IN REVERSIBLE PROCESS: CLAUSIUS THEOREM

Let us consider a complete reversible process- a Carnot's cycle ABCD as shown in figure 2. 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 the heat is absorbed by the system, Q_1 is positive and hence entropy change is positive because T_1 is positive.
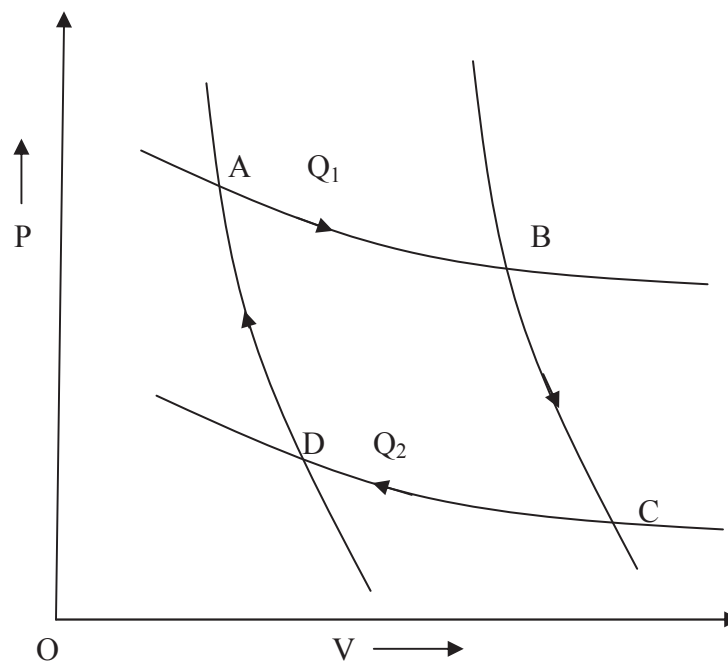
Fig. (4.2)

Hence gain in entropy of working substance from A to B $= \frac{Q_1}{T_1}$

(Source loses this heat Q_1 at temperature T_1; therefore, its entropy decreases by $\frac{Q_1}{T_1}$)

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 to the sink at a constant temperature T_2 and therefore 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, therefore its entropy increases by $\frac{Q_2}{T_2}$).

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

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 constant or the change in entropy of the system is zero i.e.

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

where the integral sign with a circle refers to a complete cycle.

Hence we conclude that in a reversible cyclic process, the entropy change is zero. This is Clausius theorem.

4.5 ENTROPY CHANGE IN IRREVERSIBLE PROCESS

Let us suppose that 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

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

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

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

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, the source losses the entropy by an amount $\frac{Q_1}{T_1}$ and the sink gains an entropy $\frac{Q_2}{T_2}$. Therefore, the net change in entropy for the 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.

As an example of irreversible process, consider the case of conduction or radiation. Suppose in a system, there are two objects A and B at temperatures T_1 and T_2 ($T_1 > T_2$) respectively. In conduction (or radiation) heat flows from the object of higher temperature to that of lower temperature. If an amount Q of heat is transferred then

Decrease in the entropy of object A $= \dfrac{Q}{T_1}$

Increase in the entropy of object B $= \dfrac{Q}{T_2}$

Therefore, the net increase in entropy $= \dfrac{Q}{T_2} - \dfrac{Q}{T_1} = Q\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ .....(4.8)

Since $T_1 > T_2$, therefore the net increase in entropy is positive.

Now we may generalize 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'. In the process of equalization of temperature, entropy always increases.

4.6 PRINCIPLE OF INCREASE OF ENTROPY DEGRADATION OF ENERGY

In the previous article, we have seen that in a reversible processes, the entropy remains unchanged while in an irreversible processes, it increases. Since, in general, most of the processes are not perfectly reversible, therefore, there is always an increase in the entropy always. If the processes occur in succession the entropy goes on increasing and tends to a maximum value. This is known as the principle of increase of entropy. It may be stated that the entropy of an isolated or self-contained system either increases or remains constant accordingly as the processes it undergoes are irreversible or reversible.

According to Clausius, the entropy of an isolated or self-contained system tends to a maximum value. Thus, the entropy of a system either increases or remains constant i.e.

$$dS \geq 0$$

where, = sign stands for reversible processes and > sign for irreversible processes. Obviously, for the stability of a system its entropy must be maximum.

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 universe in the form of heat through friction, conduction or radiation. In this way, in a distant future, on account of irreversibility, all energies existing in different forms will be transformed into heat energy and will not be available for alteration into mechanical work, i.e. the available energy of the universe will tend towards zero. It will correspond to a state of maximum entropy and all temperature difference between various bodies of the universe will be equalized due to convection etc. No heat engine will then be able to work in this state because no heat flow would be possible due to the uniformity of

temperature throughout the universe. This is known as the principle of degradation of energy and implies that although the total amount of energy is conserved, it is converted into a form which is unavailable for work.

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. As the temperature of a system is a measure of its degree of hotness, in a similar way, the entropy of a system is a measure of disorder in it. At absolute zero of temperature, the motion of the molecules of a substance ceases, the molecules become well arranged and the entropy becomes zero.

4.7 TEMPERATURE ENTROPY (T − S) DIAGRAM

The thermodynamic state of a substance can be determined by plotting the temperature as ordinate and entropy as abscissa. The resulting graph is known as temperature-entropy diagram and is used in the checking of efficient working of actual engines. The idea of T-S graph was first introduced by Gibbs.

If a thermodynamical system is given an infinitesimal amount of heat dQ , at temperature T then

$$dQ = T \, dS \qquad\qquad .....(4.9)$$

where dS is the increase in the entropy of the system.

Therefore, in a process, total amount of heat given to the system is

$$Q = \int T dS \qquad\qquad .....(4.10)$$
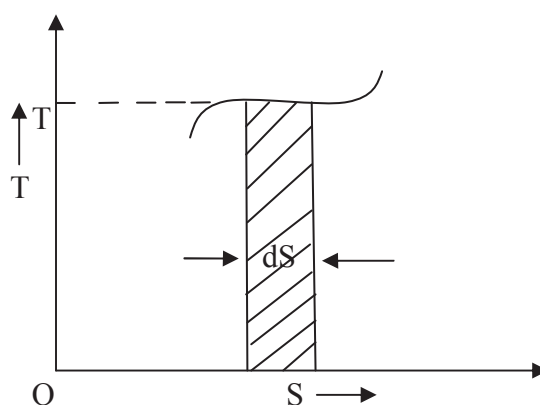
Fig. (4.3)

Obviously, the integral represents the area enclosed by the T-S diagram. Thus by finding the area of T-S diagram, we can find the amount of heat given to the system. The shape of the T-S graph depends upon the process. An isothermal change is represented by a horizontal line

parallel to the entropy axis while an adiabatic change is represented by a vertical line parallel to T-axis because in such a change S remains constant.

Let us study Carnot cycle represented by a temperature-entropy (T-S) diagram in figure (4.4).

As we know that Carnot's cycle consists of two isothermals and two adiabatics. The isothermals are represented by horizontal straight lines (parallel to entropy axis) and adiabatics by vertical straight lines (parallel to temperature axis) on a T-S diagram. In this way, in the figure, PQ represents the isothermal expansion at a constant temperature T_1 of the source, the vertical line QR is the adiabatic expansion during which there is no change in entropy but a fall of temperature from T_1 to T_2, the temperature of the sink. RS is the second
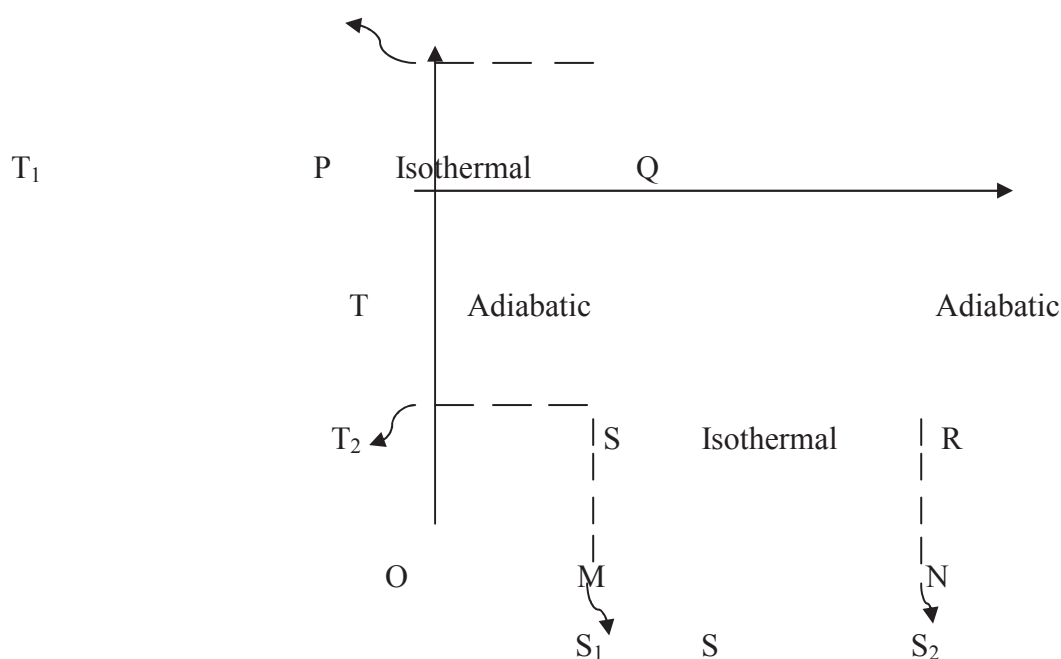
Fig. (4.4)

isothermal representing compression at constant temperature T_2 and SP is the final adiabatic compression involving a rise of temperature from T_2 to T_1, entropy remaining the same.

The amount of heat energy absorbed in isothermal expansion PQ is given by the area under PQ, i.e. PQNM. In a similar way, the heat rejected in isothermal compression RS is given by the area SRNM.

Total heat absorbed = Area PQNM = $T_1 (S_2 - S_1)$

Heat energy converted into work = heat absorbed – heat rejected

$$= \text{area PQNM} - \text{area SRNM} = \text{shaded area PQRS}$$

$$= PS \times SR = (T_1 - T_2)(S_2 - S_1)$$

Therefore, efficiency of the engine $\eta = \dfrac{\text{Heat energy converted into work}}{\text{Total heat absorbed}}$

$$= \frac{(T_1 - T_2)(S_2 - S_1)}{T_1(S_2 - S_1)} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

Thus, the T-S diagram gives an expression for efficiency of a Carnot's engine which only depends on the two working temperatures and not on the nature of the working substance.

4.8 ENTROPY OF A PERFECT GAS

Let us calculate the entropy of a perfect gas. Let us consider 1 gm. 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

$$dQ = dU + dW \qquad \qquad .....(4.11)$$

If C_v is the specific heat of the gas at constant volume, dT the rise in temperature, dV the change in volume then we can write

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

Using these values in equation (4.11) we get-

$$dQ = C_v\, dT + P\, dV$$

If S is the entropy per unit mass of the gas, then

$$S = \int \frac{dQ}{T} = \int \frac{1}{T}(C_v dT + P\, dV)$$

$$= \int C_v \frac{dT}{T} + \int \frac{P}{T} dV \qquad \qquad .....(4.12)$$

Now let us calculate the value of S in terms of temperature and volume.

We know,

PV = rT or P/T = r/V, where r is the ordinary gas constant for unit mass of the gas.

From equation (4.12), we get

$$S = \int C_v \frac{dT}{T} + \int \frac{r\, dV}{V}$$

$$= C_v \log_e T + r \log_e V + \text{constant}$$

or, $\qquad \qquad S = C_v \log_e T + (C_p - C_v)\log_e V + \text{constant} \qquad .....(4.13)$

Where, $r = C_p - C_v$, Mayer's relation. C_p is the specific heat at constant pressure.

Now let us calculate S in terms of temperature and pressure.

Again, $\qquad \qquad \qquad$ PV = rT

Differentiating, we get

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

or $$P \, dV = r \, dT - V \, dP$$

From equation (4.12), we get

$$S = \int C_v \frac{dT}{T} + \int \frac{P}{T} dV$$

$$= \int C_v \frac{dT}{T} + \int \frac{(r \, dT - V \, dP)}{T}$$

$$= \int C_v \frac{dT}{T} + \int r \left(\frac{dT}{T} - \frac{V dP}{rT} \right) = \int C_v \frac{dT}{T} + \int r \left(\frac{dT}{T} - \frac{dP}{P} \right) \qquad \text{(since } V/rT = 1/P)$$

$$= \int C_v \frac{dT}{T} + \int (C_p - C_v) \left(\frac{dT}{T} - \frac{dP}{P} \right) \qquad \text{(using } r = C_p - C_v)$$

$$= \int C_v \frac{dT}{T} + \int (C_p - C_v) \frac{dT}{T} + \int (C_p - C_v) \frac{dP}{P}$$

$$= \int C_v \frac{dT}{T} + \int C_p \frac{dT}{T} - \int C_v \frac{dT}{T} + \int (C_p - C_v) \frac{dP}{P}$$

or $$S = \int \left\{ C_p \frac{dT}{T} + (C_p - C_v) \frac{dP}{P} \right\}$$

or $$S = C_p \log_e T + (C_p - C_v) \log_e P + \text{constant} \qquad \qquad .....(4.14)$$

Now let us calculate S in terms of pressure and volume.

We know, $$PV = rT \quad \text{or } T = \frac{PV}{r}$$

Differentiating above, we get

$$dT = \frac{P.dV + V.dP}{r}$$

Putting the value of dT in relation (4.12), we get

$$S = \int \left[C_v \frac{PdV + VdP}{rT} + \frac{P \, dV}{T} \right]$$

$$= \int \left[C_v \frac{PdV + VdP}{PV} + \frac{P \, dV.r}{PV} \right] \qquad \text{(putting the value of T)}$$

$$= \int \left[C_v \left(\frac{dV}{V} + \frac{dP}{P} \right) + (C_p - C_v) \frac{dV}{V} \right]$$

or $$S = \int \left[C_v \frac{dP}{P} + C_p \frac{dV}{V} \right]$$

or $$S = C_v \log_e P + C_p \log_e V + \text{constant} \qquad \qquad .....(4.15)$$

In the above calculations, we have assumed the entropy of the gas to be zero at zero temperature. In actual practice, however, we are concerned with a change in entropy of the

gas, when the gas changes from a state of pressure P_1, volume V_1 and temperature T_1 to another of P_2, V_2 and T_2 respectively. This can be obtained by integrating relation (4.12) between the limits T_1 and T_2. If we denote the change in entropy by (S_2-S_1), then equation (4.13), (4.14) and (4.15) assumes the form, respectively, as

$$S_2\text{-}S_1 = C_v \log_e \frac{T_2}{T_1} + (C_p - C_v) \log_e \frac{V_2}{V_1} \qquad \qquad .....(4.16)$$

$$S_2\text{-}S_1 = C_p \log_e \frac{T_2}{T_1} + (C_p - C_v) \log_e \frac{P_2}{P_1} \qquad \qquad .....(4.17)$$

$$S_2\text{-}S_1 = C_v \log_e \frac{P_2}{P_1} + C_p \log_e \frac{V_2}{V_1} \qquad \qquad .....(4.18)$$

All the above relations from (4.13) to (4.18) stand for unit mass of the gas. If the entropy S and the change in entropy (S_2-S_1) for m gms. of the gas is required, it can be obtained by multiplying these relations from (4.12) to (4.18) by the given mass m.

4.9 THERMODYNAMIC OR KELVIN SCALE OF TEMPERATURE

We know that the efficiency of a reversible Carnot's engine depends only upon the two temperatures between which it works and is independent of the properties of the working substance. Thus there is a property which absolutely depends on temperature and on nothing else. Hence, if we define a temperature scale using this property of working of Carnot's engine, it is an absolute scale of temperature because it does not depend upon the particular property of any substance as in the case of other thermometric scales. Lord Kelvin worked out the theory of such an absolute scale called the Kelvin's work or thermodynamical scale and showed that it agrees with the ideal gas scale.

Let us suppose that a reversible engine takes in a quantity of heat Q_1 at temperature θ_1 and rejects a quantity of heat Q_2 at temperature θ_2, then since the efficiency of the engine is a function of these two temperatures

$$\eta = 1 - \frac{Q_2}{Q_1} = f(\theta_1, \theta_2)$$

$$\frac{Q_1}{Q_2} = \frac{1}{1 - f(\theta_1, \theta_2)} = F(\theta_1, \theta_2) \qquad \qquad .....(4.19)$$

where F is some other function of θ_1 and θ_2.

Similarly, if the reversible engine works between a pair of temperature θ_2 and θ_3 ($\theta_2 > \theta_3$) absorbing a heat Q_2 and rejecting Q_3, we have

$$\frac{Q_2}{Q_3} = \frac{1}{1 - f(\theta_2, \theta_3)} = F(\theta_2, \theta_3) \qquad \qquad .....(4.20)$$

Also, if it works between   temperatures θ_1 and θ_3 ($\theta_1 > \theta_3$), then

$$\frac{Q_1}{Q_3} = F(\theta_1, \theta_3) \qquad \qquad .....(4.21)$$

Multiplying equations (4.19) and (4.20)

$$\frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3} = \frac{Q_1}{Q_3} = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3)$$

Comparing it with equation (4.21), we have

$$F(\theta_1, \theta_3) = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3) \qquad\qquad .....(4.22)$$

Equation of type (4.22) is called the functional equation. It does not contain θ_2 on the left hand side, therefore, function F should be so chosen that θ_2 disappears from the right hand side too. This is possible if

$$F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)} \text{ and } F(\theta_2, \theta_3) = \frac{\phi(\theta_2)}{\phi(\theta_3)}$$

where ϕ is another unknown function of temperature.

Equation (4.22) then gives

$$F(\theta_1, \theta_3) = \frac{\phi(\theta_1)}{\phi(\theta_2)} \text{ X } \frac{\phi(\theta_2)}{\phi(\theta_3)} = \frac{\phi(\theta_1)}{\phi(\theta_3)}$$

Equation (4.19) gives

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)}$$

Since $\theta_1 > \theta_2$ and $Q_1 > Q_2$, the function $\phi(\theta_1) > \phi(\theta_2)$. In this way, function $\phi(\theta)$ is a linear function of θ and can be used to measure temperature. If we suppose that $\phi(\theta)$ represents a temperature τ (some multiple of θ) on a new scale, then

$$\frac{Q_1}{Q_2} = \frac{\tau_1}{\tau_2} \qquad\qquad .....(4.23)$$

Equation (4.23) defines the Kelvin's absolute thermodynamic scale of temperature. The ratio of any two temperatures on this scale is equal to the ratio of the heats absorbed and rejected by a Carnot reversible engine working between these two temperatures.

 Now equation (4.23) can also be written as

$$\frac{Q_1 - Q_2}{Q_1} = \frac{\tau_1 - \tau_2}{\tau_1} \qquad\qquad .....(4.24)$$

Since $(Q_1 - Q_2)$ represents the work done W per cycle by the reversible engine operating between the two temperature τ_1 and τ_2, temperatures are measured in terms of work and hence this scale is also known as work scale of temperature.

4.10 ABSOLUTE ZERO TEMPERATURE

We know that

$$\eta = 1\text{-}\frac{Q_2}{Q_1} = 1\text{-}\frac{\tau_2}{\tau_1} \qquad\qquad\qquad .....(4.25)$$

If $\tau_2 = 0$, then efficiency $\eta = 1\text{-}\dfrac{0}{\tau_1} = 0$

Thus, for the efficiency to be unit i.e., $\eta = 1$, $\tau_2 = 0$

This temperature of the sink at which the efficiency of the reversible engine becomes unity is called the absolute zero of temperature. This is the thermodynamic definition of absolute zero temperature.

From equation (4.25), it is clear that at the absolute zero of temperature ($\tau_2 = 0$), $Q_2 = 0$, therefore, $W = Q_1$. Therefore, the entire amount of heat absorbed by the reversible engine is converted into work and thus, the efficiency of the engine becomes unity. The temperature on this scale can never be negative i.e. $\tau < 0$ is not possible. This is because if the temperature of the sink is a negative quantity (say –m) on this scale, then from equation (4.25),

$$\eta = 1 + \frac{m}{\tau}$$

The efficiency will be more than unity ($\eta > 1$) which is impossible. Because in this situation, the engine will be producing more work than the amount of heat received. This can never be true as it will be a violation of the second law of thermodynamics. Thus, negative temperatures are not possible on the absolute scale of temperature. That is why $\tau = 0$ is the lowest possible temperature and is called the absolute zero temperature.

4.11 UNATTAINABILITY OF ABSOLUTE ZERO

It can be easily understood why the efficiency of an engine cannot be unity i.e. 100%. For this to happen we must have a sink at absolute zero temperature. But nature does not provide us with a sink at absolute zero. This temperature is neither available nor easily attainable. Therefore, 100% efficiency of an engine is not possible and thus absolute zero is also unattainable.

4.12 NERNST THEOREM (THIRD LAW OF THERMODYNAMICS)

For the study of chemical equilibrium in chemical reactions, it is necessary to determine the change in the entropy of the system when the reaction takes place at 0 K temperature. Nernst assumed that this change in entropy is zero. Nernst's this assumption is termed as Nernst Heat Theorem. Nernst and Simon presented this concept in the form of law which is given as-

"The entropy change associated with any isothermal reversible process of condensed system (solid or liquid) approaches zero as the temperature is reduced to absolute zero." This is called Third law of thermodynamics.

An important consequence of this law is that, it is impossible to attain the absolute zero temperature; it can be attained only asymptotically. Some scientists treated it as a more fundamental law and stated the third law of thermodynamics as follows

"It is impossible by any process, no matter how idealized, to reduce any system to absolute zero of temperature in a finite number of steps."

The third law of thermodynamics is also known as the law of unattainability of absolute zero of temperature. This law has many applications in physics and chemistry.

4.13 ZERO POINT ENERGY

We know that absolute zero is the lowest temperature which can be achieved. At absolute zero of temperature, the gas molecules will be devoid of all motions. So kinetic theory predicts that at absolute zero, all molecules will behave as if they were frozen in space and have no energy. This is classical picture of the situation. However, due to quantum effects (as will be taught in Fermi-Dirac statistics in later stage), there is some finite energy even at absolute zero for some typical systems. This energy is known as zero-point energy.

Because of the non-zero value of energy even at absolute zero temperature, we cannot assign zero value to the entropy even at this temperature. Therefore, we generally deal with changes in entropy, as do we talk about changes in gravitational potential energy, rather than its absolute value.

The concept of zero-point energy was developed by Max Planck in Germany in 1911 as a corrective term added to a zero-grounded formula developed in his original quantum theory in 1900.

Example 1: A Carnot engine is working between 500 K and 400 K. Calculate its efficiency

Solution: Given T_1 = 500 K, T_2 = 400 K

$$\text{Efficiency of the engine } \eta = 1 - \frac{T_2}{T_1} = 1 - \frac{400}{500} = \frac{100}{500} = 0.2 = 20\%$$

Self Assessment Question (SAQ) 1 Choose the correct option

The change in entropy of the universe in a reversible process is

(i) infinite   (ii) zero   (iii) 1   (iv) 100

Self Assessment Question (SAQ) 2 Choose the correct option

The change in entropy of the working substance in a cyclic process is

(i) 1   (ii) infinite   (iii)   zero   (iv) none of these

Self Assessment Question (SAQ) 3 Choose the correct option

In an irreversible process, the entropy of the universe

(i) remains constant   (ii) decreases   (iii) increases   (iv) none of these

Self Assessment Question (SAQ) 4 Choose the correct option

In a complete Carnot cycle, the change in the entropy of the universe is

(i) infinite   (ii) negative   (iii) positive   (iv) zero

Self Assessment Question (SAQ) 5 Choose the correct option

Entropy remains constant in

(i) isothermal process   (ii) adiabatic process   (iii) cyclic process   (iv) isobaric process

Self Assessment Question (SAQ) 6 Choose the correct option

The area of the Carnot cycle on a T-S diagram represents

(i) heat rejected to the sink   (ii) work done in a cycle   (iii) heat absorbed from the source
(iv) efficiency of the engine

4.14 SUMMARY

In this unit, you have learnt about entropy, its general concept and significance. Entropy is a measure of disorderness of a system. More entropy, more disorderness and low entropy, low disorderness. You have learnt that in an adiabatic process, the change in entropy of a system is zero or in other words, in adiabatic processes the entropy of a system remains constant. Due to this reason the adiabatic curves on the P-V diagram are also called 'isentropics' or constant entropy curves. You have studied about Clausius theorem that in a reversible cyclic process, the entropy change is zero. Also if an irreversible process occurs in a closed system, the entropy S of the system always increases and it never decreases. You have analyzed the entropy change in irreversible process and concluded that the entropy of a system increases in all irreversible processes. This is known as the law or principle of increase of entropy. In the process of equalization of temperature entropy always increases. Other than this, you have studied principle of increase of entropy or degradation of energy, temperature, entropy diagram, Kelvin scale of temperature, absolute zero temperature, Nernst theorem, zero point energy etc. In the unit, you have calculated entropy of a perfect gas. We have included examples and self assessment questions (SAQs) to check your understanding.

4.15 GLOSSARY

Entropy- In thermodynamics, quantity that is a measure of a system's disorder or the unavailability of its energy to do work. It is a measure of randomness.
Degradation- The irreversible loss of energy available to do work with a consequent increase in entropy
Absolute zero- Theoretically lowest possible temperature at which a substance has no heat energy. The pressure and volume of any gas becomes zero at this temperature.

4.16 TERMINAL QUESTIONS

1. Explain entropy. Give its general concept and physical significance. Prove that the entropy of a system increases in an irreversible process.

2. Give the definition of entropy. Prove that the entropy of a system remains constant in a reversible process.

3. "The entropy of a substance is a unique function of its state," explain

4. Prove that the dimensions of entropy are the same as the ratio of heat and temperature.

5. Show that in a reversible cyclic process, the entropy change is zero.

6. Explain the principle of increase of entropy.

7. Discuss T-S diagram and hence establish the expression for efficiency of an engine.

8. Derive entropy of a perfect gas in terms of pressure and temperature.

9. Explain Kelvin scale of temperature.

10. What is absolute zero temperature? Explain.

11. Explain unattainability of absolute zero.

12. State and prove Clausius theorem of entropy.

13. Discuss Nernst theorem.

14. Explain zero point energy. Give its significance.

15. Show that the negative temperatures are not possible on absolute scale of temperature.

16. Give short notes on

(i) Absolute scale of temperature

(ii) Law of increase of entropy

17. Why Kelvin's scale of temperature is called the absolute scale?

18. For the following processes in an ideal gas state whether the change in entropy is positive, negative or zero?

(i) Reversible adiabatic expansion

(ii) Reversible isothermal compression

(iii) Reversible isobaric expansion

(iv) Joule's free expansion

19. Fill in the blanks

   (i) The absolute scale of temperature is also called...................

   (ii) The absolute scale of temperature was proposed by..............

   (iii) ....temperatures are not possible on the absolute scale of temperature.

   (iv) The entropy of a system is a ....function.

   (v) The entropy of a system remains constant in an ....process.

   (vi) The concept of entropy was first introduced by..............

   (vii) Entropy is closely related to ....

4.17 ANSWERS

Self assessment questions (SAQs)

1. (ii) zero

2. (iii) zero

3. (iii) increases

4. (iv) zero

5. (ii) adiabatic process

6. (ii) work done in a cycle

Terminal questions

17. Because the Kelvin's scale does not depend upon the properties of any working substance.

18. (i) zero   (ii) negative   (iii) positive   (iv) zero

19. (i) thermodynamic scale of temperature

   (ii) Lord Kelvin

   (iii) negative

   (iv) point

   (v) adiabatic

   (vi) Clausius

   (vii) disorder in the system

4.18 REFERENCES

1. Thermal physics, Garg, Bansal and Ghosh, McGraw Hill, New Delhi.

2. Heat and Thermodynamics, Zemansky and Dittman, 6th ed. McGraw Hill, New York.

3. Thermal Physics, Kumar nad Taneja, R. Chand & Co., New Delhi.

4. Thermal Physics and Statistical Mechanicms, Kumar and Taneja, R. Chand & Co., New Delhi.

5. Heat Thermodynamics and Statistical Physics; Singhal, Agrawal and Prakash; Pragati Prakashan, Meerut.

4.19 SUGGESTED READINGS

1. Fundamentals of Physics; Halliday, Resnick and Walker; John Wiley and Sons (Asia) Pvt. Ltd, Singapore

2. Modern Physics, A. Beiser, Tata McGraw Hill.

UNIT 5   MAXWELL'S THERMODYNAMIC RELATIONS

CONTENTS

5.1   INTRODUCTION

Out of several properties of a thermodynamic system some of these like internal energy and entropy cannot be measured directly. So, thermodynamic relations can relate these properties with those that can be measured like pressure, temperature, compressibility etc. In thermodynamic relations un-measurable properties can be written as partial derivatives involving both intensive and extensive variables. A thermodynamic relations is a rule which is obtained by a simple thermodynamic reasoning and applies to most of the systems.

The usefulness of the above relations lies in the fact that they relate quantities which seem unrelated. They help us to link data obtained in various ways or replace a difficult measurement by another one. They can also be used to obtain values of one variable from the calculations of another variable.

These relations are very general and immensely useful as they simplify analysis of thermodynamic systems. The most convenient way to derive these relations is to use partial differentiation.

5.2   OBJECTIVES

After studying of this unit, the learner will be able to understand

- The perfect differentials and partial derivatives.
- The extensive and intensive thermodynamic variables learner
- Maxwell thermodynamic relations amongst different thermodynamic variables.
- Various thermnodynamical effects using Maxwell's relations
- To find the value of one variable calculated by the value of another variable.
- To understand the specific heat and its relations, Clausius Clapeyron latent heat equation; Joule's Law; Joule-Thomson law, Temperature inversion and Ratio of adiabatic and isothermal elasticites using Maxwell's relations.

5.3   PERFECT DIFFERENTIALS

A line integral over a *perfect differential* is path independent. The integral depends only on the end points. Let us suppose that we have a certain quantity z depending upon two other quantities x and y so that z is some single valued function of x and y. Mathematically we express it as z = f (x,y). Let us take mutually perpendicular axes of coordinates (Fig.5.1). Then for any particular point A of coordinates x, y, the quantity z has a particular and definite value. That is, when x and y are given, the quantity z is completely determined. The differential dz is then called "perfect differential". In this case, when we go from a point A to a point C, the value of z at C will be independent of the actual path adopted. There are a number of paths from A to C but the value of z changes in going from A and C by the same amount, whichever path is chosen. From this it follows that if we take the quantity z through a cycle such as ABCD, then

$$\oint dz = 0$$
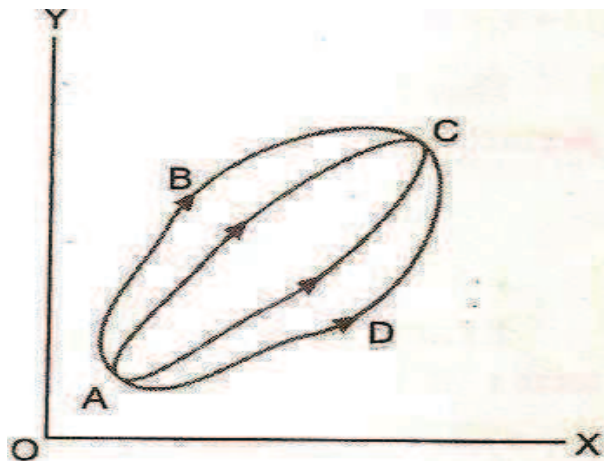
Fig. (5.1)

Mathematical Condition of Partial Differentials

Let us now find the mathematical condition for dz to be a perfect differential. Let, the variable x and y changes by infinitesimal amount dx and dy respectively. To represents this, let us draw an elementary rectangle ABCD (Fig. 5.2), the coordinates of A being (x,y) and the sides AD and AB of the rectangle being dx and dy respectively. Clearly, the coordinates of D will be (x+dx, y); the coordinates of B will be (x, y+dy), and the coordinates of C will be (x+dx, y+dy).
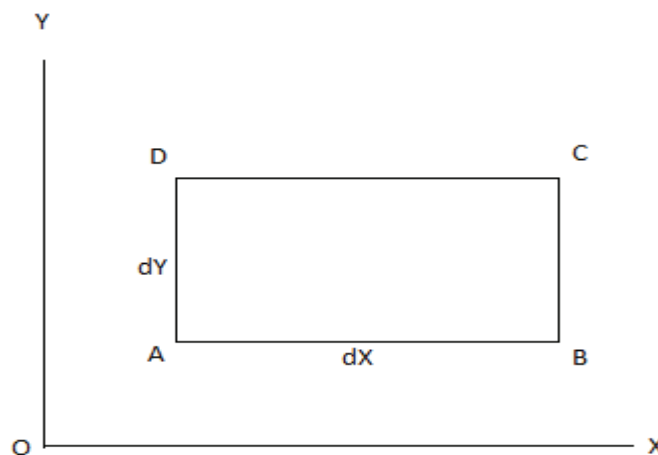
Fig. (5.2)

Suppose, we chose the path ABC to go from A to C. then if the value of the quantity is z at A, its value at B will be $z + \frac{\partial z}{\partial y} dy.$ The value of z at C will be

$$\left(z + \frac{\partial z}{\partial y} dy\right) + \frac{\partial}{\partial x}\left(z + \frac{\partial z}{\partial y} dy\right) \times dx$$

Secondly, let us choose the path ADC from A to C. The value of z at D will be $z + \frac{\partial z}{\partial x} dx$. The value of z at C will be

$$\left(z + \frac{\partial z}{\partial x}dx\right) + \frac{\partial}{\partial y}\left(z + \frac{\partial z}{\partial x}dx\right) \times \ dy$$

Now, if dz is a perfect differential, the value of z must be the same at C, whichever path is chosen. That is

$$\left(z + \frac{\partial z}{\partial y}\ dy\right) + \frac{\partial}{\partial x}\left(z + \frac{\partial z}{\partial y}dy\right)dx = \left(z + \frac{\partial z}{\partial x}dx\right) + \frac{\partial}{\partial y}\left(z + \frac{\partial z}{\partial x}dx\right)dy$$

or, $$\left(z + \frac{\partial z}{\partial y}\ dy\right) + \frac{\partial z}{\partial x}dx + \frac{\partial^2 z}{\partial x\,\partial y}\ dy\ dx = z + \frac{\partial z}{\partial x}dx + \frac{\partial z}{\partial y}dy +$$

$$\frac{\partial^2 z}{\partial y\,\partial x}\ dxdy$$

$$\frac{\partial^2 z}{\partial x\,\partial y} = \frac{\partial^2 z}{\partial y\,\partial x}$$

This is the mathematical condition for dz to be perfect differential. If dz is a perfect differential of a function (x, y); it may be shown that

$$dz = \ \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

All the five state variables P, V, T, U and S are perfect differential.

5.4   EXTENSIVE AND INTENSIVE THERMODYNAMIC VARIABLES

An intensive property is a bulk property, meaning that it is a physical property of a system that does not depends on the size or the amount of the material in the system. Examples of intensive properties include temperature, pressure, density, viscosity, hardness, refractive index, specific volume, emf, etc.

An extensive property is a physical quantity whose magnitude is additive for the system. The value of such an additive property is proportional to the size of the system or to the quantity of matter in the system. Examples of the extensive property is length, area, volume,mass, internal energy, entropy, electric charge, heat capacity, magnetisation etc.

The ratio of two extensive properties of the same object or system may be an intensive property. For example, the ratio of an object's mass and volume, which are two extensive properties, is density (M/V), or specific volume (V/M), which is an intensive property.

5.5   MAXWELL'S THERMODYNAMIC RELATIONS

The state of a homogenous system is completely determined if we know its mass and any two of the thermodynamic variables P, V, T, U and S. Thus, the internal energy U of a system is completely determined if V and T are given i.e., U is a function of the two variables V and T. Among the five thermodynamic variables certain relations exist, of which four are important and known as 'Maxwell's thermodynamic relations'. Let us deduce these relations.

From the first law of thermodynamics

$$dQ = dU + dW$$

$$dQ = dU + PdV \qquad \text{(Since } dW = PdV)$$

or $\qquad dU = dQ - PdV$

and from the second law of thermodynamics

$$dQ = TdS$$

Substituting the value of dQ in first equation

$$dU = TdS - PdV \qquad \qquad \dots (5.1)$$

Let U, S and V be the functions of two independent variables x and y. [Here x and y may be any two variables out of S, T, P and V], then

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

Substituting these values of dU, dS and dV in equation (5.1), we get

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy\right] - P\left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy\right]$$

or $\quad \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = \left[T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y\right]dx + \left[T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x\right]dy$

Equating the coefficients of dx and dy on both sides, we have

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \qquad \dots (5.2)$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \qquad \dots (5.3)$$

Differentiating equation (5.2) with respect to y and equation (5.3) with respect to x, we get

$$\frac{\partial^2 U}{\partial y \cdot \partial x} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y \cdot \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y \cdot \partial x}$$

$$\frac{\partial^2 U}{\partial x \cdot \partial y} = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x \cdot \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x \cdot \partial y}$$

As dU is a perfect differential, therefore,

$$\frac{\partial^2 U}{\partial y \cdot \partial x} = \frac{\partial^2 U}{\partial x \cdot \partial y}$$

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y \cdot \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y \cdot \partial x}$$

$$= \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x \cdot \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x \cdot \partial y}$$

…(5.4)

Since dS and dV are also perfect differentials, we have

$$\frac{\partial^2 S}{\partial y \cdot \partial x} = \frac{\partial^2 S}{\partial x \cdot \partial y} \qquad \text{and} \qquad \frac{\partial^2 V}{\partial y \cdot \partial x} = \frac{\partial^2 V}{\partial x \cdot \partial y}$$

Therefore, equation (5.4) becomes:

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \qquad \dots$$

(5.5)

This is the general expression for Maxwell's thermodynamic relations. In place of the independent variables x and y, any two of the four variables S, T, P and V can be substituted so that there may be one mechanical variable (P or V) and one thermal variable (S or T). Thus there may be four sets of possible substitutions (S, V), (T, V), (S, P) and (T, P), providing the four Maxwell's thermodynamic relations.

Maxwell's First Relation: Substitute x = S and y = V in equation (5.5), so that

$$\frac{\partial S}{\partial x} = 1, \frac{\partial S}{\partial y} = 0$$

$$\frac{\partial V}{\partial x} = 0, \frac{\partial V}{\partial y} = 1$$

Putting these values in equation (5.5), we get

$$\left(\frac{\partial T}{\partial y}\right)_x = -\left(\frac{\partial P}{\partial x}\right)_y$$

But $\partial y = \partial V$ (as y = V) and $\partial x = \partial S$ (as x =S). Hence

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

(i)

This is Maxwell's first thermodynamic relation.

Maxwell's Second Relation: Substitute x = T and y = V in equation (5.5), so that

$$\frac{\partial T}{\partial x} = 1, \ \frac{\partial T}{\partial y} = 0$$

$$\frac{\partial V}{\partial x} = 0, \ \frac{\partial V}{\partial y} = 1$$

Putting these values in equation (5.5), we get

$$0 = \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y$$

or $\qquad \left(\frac{\partial S}{\partial y}\right)_x = \left(\frac{\partial P}{\partial x}\right)_y$

But $\partial y = \partial V$ (as y = V) and $\partial x = \partial T$ (as x =T). Hence

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

(ii)

This is Maxwell's second thermodynamic relation.

Maxwell's Third Relation: Substitute x = S and y = P in equation (5.5), so that

$$\frac{\partial S}{\partial x} = 1, \ \frac{\partial S}{\partial y} = 0$$

$$\frac{\partial P}{\partial x} = 0, \ \frac{\partial P}{\partial y} = 1$$

Putting these values in equation (5.5), we get

$$\left(\frac{\partial T}{\partial y}\right)_x - \left(\frac{\partial V}{\partial x}\right)_y = 0$$

$$\left(\frac{\partial T}{\partial y}\right)_x = \left(\frac{\partial V}{\partial x}\right)_y$$

But $\partial y = \partial P$ (as y = P) and $\partial x = \partial S$ (as x = S). Hence

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

(iii)

This is Maxwell's third thermodynamic relation.

Maxwell's Fourth Relation: Substitute x = T and y = P in equation (5.5), so that

$$\frac{\partial T}{\partial x} = 1, \ \frac{\partial T}{\partial y} = 0$$

$$\frac{\partial P}{\partial x} = 0, \ \frac{\partial P}{\partial y} = 1$$

Putting these values in equation (5.5), we get

$$-\left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial S}{\partial y}\right)_x$$

But $\partial y = \partial P$ (as y = P) and $\partial x = \partial T$ (as x = T). Hence

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \hspace{3cm} …$$

(iv)

This is Maxwell's fourth thermodynamic relation.

Relations (i), (ii), (iii) and (iv) are the four important thermodynamic relations and any of these relation depending on its suitability, can be used while solving a particular problem.

5.6 APPLICATIONS OF MAXWELL'S THERMODYNAMIC RELATIONS

5.6.1 SPECIFIC HEAT OF A SUBSTANCE

Heat capacity per unit mass is known as specific heat and is represented by the letter C. Thus

$$C = \frac{\text{Heat Capacity}}{\text{Mass}} = \frac{Q/\Delta T}{m} = \frac{Q}{\Delta T.m} \hspace{2cm} … \ (5.6)$$

Thus specific heat of a material is the quantity of heat required so as to raise the temperature of unit mass of the materials through 1 degree. The unit of specific heat in M.K.S system is joule per kg per °C' (J/kg°C).

The above definition of specific heat is sufficient for solids and liquids but not for gases because from equation (5.6), specific heat of gas may vary from zero to infinity.

For example, if a gas is compressed there is rise in temperature without supplying any heat to the gas. Thus

$$C = \frac{Q}{\Delta T.m} = 0 \hspace{3cm} (\because Q=0) \quad … (5.7)$$

On the other hand if heat is supplied to the gas and the gas is allowed to expand such that there is no rise in temperature, then

$$C = \frac{Q}{\Delta T.m} = \infty \hspace{3cm} (\because \Delta T =0) \quad … (5.8)$$

Hence, in order to find the value of the specific heat of a gas, either the pressure or the volume has to be kept constant. Consequently we have two specific heats.

The **Specific heat at constant volume** which is defined as the amount of heat required to raise the temperature of unit mass of a gas through 1 °C when its volume is kept constant. It is denoted by C_v and given as

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \qquad\qquad (5.9)$$

The **Specific heat at constant pressure** which is defined as the amount of heat required to raise the temperature of unit mass of a gas through 1 °C when its pressure is kept constant. It is denoted by C_P and given as

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \qquad\qquad (5.10)$$

5.6.2 RELATION BETWEEN C_P AND C_V

(i)   The specific heats at constant pressure and at constant volume are given as

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad (\because \partial Q = T\,\partial S) \qquad (5.11)$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad\qquad (5.12)$$

Now, if the entropy S is regarded as a function of T and V and since dS is a perfect differential

or, $$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Differentiating with respect to T at constant P, we get

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

Multiplying both sides by T, we have

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

From Maxwell's second relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, so that

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

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

Using equations (5.11) and (5.12), we get

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \qquad (5.13)$$

(ii)   But pressure P is a function of T and V, and dP is perfect differential, hence

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

If the change takes place at constant pressure, $dP = 0$. Then

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

Differentiating with respect to T at constant P, we get

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

Substituting this value in equation (5.13), we get

$$C_P - C_V = T\left[-\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right] \left(\frac{\partial V}{\partial T}\right)_P$$

or $$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 \qquad (5.14)$$

But the coefficient of volume elasticity $E = -\left(\frac{\partial P}{\partial V/V}\right)_T = -V\left(\frac{\partial P}{\partial V}\right)_T$ and coefficient of volume expansion $\alpha = \left(\frac{\partial V/V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, then equation (5.14) becomes

$$C_P - C_V = TE\alpha^2 V \qquad (5.15)$$

(iii)   For a perfect gas, the equation of state is

$$PV = RT$$

Differentiating it with respect to T at constant V, and at constant P, we have

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \text{ and } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Hence equation (5.13) becomes

$$C_P - C_V = T\left(\frac{R}{V}\right)\left(\frac{R}{P}\right) = \frac{R^2 T}{PV} = \frac{R^2 T}{RT}$$

or $$C_P - C_V = R \qquad (5.16)$$

(iv)   For a van der Waal's gas, the equation of state is

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

Where a and b are constants

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

or, $\qquad P = \frac{RT}{(V - b)} - \frac{a}{v^2}$ $\qquad\qquad\qquad\qquad\qquad$ (5.17)

Differentiating equation (5.17) with respect to T at constant V, we obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{(V - b)} \qquad\qquad\qquad\qquad (5.18)$$

Differentiating equation (5.18) with respect to T at constant P, we obtain

$$0 - \frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{(V - b)} - \frac{RT}{(V - b)^2}\left(\frac{\partial V}{\partial T}\right)_P$$

or $\qquad \left(\frac{\partial V}{\partial T}\right)_P\left[\frac{RT}{(V - b)^2} - \frac{2a}{V^3}\right] = \frac{R}{(V - b)}$

or $\qquad \left(\frac{\partial V}{\partial T}\right)_P = \dfrac{\left(\frac{R}{(V - b)}\right)}{\left[\frac{RT}{(V - b)^2} - \frac{2a}{V^3}\right]}$ $\qquad\qquad$ … (5.19)

Substituting the value of $\left(\frac{\partial P}{\partial T}\right)_V$ from equation (5.18) and the value of $\left(\frac{\partial V}{\partial T}\right)_P$ from equation (5.19) in equation (5.13), we get

$$C_P - C_V = \dfrac{T\left(\frac{R}{(V - b)}\right)\left(\frac{R}{(V - b)}\right)}{\left[\frac{RT}{(V - b)^2} - \frac{2a}{V^3}\right]}$$

Dividing by $\dfrac{RT}{(V - b)^2}$ in numerator and denominator in RHS of the above equation

$$C_P - C_V = \dfrac{R}{\left[1 - \frac{2a}{V^3} \cdot \frac{(V - b)^2}{RT}\right]}$$

Neglecting b in comparison to V

$$C_P - C_V = \dfrac{R}{1 - \frac{2a}{V^3} \cdot \frac{V^2}{RT}} = \dfrac{R}{1 - \frac{2a}{VRT}} = R\left(1 - \frac{2a}{VRT}\right)^{-1}$$

Expanding binomially and neglecting the higher power terms, we obtain

$$C_P - C_V = R\left(1 + \frac{2a}{VRT}\right) \qquad\qquad\qquad …(5.20)$$

5.6.3 CLAUSIUS-CLAPEYRON LATENT HEAT EQUATION

Maxwell's second thermodynamic relation is written as:

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

Multiplying both sides by T, we have

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

But, $T\partial s = \partial Q$ (from second law of thermodynamics). Hence

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

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 mean that at constant temperature the heat absorbed or liberated bring out simply a change in the volume of the substance. Therefore, this quantity of heat absorbed or liberated at constant temperature must be the latent heat and the change in volume must be due to a change of state. Considering a unit mass of substance, let L be the latent heat when the substance changes its volume from V_1 to V_2 at constant temperature, then

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

Substituting these values in the above expression

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

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

or $$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \qquad \qquad \text{…(5.21)}$$

This is the Clausius-Clapeyron latent heat equation.

5.6.4 ENERGY EQUATION

Let, a thermodynamic system undergoes an infinitesimal reversible process between two equilibrium states. Its general behavior may be expressed by the first and second laws of thermodynamics, which are

$$dQ = dU + PdV$$

and $$dQ = TdS$$

These give $dU + PdV = TdS$

or $dS = \dfrac{dU + PdV}{T}$

Making this substitution in Maxwell's 2nd relation $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$, 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 $\left(\dfrac{\partial U}{\partial V}\right)_T + P = T\left(\dfrac{\partial P}{\partial T}\right)_V$

or $\left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial P}{\partial T}\right)_V - P$ … (5.22)

This is called the first energy equation which infact shows the variation of internal energy with volume.

Again taking equation

$$dU = TdS - PdV$$

and dividing by dP, we get

$$\frac{dU}{dP} = T\frac{dS}{dP} - P\frac{dV}{dP}$$

where U, S and V are regarded as function of T and P. If T is kept constant then the derivatives becomes partial derivatives, and then

$$\left(\frac{dU}{dP}\right)_T = T\left(\frac{dS}{dP}\right)_T - P\left(\frac{dV}{dP}\right)_T$$

From Maxwell's fourth relation

$$\left(\frac{dS}{dP}\right)_T = -\left(\frac{dV}{dT}\right)_P$$

Therefore,

$$\left(\frac{dU}{dP}\right)_T = -T\left(\frac{dV}{dT}\right)_P - P\left(\frac{dV}{dP}\right)_T$$ (5.23)

This is the second energy equation which shows the variation of internal energy with pressure.

5.6.4.1 FOR IDEAL GAS

For 1 mole of an ideal gas, we have

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

or $$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

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

Putting this in eq. (5.22), we get

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad\qquad \dots (5.24)$$

Thus, the internal energy of an ideal gas is independent of its volume at constant temperature, which is Joule's Law.

5.6.4.2 FOR VAN DER WAALS' GAS

For 1 mole of a real gas, we have

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

Putting this value in eq. (5.22), 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 van der Waal's equation, we have

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} \qquad\qquad \dots(5.25)$$

which is positive. This means that the internal energy of an actual gas does depend on its volume at constant temperature.

5.6.5 JOULE-THOMSON EFFECT

When a gas under a constant pressure is made to pass through an insulated porous-plug to a region of lower constant pressure, it suffers a change in temperature. This is called the 'Joule - Thomson or Joule-Kelvin effect'. The process is called the 'throttling process'. The change in temperature is proportional to the pressure-difference between the two sides of the plug. At ordinary temperature, all gases, expect hydrogen and helium, show a cooling effect while hydrogen and helium show a heating effect.

Let us consider 1 mole of gas. Let P_1 and V_1 be its pressure and volume before passing and P_2 and V_2 the pressure and volume after passing through the porous plug. The net external work done by the gas in passing through the plug is then $P_2V_2 - P_1V_1$. Since there is no heat-exchange between the gas and its surroundings, this work must come from the internal energy of the gas. Thus, if U_1 and U_2 be the internal energies of the gas before and after passing through the plug, we have from the first law of thermodynamics

$$U_1 - U_2 = P_2V_2 - P_1V_1$$

or $\qquad U_1 + P_1V_1 = U_2 + P_2V_2$

$$U + PV = constant$$

The quantity $(U + PV)$ which remains constant during a throttling process, is called the enthalpy (H) of the gas. Thus, we may write

$$dH = d(U + PV) = 0$$

$$dU + PdV + VdP = 0$$

But $dU + PdV = dQ$ and $dQ = TdS$ (first and second law respectively). Therefore,

$$TdS + VdP = 0 \qquad\qquad\qquad …(5.26)$$

Let as assume that the entropy S is the function of variables P and T. Since dS is a perfect differential, we have

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

Substituting this value of dS in equation (5.26), we get

$$T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP + VdP = 0 \qquad\qquad …(5.27)$$

But $dQ = TdS$. Therefore, $T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$ where C_P is the specific heat at constant pressure.

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

Therefore equation (5.27) becomes

$$C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP + VdP = 0$$

or $\qquad C_P dT = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$

$$\frac{dT}{dP} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \qquad\qquad … (5.28)$$

Since, the enthalpy H remains constant during throttling process, we write $\frac{dT}{dP}$ as $\left(\frac{\partial T}{\partial P}\right)_H$ which is called the Joule-Thomson coefficient μ. Thus,

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \qquad \text{… (5.29)}$$

Integrating it, we get the temperature-change for finite drop in pressure from P_1 to P_2 as

$$\Delta T = \frac{1}{C_P}\int_{P_1}^{P_2}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]dP \qquad \text{…(5.30)}$$

5.6.5.1 FOR IDEAL GAS

For 1 mole of a perfect gas, the equation of state is PV=RT.

Differentiating it with respect to T, taking P constant, we have

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$T\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}T = V \qquad \text{(since PV=RT)}$$

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = 0$$

Substituting this value for Joule-Thomson coefficient, we get

$$\mu = 0 \qquad \text{…(5.31)}$$

Thus, the Joule-Thomson effect for a perfect gas is zero.

5.6.5.2 FOR VAN DER WAALS' GAS

For a van der Waals' gas, we have

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

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, $$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\left(P + \frac{a}{V^2}\right) - \frac{2a}{V^3}(V - b)}$$

$$= \frac{R}{\frac{RT}{V-b} - \frac{2a}{V^3}(V-b)} = \frac{R(V-b)}{RT - \frac{2a}{V^3}(V-b)^2}$$

or, $$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{RT(V-b)}{RT - \frac{2a}{V^3}(V-b)^2} - V$$

$$= \frac{-RTb + \frac{2a}{V^2}(V-b)^2}{RT - \frac{2a}{V^3}(V-b)^2}$$

$$= \frac{2aV(V-b)^2 - RTV^3 b}{RTV^3 - 2a(V-b)^2} \qquad \text{…(5.32)}$$

Since, a and b are very small quantities, we replace $2aV(V - b)^2$ by $2aV^3$ in the numerator and ignore $2a(V - b)^2$ in comparison with RTV^3 in the denominator. Then, we get

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2aV^3 - RTV^3b}{RTV^3}$$

$$= \frac{2a}{RT} - b$$

Substituting this result in equations (5.28) and (5.29), we get

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right] \qquad \qquad \dots(5.33)$$

and $$\Delta T = \frac{1}{C_P}\int_{P_1}^{P_2}\left[\frac{2a}{RT} - b\right]dP = \frac{\frac{2a}{RT} - b}{C_P}(P_2 - P_1).$$

The pressure is lower on the emergent side of the porous plug ($P_2 < P_1$). Hence, we may write as

$$\Delta T = -\frac{\frac{2a}{RT} - b}{C_P}(P_2 - P_1) \qquad \qquad \dots(5.34)$$

This expression shows the Joule-Thomson effect for real gas.

Joule-Thomson Effect as due to deviation from Joule's law and Boyle's law

The Joule-Thomson effect, as deduced in the last equation, is expressed as

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

By Maxwell's fourth relation $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$.

On substitution,

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right]$$

Now $dU + PdV = dQ$ and $dQ = TdS$. Therefore

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{P\,\partial V}{\partial P}\right)_T + V\right]$$

$$C_P\left(\frac{\partial T}{\partial P}\right)_H = -\left[\left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T\right] \qquad \qquad \dots(5.35)$$

According to Joule's law, U_T is constant, while according to Boyle's law $(PV)_T$ is constant. Thus, the first term on the right-hand side represents deviation from the Joule's law while the second term represents deviation from the Boyle's law. The Joule-Thomson effect is thus the resultant of these two deviations.

5.6.6 TEMPERATURE OF INVERSION

The expression (5.34) shows that if $\frac{2a}{RT} > b \; or \; T < \frac{2a}{Rb}$ then ΔT will be negative i.e., the gas will be cooled on passing through the porous plug. If $T > \frac{2a}{Rb}$, then ΔT will be positive and the gas will be warmed. At $T = \frac{2a}{Rb}$, we have $\Delta T = 0$ i.e., there is no change in the temperature of the gas on passing through the porous plug. This temperature is called the *temperature of inversion* T_i. At this temperature, the Joule-Thomson coefficient $\mu = 0$.

The temperature of inversion T_i, the Boyle temperature T_B and the critical temperature T_c are related by the relation

$$T_i = \frac{2a}{Rb} = \frac{27}{4} T_c = 2T_B \qquad \qquad \ldots(5.36)$$

which gives expressions for these quantities in terms of the van der Waals' constants as

$$T_B = \frac{a}{Rb} \qquad T_c = \frac{8a}{27Rb} \quad \text{and} \quad T_i = \frac{2a}{Rb} \qquad \ldots (5.37)$$

For most gases, the temperature of inversion is greater than the ordinary temperature. Hence, a cooling effect is obtained. However, for hydrogen and helium, the T_i is much lower than the ordinary temperature and hence they show heating effect in porous plug experiment. If they are pre-cooled below their temperature of inversion, they will also show a cooling effect.

An accurate expression for inversion temperature may be obtained by equating the exact value of $T\left(\frac{\partial V}{\partial T}\right)_P - V$, given by eq. (5.32), to zero. That is

$$2aV(V - b)^2 - RT_i V^3 b = 0$$

or, $\qquad T_i = \frac{2a(V-b)^2}{RV^2 b}$ $\qquad \qquad \ldots(5.38)$

5.6.7   RATIO OF ADIABATIC AND ISOTHERMAL ELASTICITIES

The coefficient of volume elasticity is defined by

$$E = \frac{\text{Stress}}{\text{Volume strain}} = -\frac{dP}{dV/V} = -V\frac{dP}{dV} \qquad \ldots (5.39)$$

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

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

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

Hence, $\qquad \dfrac{E_S}{E_T} = \dfrac{\left(\frac{\partial P}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial V}\right)_T} = \dfrac{\left(\frac{\partial P}{\partial T}\cdot\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial S}\cdot\frac{\partial S}{\partial V}\right)_T} = \dfrac{\left(\frac{\partial P}{\partial T}\right)_S}{\left(\frac{\partial P}{\partial S}\right)_T} \times \dfrac{\left(\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial S}{\partial V}\right)_T}$

But $\qquad \left(\frac{\partial P}{\partial T}\right)_S = \left(\frac{\partial S}{\partial V}\right)_P$ From Maxwell's third relation

$\qquad\qquad\quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$ From Maxwell's first relation

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

$\qquad\qquad\quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ From Maxwell'second relation

Making use of these relations, we have

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

or $\qquad\qquad \frac{E_S}{E_T} = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_V = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V}$

$$\frac{E_S}{E_T} = \frac{T\left(\frac{\partial S}{\partial T}\right)_P}{T\left(\frac{\partial S}{\partial T}\right)_V} = \frac{\left(\frac{\partial Q}{\partial T}\right)_P}{\left(\frac{\partial Q}{\partial T}\right)_V} \qquad\qquad\qquad (T\,\partial S = \partial Q)$$

But $\qquad\qquad \left(\frac{\partial Q}{\partial T}\right)_P = C_p$ and $\left(\frac{\partial Q}{\partial T}\right)_V = C_v$

Hence $\qquad\qquad \frac{E_S}{E_T} = \frac{C_p}{C_v} = \gamma \qquad\qquad\qquad\qquad$ … (5.40)

Thus, the ratio of adiabatic and isothermal elasticities for any substance is equal to the ratio of the specific heats of the substance at constant pressure and at constant volume.

Self Assessment Questions (SAQ)

1 Show that Joule-Thomson effect for a perfect gas is zero.

2 If the process is isobaric, prove that $\left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_S$

3 If the process is isobaric, prove that $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$

5.7 EXAMPLES

Example 1. For a metallic copper disc at 300 K, the following values are known: Isothermal compressibility, $K = 7.78 \times 10^{-12}$ N/m^2; Specific heat at constant pressure, $C_P = 24.5$ J/mol K; Volume, V = 7.06 cm^3/mol and coefficient of volume expansion, $\alpha = 50.4 \times 10^{-6}$ K^{-1}.

Determine Specific heat at constant volume, C_V.

Solution: We know that

$$C_P - C_V = TE\alpha^2 V$$

and $E = \frac{1}{K}$

so that $C_P - C_V = \frac{T\alpha^2 V}{K}$

Here V = 7.06 cm³/mol = 7.06 × 10⁻⁶ m³/mol

Hence $C_P - C_V = \frac{300 \times 7.06 \times 10^{-6} \times (50.4 \times 10^{-6})^2}{7.78 \times 10^{-12}}$

$C_P - C_V = 0.6915$ J/mol-K

$C_V = C_P - 0.6915$ J/mol-K

$C_V = (24.5 - 0.6915)$ J/mol-K

$C_V = 23.8085$ J/mol-K

Example 2. Calculate under what pressure water would boil at 150⁰C if the change in specific volume when 1 gram of water is converted into steam is 1676 c.c. Given latent heat of vaporization of steam = 540 cal per gram; J = 4.2 × 10⁷ erg/cal, and one atmosphere pressure = 10⁶ dynes/cm².

Solution: From Maxwell's second relation

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

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

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

Here ∂Q = 540 cals. = 540×4.2×10⁷ ergs.

∂V = 1676 c.c.   T = 100 ⁰C = 373 K.   and 150 ⁰C = 423 K.

Hence ∂T = 423 – 373 = 50 K, ∂P = ?

Substituting these values in above equation

$$\frac{540 \times 4.2 \times 10^7}{1676} = 373\left(\frac{\partial P}{50}\right)$$

$$\partial P = \frac{50 \times 540 \times 4.2 \times 10^7}{373 \times 1676}$$

$\partial P = 1.815 \times 10^6$ dynes/cm²

= 1.815 atmosphere.

Hence the required pressure at which water would boil at 150 ⁰C = 1.815 + 1

= 2.815 atm.

5.8   SUMMARY

A thermodynamic relations is a rule which is obtained by a simple thermodynamic reasoning and applies to most of the systems. The usefulness of the above relations lies in the fact that they relate quantities which seem unrelated. They help us to link data obtained in various ways or replace a difficult measurement by another one. They can also be used to obtain values of one variable from the calculations of another variable. These relations are very general and immensely useful as they simplify analysis of thermodynamic systems. The most convenient way to derive these relations is to use partial differentiation. They can also be derived from other methods.

5.9   GLOSSARY

Perfect Differential	A quantity whose line integral over it is path independent.
Homogeneous System	A system whose chemical composition and physical properties are the same in all parts of the system, or change continuously from one point to another.
State Variable	Temperature, pressure, volume, internal energy, enthalpy and entropy are state variables.
Internal Energy	Energy contained within the system.
Enthalpy	Total heat content of the system.
Entropy	Lack of order or predictability; gradual decline into disorder.
Isothermal Process	A change of a system in which the temperature remains constant.
Adiabatic Process	One that occurs without transfer of heat or matter between a thermodynamic system and its surrounding.
Specific Heat	Amount of heat per unit mass required raising the temperature by 1^0 C.
Heat Capacity	Amount of heat needed to raise the system's temperature by 1^0 C.
Latent Heat	Energy released or absorbed by a thermodynamic system during a isothermal process.
Cyclic Process	A process consists of a series of changes which returned the system back to its initial state.
Throttling Process	In this process enthalpy remains constant, work done is zero.
Young's Modulus	It is a measure of the stiffness of a solid material.
Volume Expansion Coefficient	It is increase in volume per unit original volume per Kelvin rise in temperature.

5.10 ANSWERS TO SELF ASSESSMENT QUESTIONS

1.   For 1 mole of a perfect gas, the equation of state is PV=RT.

Differentiating it with respect to T, keeping P constant, we have

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$T\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}T = V \qquad \text{(since PV=RT)}$$

or, $$T\left(\frac{\partial V}{\partial T}\right)_P - V = 0$$

Substituting this valve in Joule-Thomson coefficient, we get

$$\mu = 0$$

Thus, the Joule-Thomson effect for a perfect gas is zero.

2.   The pressure P as a function of two independent variables S and T i.e.,

$$P = P(S, T)$$

so that $$dP = \left(\frac{\partial P}{\partial S}\right)_T dS + \left(\frac{\partial P}{\partial T}\right)_S dT$$

If the process is isobaric i.e., dP = 0, then

$$\left(\frac{\partial P}{\partial S}\right)_T dS + \left(\frac{\partial P}{\partial T}\right)_S dT = 0$$

$$\left(\frac{\partial P}{\partial S}\right)_T dS = -\left(\frac{\partial P}{\partial T}\right)_S dT$$

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

5.3   The pressure P as a function of two independent variables T and V i.e.,

$$P = P(T, V)$$

so that $$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

If the process is isobaric i.e., dP = 0, then

$$\left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV = 0$$

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

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

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

5.11 REFERENCES

Chakrabarti, P.K., (2006), Theory and Experiment on Thermal Physics, New Central Book Agency (P) Ltd., Howrah.

Garg, S.C., Bansal, R.M. and Ghosh, C.K., (2006), Thermal Physics, Tata McGraw-Hill, New Delhi.

Kittel, C., (2007), Thermal Physics, Dover Publications, Inc. Mineola, New York.

Lal, B., Subrahmanyam, N. and Hemne, P.S. (2015), Heat, Thermodynamics and Statistical Physics, S. Chand Publishing, New Delhi.

Reif, F., (2013), Fundamental of Statistical and Thermal Physics, Tata McGraw-Hill, New Delhi.

Tripathi, D.N. and Singh, R.B., (2012), Thermal Physics, Kedar Nath Ram Nath, Meerut.

Zemansky, M.W., Dittman, R.H. and Chattopadhyay, A.K. (2011), Heat and Thermodynamics, Tata McGraw-Hill, New Delhi.

Kumar, A. and Taaneja, S.P. (2016), Thermal Physics and Statistical Mechanic, R. Chand & Co., New Delhi.

5.12 TERMINAL QUESTIONS

s1. Using Maxwell's thermodynamic relations, prove that for any substance, the ratio of the adiabatic and isothermal elasticities is equal to the ratio of its two specific heats.

2. Derive Maxwell's thermodynamic equations connecting the thermodynamic quantities.

3.   What is Joule-Thomson effect? Derived Joule Thomson effect with the help of Maxwell's thermodynamic relations.

4. Write shorts notes on

(i)   Clausius Clapeyron Latent Heat equation

(ii)   Temperature Inversion

(iii)   Joule-Thomson Effect

5.   Prove that enthalpy remains constant in a throttling process.

6.   Define Joule Effect. Derive the Joule effect of an Ideal gas with the help of Maxwell's thermodynamic relations

7.   By the use of relevant Maxwell equation, show that an adiabatic expansion always produces cooling effect.

8.   There is no Joule-Thomson effect for a perfect gas. Explain.

9.   What is the most important application of Joule-Kelvin effect.

10.   Show that for a perfect gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

11.   What do you mean by energy equation? Show the internal energy

(i) of an ideal gas is independent of pressure and volume and

(ii) of a van der Waals' gas depends on volume as $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$

12.   Show that $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = TE\beta - P$

13.   Using Maxwell's thermodynamical relations, prove that the ratio of the adiabatic to the isochoric pressure coefficient of expansion is equal to $\frac{\gamma}{\gamma-1}$

14.   Establish the Clausius-Clapeyron's equation

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

From Maxwell's thermodynamical relation, explain the effect of pressure on (i) boiling point of liquid and (ii) melting point of a solid.

15. 0.5 kg of water is subjected to reversible compression from 1 to 5×10^8 Pa at 0^0C. Calculate the (i) heat transferred (ii) work done (iii) change in internal energy (iv) rise in temperature if the compression were adiabatic.

16. The pressure of 100g of water is increased reversibly and adiabatically from 0 to 10^{-8} Pa. Calculate the rise in temperature when the initial temperature is 0^oC

Specific volume v $= 1\times10^{-3}$ m^3/kg, expansitivity $= -68\times10^{-6}$ K^{-1}, $C_p = 4.2$ kJ/(kg.K)

17. At a constant temperature 300K, one mole of mercury is subjected to compression from 0 to 1000 atm. Calculate (i) the quantity of heat rejected (ii) the work done (iii) the change in internal energy. Given Compressibility of mercury K$= 3.84\times10^{-11}$ N^{-1}m^2, coefficient of volume expansion $\beta = 18\times10^{-5}$ K^{-1}, volume per mole $= 14.7\times10^{-6}$ m^3

18. Calculate the drop in temperature produced by adiabatic throttling process in the case of oxygen when the pressure is reduced by 50 atm. Initial temperature of the gas is 27^0C. Given that the gas obeys van der Waals' equation and

$a = 1.32\times10^{12}$ cm^4 dynes/ mole^2

$b = 31.2$ cm^3/mole

$C_p = 7.0$ cal/mole-K

19. Find the change in boiling point of water for 100 cm change in mercury pressure if the specific volume of steam is 1601 cm^3/gram at 100^0 C and 76 cm mercury pressure. Take latent heat as 5366 cal/gram.

20. Show that for a homogenous fluid $C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

where C_P and C_V are the specific heats at constant pressure and constant volume respectively, and other symbols have their usual meanings.

(i) Also show that $C_P - C_V = TE\alpha^2 V$

where E is the bulk modulus of isothermal elasticity, and α the coefficient of volume expansion.

(ii) Hence prove that for a perfect gas $C_P - C_V = R$

(iii) Hence prove that for a real (van der Waal's) gas $C_P - C_V = R\left(1 + \frac{2a}{VRT}\right)$

21. Objective Questions

(i)   From Maxwell's thermodynamic relations $\frac{E_S}{E_T} = ?$

   (a) 1   (b) $\frac{1}{\gamma}$ (c) γ (d) 0

(ii)   The value of $C_P - C_V$ for an ideal gas is

   (a) $TE\alpha V^2$ (b) $T^2 E\alpha V$ (c) $TE\alpha^2 V$ (d) $TE^2 \alpha V^2$

(iii)   Hydrogen and helium at normal temperature is porous plug experiment show

   (a) Heating effect   (b) Cooling effect

   (c) Sometimes cooling and sometimes heating   (d) None of these

(iv)   Which of the following is not a Maxwell thermodynamical relation

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

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

(v)   The temperature of inversion of a gas is

   (a) $\frac{a}{Rb}$ (b) $\frac{2a}{Rb}$ (c) $\frac{b}{Ra}$ (d) $\frac{2b}{Ra}$

UNIT 6 THERMODYNAMIC POTENTIALS AND THEIR APPLICATIONS

CONTENTS

6.1   INTRODUCTION

We know that the internal energy (U) of a thermodynamic system is a state function which means that a system undergoes the same change in U when moved from one equilibrium state to another, irrespective of the path followed. This path independence of internal energy makes it very useful, however, not a uniquely useful quantity. There could be some other combinations of the state variables (i.e. pressure p, volume V, temperature T, and entropy S) which when added with the internal energy function may result quantities having dimensions of energy and preserve the nature of path independence. These new state functions are very useful and termed as thermodynamic potentials. However, all such combinations may not be helpful in the study of a thermodynamic system but the combinations like U + PV, U – TS and U + PV – TS are found to have significant role and are named as enthalpy (H), Helmholtz function (F), and Gibbs function (G) respectively. All the thermodynamic properties of a system can be calculated by differentiating these functions. In this unit, we explored the importance and usefulness of these potentials.

For a paramagnetic specimen, the tiny dipoles may be aligned uniformly in the applied field direction at lower temperatures. However, at higher temperatures, the dipoles point in random directions because the thermal energy is much larger than the magnetic energy irrespective of applied magnetic field. Interestingly, the temperature dependence of alignment of paramagnetic dipole moments could be utilized to cool the specimen to ultra-low temperatures and method of the same is discussed in this unit. Detailed idea about latent heat equations, triple point and phase transitions are also discussed in this unit.

6.2   OBJECTIVES

By reading this unit, the learner will be able to understand.

- How thermodynamic variables can be combined to have state functions with units of energy?
- The definitions of thermodynamic potentials.
- The significance and applications of thermodynamic potentials.
- How Maxwell's equations can be obtained using thermodynamic potentials?
- How adiabatic demagnetisation leads to cooling effect?
- What is Clausius Clapeyron equation?
- The significance of studying phase transition in thermodynamics.
- The triple point and its properties; TdS equations and stretching of wire.

6.3   THERMODYNAMIC VARIABLES

The thermodynamic state of a system can be determined by quantities like temperature (T), Volume (V), pressure (P), internal energy (U), entropy (S) etc. These quantities are known as

thermodynamic variables, or parameters of the system. Any change in one of the variables results in a change in the thermodynamic state of the system.

Thermodynamic variables are the quantities like pressure, volume and temperature, which help us to study the behaviour of a thermodynamic system. There are some other thermodynamic variables such as entropy, internal energy etc. but these thermodynamic variables can be expressed in terms of pressure, volume and temperature. These properties undergo change when the system passes from one state to another i.e., thermodynamic variables are path dependent. These variables are also known as macroscopic co-ordinates.

6.4   *THERMODYNAMIC POTENTIALS*

A thermodynamic potential is a scalar quantity used to represent the thermodynamic state of a system. The concept of thermodynamic potentials was introduced by Pierre Duhem in 1886. Four common thermodynamic potentials are:

Internal energy (U) is the capacity to do work plus the capacity to release heat.

Gibbs energy (G) is the capacity to do non-mechanical work.

Enthalpy (H) is the capacity to do non-mechanical work plus the capacity to release heat.

Helmholtz free energy (F) is the capacity to do mechanical plus non-mechanical work.

Thermodynamic potentials are of practical importance in studying the equilibrium conditions of a thermodynamic system. 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. Taking two of the four state variables P,V,T and S at a time, there are six variable pairs, i.e., (P,V), (P,T), (P,S), (V,T), (V,S), (T,S) corresponding to each pair, we can write a thermodynamic relation.

There exists certain relation between these thermodynamic variables. The first and second law of thermodynamics provide two relations given as

$$dQ = dU + PdV$$

and $$dQ = TdS$$

Therefore, $$TdS = dU + PdV$$

or, $$dU = TdS - PdV$$

This expresses the change in internal energy of the system in terms of four thermodynamic variables. However, for a complete knowledge of the system, certain other

relations are required and for this purpose we introduce some functions of the variables P, V, T and S which are known as thermodynamic potentials or the thermodynamic functions. There are four principal thermodynamic potentials and we shall discuss them one by one.

6.4.1 INTERNAL ENERGY (U)

The internal energy U of the system is a thermodynamic variable which characterises the system. This is also called the intrinsic energy or internal energy. When the system passes from one state to another, the change in the internal energy is independent of the path followed in between the two states. The internal energy of a system is defined as the equation

$$dU = dQ - dW$$

where $dW = PdV$ is the external work done while $dQ = TdS$

$$dU = TdS - PdV \qquad\qquad ... (6.1)$$

(a) For an adiabatic process

$$dQ = 0$$

$$dU = -PdV$$

i.e., the work done by the system in an adiabatic process is at the expense of its internal energy.

(b) For an isochoric adiabatic process

$$dV = 0 \text{ and } dQ = 0$$

$$dU = 0 \text{ or } U= \text{constant}$$

i.e., the internal energy of system remains constant in an isochoric adiabatic process.

6.4.2 HELMHOLTZ FREE ENERGY (F)

The Helmholtz free energy is also called as 'Helmholtz function' or 'Thermodynamic Potential at constant volume' and It is defined by the equation

$$F = U - TS.$$

Since U, T and S are perfect differentials, F is also a perfect differential. When a system undergoes an infinitesimal reversible change from an initial equilibrium state to a final equilibrium state, the Helmholtz free energy changes by an amount given by differentiating the above relation as

$$dF = dU - TdS - SdT$$

But $dU = TdS - PdV$, as shown in the earlier case.

$$dF = (TdS - PdV) - TdS - SdT$$

$$dF = -SdT - PdV \qquad\qquad ... (6.2)$$

This equation gives the change in Helmholtz free energy during an infinitesimal reversible process.

(a) For Reversible isothermal process

$$dT = 0$$

$$dF = -PdV \text{ or } PdV = -dF$$

Thus the work done in a reversible isothermal process is equal to the decrease in Helmholtz free energy.

(b) For isothermal isochoric process

$$dT = 0 \text{ and } dV = 0$$

$$dF = 0 \text{ or } F = \text{Constant}$$

i.e., the Helmholtz free energy remains constant during isothermal isochoric process.

6.4.3 ENTHALPY (H)

Enthalpy is an extensive thermodynamical property and is of particular significance. It is defined as

$$H = U + PV$$

For an infinitesimal reversible change, we get

$$dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP \qquad\qquad (\text{Equation 6.1})$$

$$dH = TdS + VdP \qquad\qquad ... (6.3)$$

(a) For reversible isobaric process

$$dP = 0$$

$$dH = TdS = dQ$$

i.e., for an isobaric process, the change in enthalpy is equal to the heat absorbed.

(a) For an isobaric adiabatic process

$$dP = 0 \text{ and } dQ = 0$$

$$dH = 0 \text{ or } H = \text{Constant}$$

i.e., enthalpy remains constant in a reversible isobaric adiabatic process.

6.4.4 GIBBS' FREE ENERGY (G)

This is also known as 'Gibb's Function' or 'Thermodynamic Potential at constant pressure'. It is defined as

$$G = H - TS$$

For an infinitesimal reversible process

$$dG = dH - TdS - SdT$$

But $dH = TdS + VdP$

$$dG = VdP - SdT \qquad \qquad \text{... (6.4)}$$

(a) For an isothermal isobaric process

$$dT = 0 \text{ and } dP = 0$$

$$dG = 0 \text{ or } G = \text{Constant}$$

Thus, Gibbs free energy remains constant in an isothermal isobaric process.

6.5 *RELATIONS OF THERMODYNAMIC POTENTIALS AND VARIABLES*

The four quantities U(S,V), F(T,V), H(S, P), and G (P, T) are called thermodynamic potentials because the thermodynamic variables S, T, P and V can be derived from them by their differentiations with respect to the independent variables associated with them. Let us derive them.

6.5.1 THERMODYNAMIC POTENTIAL U (S, V)

Taking partial derivatives of the intrinsic energy equation (6.1) with respect to variable S, and V, we get

$$\left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -P \qquad \qquad \text{... (6.5)}$$

These are the relation connecting the internal energy U with the thermodynamic variable S, V, T and P.

Now since dU is perfect differential, we must have

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \text{(using equation 6.5)} \qquad ...(6.6)$$

This is the first thermodynamic relation of Maxwell.

6.5.2 THERMODYNAMIC POTENTIAL F (T, V)

Taking the partial derivatives of F from equation (6.2), we have

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial F}{\partial V}\right)_T = -P \qquad\qquad ... (6.7)$$

Since dF is a perfect differential, we have

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

or, $\qquad$ $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ $\qquad$ (using equation 6.7) $\qquad$ ... (6.8)

This is the second thermodynamic relation of Maxwell.

6.5.3 THERMODYNAMIC POTENTIAL H (S, P)

The partial derivatives of H from equation (6.3) are

$$\left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V \qquad\qquad ...(6.9)$$

Since dH is a perfect differential, we have

$$\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S$$

or, $\qquad$ $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ $\qquad$ (using equation 6.9) $\qquad$ ... (6.10)

This is the third thermodynamic relation of Maxwell.

6.5.4 THERMODYNAMIC POTENTIAL G (P, T)

The partial derivatives of G from equation (6.4) are

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S \qquad\qquad ... (6.11)$$

Since dG is a perfect differential, we have

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

or, $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ (using equation 6.11)   ... (6.12)

This is fourth thermodynamic relation of Maxwell.

Thus, the thermodynamical variables S, T, P and V can be written by using equation (6.5), (6.7), (6.9) and (6.11) as

$$S = -\left(\frac{\partial G}{\partial T}\right)_P = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial F}{\partial V}\right)_T$$

and $V = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$ ... (6.13)

These equations (6.13) give the value of thermodynamic variables in terms of thermodynamic potentials.

6.6   TDS EQUATIONS

6.6.1 FIRST TdS EQUATION

The entropy S of a pure substance can be taken as a function of temperature and volume. Then we can write

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Multiplying both side by T

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV$$

But $T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = C_V$ and from Maxwell's relations $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$. Substituting these values in the above equation, we get

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$ ... (6.14)

Equation (6.14) is called the First TdS equation

6.6.2 SECOND TdS EQUATION

The entropy S of a pure substance can also be regarded as a function of temperature and pressure. Therefore

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

Multiplying both side by T

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

But $T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$ and from Maxwell's relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$. Substituting these values in the above equation, we get

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \qquad\qquad ... (6.15)$$

Equation (6.15) is called the second TdS equation.

6.7   ADIABATIC STRETCHING OF A WIRE

Stretching a wire by applying tension is equivalent to the application of a negative pressure. Therefore, as in the case of adiabatic compression of a gas, there is a heating effect, an adiabatic stretching should result into a cooling effect. If F be the tension on a uniform wire causing an increase in its length dl, then the amount of work done is

$$dW = -Fdl.$$

The negative sign indicates that in this case the work is being done on the system i.e., the wire. Comparing this expression with the work done in a gas,

$$dW = PdV$$

The two situations are identical. We can obtain an expression by simply replacing V by l and P by $-F$ in the above equation. And then the combined first and second law of thermodynamics assumes the form

as $TdS = dU - Fdl$

or $dU = TdS + Fdl$

Now writing -F and l in place of P and V respesctively, in Maxwell's first thermodynamic relation

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

$$\left(\frac{\partial T}{\partial l}\right)_S = \left(\frac{\partial F}{\partial S}\right)_l = T\left(\frac{\partial F}{T\,\partial S}\right)_l = T\left(\frac{\partial F}{\partial Q}\right)_l$$

$$\left(\frac{\partial T}{\partial l}\right)_S = T\left(\frac{\partial F}{\partial T}\right)_l \left(\frac{\partial T}{\partial Q}\right)_l \qquad \text{... (6.16)}$$

Now considering length l as a function of F and T, we put dl as sum of partial differentials with respect to F and T and thus

$$dl = \left(\frac{\partial l}{\partial F}\right)_T dF + \left(\frac{\partial l}{\partial T}\right)_F dT$$

Under condition dl = 0, we get

$$0 = \left(\frac{\partial l}{\partial F}\right)_T \left(\frac{\partial F}{\partial T}\right)_l + \left(\frac{\partial l}{\partial T}\right)_F$$

or, $$\left(\frac{\partial F}{\partial T}\right)_l = \frac{-\left(\frac{\partial l}{\partial T}\right)_F}{\left(\frac{\partial l}{\partial F}\right)_T}$$

Putting the value of $\left(\frac{\partial F}{\partial T}\right)_l$ in eq. (6.16) we get

$$\left(\frac{\partial T}{\partial l}\right)_S = -\frac{T\left(\frac{\partial l}{\partial T}\right)_F}{\left(\frac{\partial l}{\partial F}\right)_T} \left(\frac{\partial T}{\partial Q}\right)_l \qquad \text{...(6.17)}$$

But the coefficient of linear expansion $\beta = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_T$ and the isothermal Young's modulus $Y_T = \frac{l}{A}\left(\frac{\partial F}{\partial l}\right)_T$; so that $\left(\frac{\partial F}{\partial l}\right)_T = \frac{l}{Y_T A}$ where A is area of cross section of the wire. Also $\left(\frac{\partial Q}{\partial T}\right)_l = C_l$, the specific heat at constant length in erg.deg^{-1}cm^{-1} .Putting these value in eq. (6.17), we have

$$\left(\frac{\partial T}{\partial l}\right)_S = -\frac{T\beta l Y_T A}{l}\frac{1}{C_l} = \frac{T\beta Y_T A}{C_l} = -\frac{T\beta Y_T A}{mC} \qquad \text{... (6.18)}$$

Where m is the mass per unit length and C is usual specific heat in ergs deg^{-1} gm^{-1}

Relation (6.18) may also be put in the form $\left(\frac{\partial T}{\partial F}\right)_S$. Thus

$$\left(\frac{\partial T}{\partial F}\right)_S = \left(\frac{\partial T}{\partial l}\right)_S \left(\frac{\partial L}{\partial F}\right)_S$$

$$= -\frac{T\beta Y_T A}{mC}\frac{1}{Y_S A}. \qquad\qquad [Y_S = \frac{l}{A}\left(\frac{\partial F}{\partial l}\right)_S]$$

$$= -\frac{T\beta}{mC}$$

where we have put $Y\_S = Y\_T$, which is closely true for all solids.

Thus $$dT = -\frac{T\beta}{mC}dF$$ … (6.19)

It is clear from this equation that if β is positive, an increase in tension would cool the wire. Thus, the wires of substances which expand on heating, should show a cooling when stretched adiabatically.

6.8   COOLING DUE TO ADIABATIC DEMAGNETISATION

In 1926, Debye and Giauque showed theoretically that the temperatures considerably below 1 K could be obtained by the process known as adiabatic demagnetisation of a paramagnetic salt (i.e., those substances for which the magnetic susceptibility χ is small, but positive).

Experimental Method

The apparatus used is shown in Figure 6.1. The paramagnetic specimen (salt) is suspended in a vessel A, which is surrounded by liquid helium. Liquid helium taken in Dewar flask D, is boiled under reduced pressure. It is surrounded by Dewar flask D_2 containing liquid hydrogen. The salt is in contact with the helium gas. A magnetic field of the order of 30,000 Gauss is applied.

When the magnetic field is switched on, the specimen (salt) is magnetised. The heat due to magnetisation is removed by first introducing hydrogen gas into A and then pumping it off with high vacuum pump, so that the specimen is thermally isolated. In the mean time, the specimen picks up the temperature. Now the magnetic field is switched off. Adiabatic demagnetisation of the specimen takes place and its temperature falls. The temperature of the specimen is determined by fitting a coaxial solenoid coil around the tube A and measuring the self-inductance and hence susceptibility of the substance at the beginning and the end of experiment. Then temperature T is called by Curie law $\chi = C/T$.

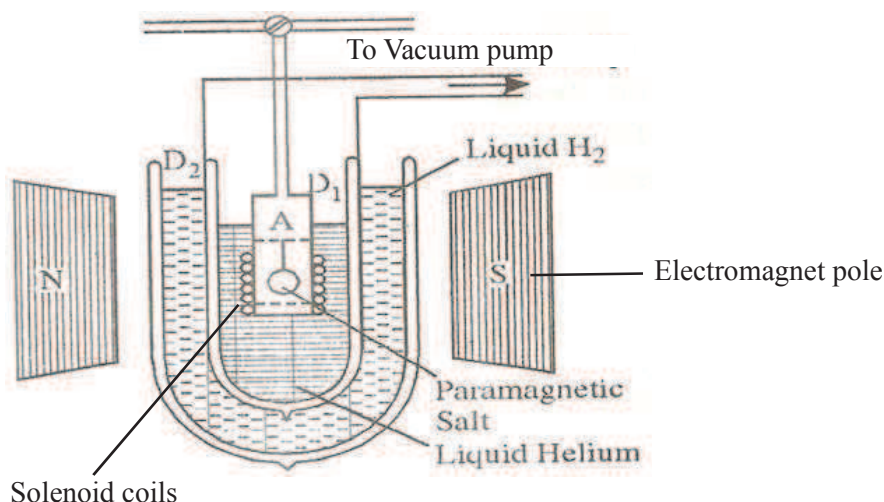The entire phenomena is also called Magneto-Caloric effect.

Fig. 6.1

Haas, in 1994, was able to produce temperature upto 0.002 K using a double sulphate of potassium and aluminium. Klerk, Stenland and Gorter used powder mixed crystal of chromium alum and aluminium alum and went down to a temperature of 0.0014 K.

Theory

When a paramagnetic material is placed in a magnetising field H, its elementary magnetic dipoles align parallel to the direction of the field. The magnetic moment thus produced per unit volume is called the intensity of magnetisation (I). According to Curie's law, this intensity of magnetisation is directly proportional to the magnetising field H and inversely proportional to temperature T of the paramagnetic substance. Thus

$$I \, \alpha \, \frac{H}{T}$$

$$I = C\left(\frac{H}{T}\right) \qquad \qquad ...(6.20)$$

where C is a constant, known as Curie constant.

If V is the volume of I mole of the substance then intensity of magnetisation of I mole of paramagnetic substance

$$M = IV$$

Substituting for I from equation (6.20), we get

$$M = CV\left(\frac{H}{T}\right) \qquad \qquad ...(6.21)$$

In the experiment, let 1 mole of paramagnetic substance is placed in magnetising field H. Then its thermodynamic behaviour can be expressed in terms of thermodynamic variables P, V, T and S. In thermodynamic system, an increase in pressure P results in decrease in volume V, analogously in our case any increase in H results in an increase in M. Hence 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 have $\qquad \left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H$

or, $\qquad \left(\frac{\partial T}{\partial H}\right)_S = \frac{-\left(\frac{\partial M}{\partial T}\right)_H}{\left(\frac{\partial S}{\partial T}\right)_H}$

Multiplying numerator and denominator by T, we get

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{-T\left(\frac{\partial M}{\partial T}\right)_H}{T\left(\frac{\partial S}{\partial T}\right)_H}$$

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{-T\left(\frac{\partial M}{\partial T}\right)_H}{\left(\frac{\partial Q}{\partial T}\right)_H} \qquad \qquad (T\partial S = \partial Q)$$

$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H \qquad \text{... (6.22)}$$

where $\left(\frac{\partial Q}{\partial T}\right)_H = C_H$, the specific heat of the substance at constant magnetic field H.

Since the process is carried out adiabatically (S = constant), we may write for infinitesimal change,

$$dT = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H dH$$

Therefore, when a field changes from H_1 to H_2, the change in temperature

$$\Delta T = -\frac{T}{C_H}\int_{H_1}^{H_2}\left(\frac{\partial M}{\partial T}\right)_H dH \qquad \text{... (6.23)}$$

Differentiating equation (6.21) with respect to T at constant H, we get

$$\left(\frac{\partial M}{\partial T}\right)_H = -\frac{CVH}{T^2} \qquad \text{... (6.24)}$$

Substituting this value in equation (6.23), we have

$$\Delta T = -\frac{T}{C_H}\int_{H_1}^{H_2}\left(-\frac{CVH}{T^2}\right) dH$$

$$\Delta T = \frac{CV}{C_H T}\int_{H_1}^{H_2} H dH$$

$$\Delta T = \frac{CV}{2C_H T}\left(H_2^2 - H_1^2\right) \qquad \text{...}$$

(6.25)

If the magnetic field is reduced from $H_1 = H$ to $H_2 = 0$, then the change in temperature will be

$$\Delta T = \frac{CV}{2C_H T}H^2 \qquad \text{... (6.26)}$$

The following conclusions can be drawn from the equation (6.26)

(i)   The temperature of paramagnetic solid decreases as the magnetising field is reduced (indicated by negative sign of ΔT)

(ii)   Greater is the initial field H and lower is the initial temperature T, greater is the temperature fall ΔT.

It is to be noted that here CV is the Curie constant per mole. If 1 gm of paramagnetic substance is taken, then CV would stand for Curie constant per gm.

6.9   CLAUSIUS CLAPEYRON LATENT HEAT EQUATION USING CARNOT'S CYCLE

6.9.1 THE FIRST LATENT HEAT EQUATION

Clapeyron in 1834, and Clausius in 1850, deduced an important equation which describes conditions governing changes of state, such as melting of solids and boiling of liquids. This is known as the 'Clausius-Clapeyron equation' or the 'first latent heat equation'

Let ABCD and EFGH represent the two isothermals at infinitely close temperatures T and (T+dT) respectively. Referring to Figure 6.2, the parts AB and EF correspond to the liquid state of the substance. At B and F, substance is purely in the liquid state. Along BC and FG, the change of state is in progress and the liquid and vapour states coexist in equilibrium. At C and G the substance is purely in vapour state. From C to D and G to H the substance is in the vapour state. Let P and (P+dP) be the saturated vapour pressures of the liquid at temperatures T and (T+dT) respectively and let V_1 and V_2 be the volumes of the substance at F and G respectively.

Let us draw two adiabatics from F and G meeting the lower isothermal at M and N respectively. Let us suppose that 1 gm of the substance is taken round a reversible Carnot cycle FGNMF, allowing it to expand isothermally along FG, adiabatically along GN, compressing it isothermally along NM and adiabatically along MF.

The amount of heat Q_1 absorbed along FG is equal to the latent heat of vaporisation (L+dL) at temperature (T+dT), as substance changes completely from liquid state at F to the vapour state at G. Also the quantity of heat Q_2 rejected along the isothermal compression NM, is L, the latent heat at temperature T. Here latent heat is supposed to vary with temperature.
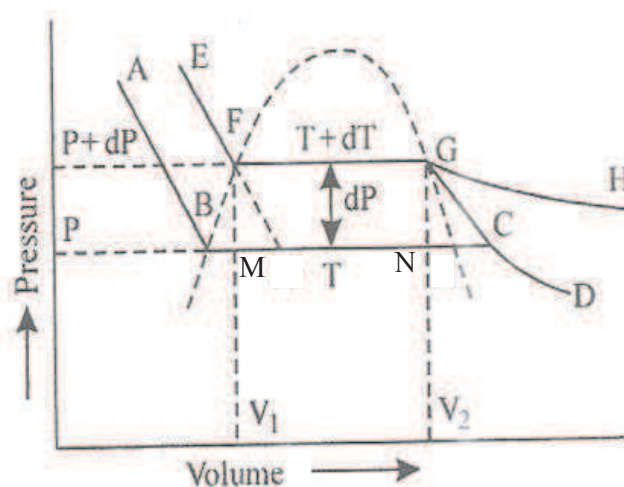
Fig. (6.2)

Applying the principle of Carnot's reversible cycle

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \qquad \text{or} \qquad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

or, $\qquad \frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2}$

We have $Q_1 = L + dL, Q_2 = L, T_1 = T + dT$ and $T_2 = T$

$$Q_1 - Q_2 = L + dL - L = dL \text{ and } T_1 - T_2 = T + dT - T = dT$$

$$\frac{dL}{L} = \frac{dT}{T}$$

$$dL = \frac{L}{T}dT \qquad \qquad ... (6.27)$$

The amount of heat converted into work during the cycle FGMNF is

$$Q_1 - Q_2 = L + dL - L = dL$$

But the work done during the Carnot cycle is given by the area FGMNF, which may be treated as a parallelogram.

Hence,

dL (in work unit) = Area FGMNF = FG × perpendicular distance between FG and NM

$$= (V_2 - V_1) \times dP$$

where V_2 and V_1 are the specific volumes in vapour and liquid state respectively, dP expresses the difference of pressure between FG and NM.

Substituting this value of dL in equation (6.27)

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

or, $\qquad \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \qquad \qquad ... (6.28)$

Eq. (6.28) is called the Clapeyron's latent heat equation and holds for both the changes of state, i.e., from liquid to vapour and solid to liquid.

Applications

1. Effect of change of pressure on the melting point

When a solid is converted into a liquid, there is change in volume

(i)   If V_2 is greater than V_1, then $\frac{dP}{dT}$ is a positive quantity. It means that the rate of change of pressure with respect to temperature is positive. In such cases, the melting point of the substance will increase with increase in pressure and vice versa

(ii)   If V_2 is less than V_1, then $\frac{dP}{dT}$ is a negative quantity. It means that the rate of change of pressure with respect to temperature is negative. In such cases, the melting point of the substance will decrease with increase in pressure and vice versa. In the case of melting of ice, the volume of water formed is less than the volume of ice taken. Hence V_2 is less than V_1.

Therefore, the melting point of ice decreases with increases in pressure. Hence ice will melt at a temperature lower than zero degree centigrade at a pressure higher than the normal pressure.

2. Effect of change of pressure on the boiling point

When a liquid is converted into a gaseous state, the volume V_2 of the gas is always greater than the corresponding volume V_1 of the liquid i.e $V_2 > V_1$. Therefore, $\frac{dP}{dT}$ is a positive quantity. With increase in pressure, the boiling point of a substance increases and vice versa. The liquid will boil at a lower temperature under reduced pressure. In the case of water, the boiling point increases with increase in pressure and vice versa. Water bolis at 100 ^{0}C only at 76 cm of Hg pressure. In the laboratories, while preparing steam, the boiling point is less than 100 c because the atmospheric pressure is less than 76 cm of Hg. In pressure cookers, the liquid boils at higher temperature because the pressure inside is more than the atmospheric pressure.

6.9.2 THE SECOND LATENT HEAT EQUATION

The second latent heat equation, or the equation of Clausius, gives the variation of latent heat of a substance with temperature and connects it with the specific heat of the substance in the two states.

Let C_1 denote the specific heat of liquid in contact with its vapours and C_2 the specific heat of saturated vapours in contact with its liquid. Let us consider that 1 gm of the substance is taken round the cycle BFGCB. The quantity of heat absorbed by the substance in passing from B to F, when its temperature rises by dT is C_1dT. In passing along FG, when the substance changes from liquid to vapour at constant temperature T+dT, it absorbs a quantity of heat L+dL.

In passing from G to C, the temperature of the substance (vapours) falls by dT and hence it gives out a quantity of heat C_2dT, while in passing along CB, when it condenses from vapour to liquid at constant temperature T, gives out a quantity of heat L.

Hence the net amount of heat absorbed during the cycle is

$$C_1dT + L + dL - C_2dT - L = (C_1 - C_2)dT + dL.$$

This must be equal to the work done which is equal to the area of the cycle or the area FGNMF in the limiting case and hence from equation (6.28)

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

$$(C_1 - C_2)dT + dL = \frac{L}{T}dT$$

$$(C_1 - C_2)dT = \frac{L}{T}dT - dL$$

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T} \qquad \qquad \text{... (6.29)}$$

This is a second latent heat equation of Clausius.

6.10 TRIPLE POINT

The triple point is the temperature and pressure at which the three phases of that substance coexist in thermodynamic equilibrium.

(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 (Figure 6.3). 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.

(ii)   The melting point of ice decreases with increase in pressure i.e. ice melt below 0^0C 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.
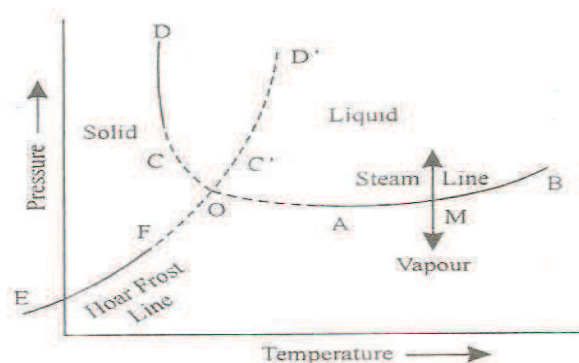

Fig. (6.3)

(iii)   When the pressure on ice is raised, evaporation from its surface slow down. The equilibrium between the solid and the vapour state of a substance can be represented by a curve EF called the Hoar Frost 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 Figure (6.3). 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 exit simultaneously in equilibrium

To show that there is only one triple point

Suppose that three curves do not meet at a point but interest enclosing an area ACF shown in shaded region in Figure 6.4 then according to ice line CD, the substance must be entirely solid in the shade area as it is to the left of CD. According to the steam line AB the substance must be entirely liquid 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 triangle ACF cannot exist. Thus, the three curves should meet in a single point O called the triple point.
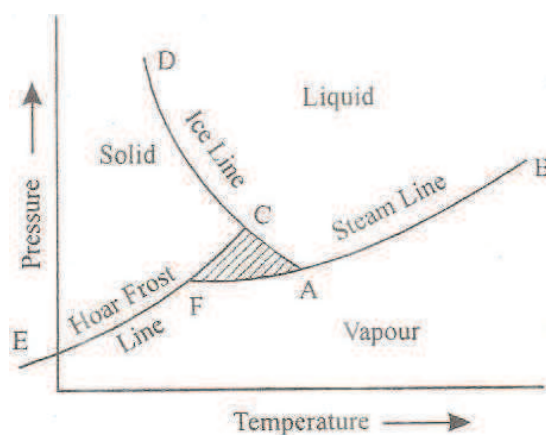
Fig. (6.4)

It should be noted that the triple point of water is not fixed but is different for different allotropic forms of ice. For pure water, the triple point corresponds to $T = 0.0075°C$ and $P = 4.58$ mm of Hg.

6.11 PHASE TRANSITIONS

A phase of the matter may be defined as a thermodynamic system of which all the physical properties (such as density, refractive index, magnetization and chemical composition etc.) are essentially uniform. In simple words, a region of matter that is chemically uniform, physically distinct, and mechanically separable may be thought of a phase. We are familiar with different forms of water i.e., ice (solid), water (liquid), and vapor/steam (gas). These three forms are three different phases of the water. In general, the distinct phases may be described as different states of such as gas, liquid and solid. Apart from these three, some other states or phases of mater are also known namely plasma or Bose–Einstein condensate. The uniformity in the physical properties of certain phase is due to the uniform interactions such as attractive forces between the constituents forming the phase under some fixed external thermodynamic conditions i.e., temperature, pressure etc. However, the change in the external conditions may result into the change in the kind and/or

strength of the interactions, which in turn, gives some different phase. The ice (solid phase) when heated up to its melting point, changes into water (liquid phase) and water when further heated up to its boiling point changes into the gaseous phase. This phenomenon of transition of the matter from one to another phase is termed as phase transition. During a phase transition of a given medium, certain properties of the medium change and these are common occurrences observed in nature. The studies about the phase transitions of the materials are very important as they provide proper understanding of the material's behaviour and their applications in thermodynamics. Here, we will discuss different aspects of phase transitions and their significance.

6.11.1 CLASSIFICATION OF PHASE TRANSITIONS

Most of the natural phase transitions occur at constant temperature and latent heat is required for such transitions to take place. On the other hand, some phase changes such as transition of material from ferromagnetic to paramagnetic phase at its Curie temperature, transition of a compound from super-conducting state to non-superconducting state, transition from liquid He I to liquid He II etc., do not require latent heat. Depending upon whether latent heat is involved or not during a phase transition, P. Ehrenfest proposed a classification of phase transitions and categorized them as first and second order phase transitions.

6.11.1.1 FIRST ORDER PHASE TRANSITION

First order phase transition can be defined as that one in which the Gibbs function with respect to pressure and temperature change discontinuously at the transition point. In other words the first derivatives of Gibb's function are discontinuous. However, the value of the Gibbs function is the same in both the phases at equilibrium. In these processes, there is transference of heat and hence there is change in entropy and volume. These changes are represented graphically in Figure 6.5.
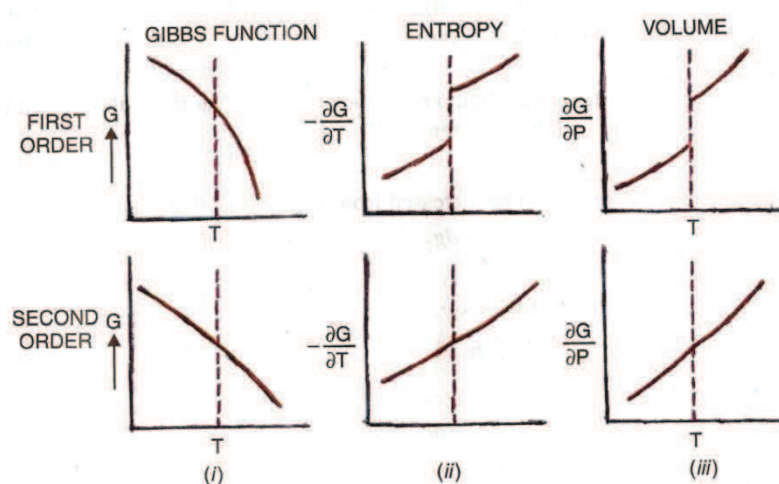

Fig (6.5)

6.11.1.2 SECOND ORDER PHASE TRANSITION

According to the definition proposed by Ehrenfest, the phase transitions in which the second derivatives of Gibbs function are discontinuous whereas the Gibbs function and its first derivatives are continuous at phase transition are termed as second order phase transitions. Second order phase transitions can be defined as the phenomenon that takes place with no change in entropy and volume at constant temperature and pressure. It has been found in case of transition from liquid helium I to liquid helium II, that there is no transfer of heat and no change in volume. Such transitions are called second order phase transitions. These changes are represented graphically in Figure 6.5.

The details of the phenomena are out of scope at this level and will be taught at later stage.

6.12 APPROACHES TO ABSOLUTE ZERO

The third law of thermodynamics refers to a state known as "absolute zero." This is the bottom point on the Kelvin temperature scale. The Kelvin scale is absolute, meaning 0° Kelvin is mathematically the lowest possible temperature in the universe. This corresponds to −273.15° Celsius, or -459.7 Fahrenheit.

In actuality, no object or system can have a temperature of zero kelvin, because of the constraint of the second law of thermodynamics. The second law, in part, implies that heat can never spontaneously move from a colder body to a hotter body. So, as a system approaches absolute zero, it will eventually have to draw energy from whatever systems are nearby. If it draws energy, it can never obtain absolute zero. So, this state is not physically possible, but is a mathematical limit of the universe.

From the Nernst heat theorem, we have

$$\lim_{T \to 0} \Delta S = 0$$

The above equation says that "The entropy of a pure perfect crystal is zero (0) at zero kelvin (0 K)" Entropy is a property of matter related with molecular random its and energy. The Third Law of Thermodynamics means that as the temperature of a system approaches absolute zero, its entropy also approaches zero. A pure perfect crystal is one in which molecules have zero energy. For non-pure crystals, or those with less-than perfect structure, there will be some energy associated with the imperfections, so the entropy cannot become zero. Since a pure perfect crystal is impossible hence absolute zero also cannot be attained.

The third law of thermodynamics can be visualized by thinking about water. Water in gas form has molecules that can move around very freely. Water vapor has very high entropy (randomness). As the gas cools, it becomes liquid. The liquid water molecules can still move around, but not as freely. They have lost some entropy. When the water cools further, it becomes solid ice. The solid water molecules can no longer move freely, but can only vibrate within the ice crystals. The entropy is now very low. As the water is cooled more, closer and closer to absolute zero, the vibration of the molecules diminishes. If the solid water reached absolute zero, all molecular motion would stop completely. At this point, the water would

have no entropy (randomness) at all. Since it is not possible so the absolute zero is unattainable.

6.13 SELF ASSESSMENT QUESTIONS

1 Prove that $C_P = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P$

2 Prove that $C_P = \left(\frac{\partial H}{\partial T} \right)_P$

3 Discuss the effect of change of pressure on the boiling point of a liquid.

6.14 EXAMPLES

Example 1. The vapour pressure P (in mm. of mercury) of solid ammonia is given by
$$\log_e P = 23.03 - \frac{3754}{T} \text{ while that of liquid ammonia is given by}$$

$$\log_e P = 19.49 - \frac{3063}{T} \text{ where T is in K. Calculate the triple point of ammonia.}$$

Solution: At triple point, the vapour pressure of the substances in each of the three states is identical. Hence equating the vapour pressure of solid ammonia with that of liquid ammonia.

we have $23.03 - \frac{3754}{T} = 19.49 - \frac{3063}{T}$

or $\frac{1}{T}(3754 - 3063) = 23.03 - 19.49$

or $\frac{691}{T} = 3.54$

or,   T= 195.2 K

Example 2. Prove that in isothermal process for an ideal gas

(1) $G_2 - G_1 = \int RT \frac{dP}{P}$

(2) $G_2 - G_1 = RT \ln \frac{V_1}{V_2}$

Solution: Gibbs function for an ideal gas is defined as

$$G = H - TS$$

For an infinitesimal reversible process

$$dG = dH - TdS - SdT$$

But $dH = TdS + VdP$

$$dG = VdP - SdT$$

For isothermal process, dT = 0, so **dG = VdP**   ... (i)

(1)   For ideal gas, PV = RT, then equation (i) becomes $dG = \dfrac{RT}{P}dP$

Integrating it, we get $\int_{G_1}^{G_2} dG = \int \dfrac{RT}{P}dP$

$$G_2 - G_1 = \int \dfrac{RT}{P}dP$$

(2)   For ideal gas, PV = RT or P = RT/V, differentiating it isothermally with respect to V,

$$\dfrac{dP}{dV} = -\dfrac{RT}{V^2}$$

Substituting this value in equation (i), we get

$$dG = V\left(-\dfrac{RT}{V^2}dV\right)$$

$$dG = -\dfrac{RT}{V}dV$$

Integrating it, we get

$$\int_{G_1}^{G_2} dG = -RT \int_{V_1}^{V_2}\left(\dfrac{dV}{V}\right)$$

$$G_2 - G_1 = -RT\ln\left(\dfrac{V_2}{V_1}\right)$$

$$G_2 - G_1 = RT\ln\left(\dfrac{V_1}{V_2}\right)$$

Example 3. Calculate the cooling produced by adiabatic demagnetisation of a paramagnetic salt as the field is reduced from 10000 oersted to zero at initial temperature of 2 K. (Given: Curie constant per gm.mol per c.c. = 0.042 erg degree/gm oersted^{-2} and C_H = 0.42 joule gm^{-1}deg^{-1})

SOLUTION: The cooling produced is given by

$$\Delta T = \dfrac{CV}{2C_H T}.H^2$$

Here T = 2K, C_H = 0.42 joule gm^{-1}deg^{-1} = 0.42 x 10^7 erg gm^{-1}deg^{-1}, H = 10000 oersted

Curie constant CV = 0.042 erg degree/gm oersted^{-2}

So that $\Delta T = -\dfrac{0.042\times(10000)^2}{2\times\left(0.42\times10^7\right)\times2}$

$$\Delta T = -0.25\ K$$

Example 4. Calculate the specific heat of saturated steam. Given that the specific heat of water at 100 ^{0}C = 1.01 and latent heat of vaporisation decreases with rise in temperature at the rate of 0.64 cal/K. Latent heat of vaporisation of steam is 540 cal/gm.

Solution: Here C_1 = 1.01, C_2 = ?, T = 273 + 100 = 373 K, $\frac{dL}{dT} = -0.64$ cal/K

$$L = 540 \text{ cal/gm.}$$

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}$$

$$C_2 = C_1 + \frac{dL}{dT} - \frac{L}{T}$$

$$C_2 = 1.01 - 0.64 - \frac{540}{373}$$

$$C\_2 = -1.077 \text{ cal/gmK}$$

Example 5. Calculate under what pressure ice freezes at 272 K if the change in specific volume when 1 kg of water freezes is 91 x 10^{-6} m^3. Given latent heat of ice = 3.36 x 10^5 Jkg^{-1}.

Solution: L = 3.36 X 10^5 Jkg^{-1},

Freezing point of ice under normal pressure T = 273 K

Change in freezing point dT = 273 – 272 = 1 K

Change in specific volume $V_2 - V_1$ = 91 x 10^{-6} m^3

According to Clapeyron's latent heat equation

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

$$dP = \frac{dT \times L}{T(V_2-V_1)} = \frac{1 \times 3.36 \times 10^5}{273 \times 91 \times 10^{-6}} = 1.352 \times 10^7 \text{N/m}^2$$

Taking 1 atm = 10^5 N/m^2, we have

$$dP = \frac{1.352 \times 10^7}{10^5} = 135.2 \text{ atm.}$$

Hence, pressure under which ice would freeze at 272 K

$$= 1 + 135.2$$

$$= 136.2 \text{ atm.}$$

6.15 SUMMARY

- The combinations of state variables and internal energy such as U, U + PV = H, U – TS = F, and H – TS = G are called thermodynamic potentials.

- Like internal energy U, enthalpy H, Helmholtz function F, and Gibbs function G are state functions and hence are exact differentials also.
- The differentials of the thermodynamic potentials are expressed as $dU = TdS - PdV$, $dH = TdS + VdP$, $dF = -SdT - PdV$, and $dG = VdP - SdT$
- Maxwell's relation can directly be deduced using thermodynamic potentials. The relations are $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$, and $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$.
- Phase transition is a process in which a thermodynamic system changes from one state to another with different physical properties.
- Latent heat is related to the change in entropy at a first order phase transition.
- The phase transition, in which the second derivatives of Gibbs free energy are discontinuous at phase transition, are second order phase transitions.
- The Clausius Clapeyron first latent heat equation is used to determine the shape of the phase boundry
- The phenomenon of the alignment of magnetic dipoles in external magnetic field is termed as magnetization. However, the magnetic dipoles restore their original state when field is switched off. This is called demagnetization.
- If the demagnetization of a paramagnetic substance occurs adiabatically, the atomic dipoles attain their original distribution in expense of their internal energy which results the drop in the temperature of the substance. The process of heating/cooling of a paramagnetic substance due to magnetization/demagnetization is known as magneto-caloric effect.
- The process of adiabatic demagnetization of paramagnetic substances may result ultra low temperatures.

6.16   GLOSSARY

Thermodynamic variables	The physical quantities which help us to study the behavior of thermodynamic system.
Thermodynamic potential	A scalar quantity used to represent the thermodynamic state of a system.
Gibbs free energy	The energy associated with a chemical reaction that can be used to do work.
Internal energy	Energy contained within in the system.
Enthalpy	Total heat content of the system.
Helmholtz free energy	A thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature and volume
Entropy	Lack of order or predictability; measure of degree of disorder proportionally
Isothermal process	A change of a system in which the temperature remains constant.
Adiabatic process	One that occurs without transfer of heat or matter between a thermodynamic system and its surrounding.
Isobaric process	A thermodynamic process in which the pressure remains constant.

Isochoric process	A thermodynamic process in which the volume remains constant.
Specific heat	Amount of heat per unit mass required in raising the temperature by 1^0 C.
Heat capacity	Amount of heat needed to raise the system's temperature by 1^0 C.
Latent heat	Energy released or absorbed by a thermodynamic system during an isothermal process.
Cyclic process	A process consisting of a series of changes which returns the system back to its initial state.
Adiabatic demagnetisation	Process by which the removal of a magnetic field from certain materials serves to lower their temperature.
Inversion temperature	It is the critical temperature below which a real gas that is expanding at constant enthalpy will experience a temperature decrease, and above which will experiences a temperature increases.
Phase transition	A process in which a substance changes from its one state to the other. Most commonly used to describe transitions between solid, liquid and gaseous state of matter.
Triple point	The temperature and pressure at which the three phases of that substance coexist in thermodynamic equilibrium.

6.17   ANSWERS TO SELF ASSESSMENT QUESTIONS

1   We know that

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P, \quad TdS = dQ, \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = -T\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

2   We know that

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

and $H = U + PV$

Differentiating it at constant pressure, we get

$$dH = dU + PdV = (TdS - PdV) + PdV = TdS$$

or $\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = C_P$

3   From Clausius-Clapeyron latent heat equation

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

When a liquid is converted into a gaseous state, the volume V_2 of the gas is always greater than the corresponding volume V_1 of the liquid i.e., $V_2 > V_1$.

Therefore, $\frac{dP}{dT}$ is a positive quantity.

With increase in pressure, the boiling point of a substance increases and vice versa. The liquid will boil at a lower temperature under reduced pressure. In case of water, the boiling point increases with increase in pressure and vice versa.

6.18   REFERENCES

Agrawal, J.P. and Prakash, S. (2012), Thermal Physics, Pragati Prakashan, Meerut.

Chakrabarti, P.K., (2006), Theory and Experiment on Thermal Physics, New Central Book Agency (P) Ltd., Howrah.

Garg, S.C., Bansal, R.M. and Ghosh, C.K., (2006), Thermal Physics, Tata McGraw-Hill, New Delhi.

Kittel, C., (2007), Thermal Physics, Dover Publications, Inc. Mineola, New York.

Reif, F., (2013), Fundamental of Statistical and Thermal Physics, Tata McGraw-Hill, New Delhi.

Sharma, J.K. and Sarkar, K.K. (2008), Thermodynamics and Statistical Physics, Himalaya Publishing House, Mumbai.

Zemansky, M.W., Dittman, R.H. and Chattopadhyay, A.K. (2011), Heat and Thermodynamics, Tata McGraw-Hill, New Delhi.

Kumar and Taneja, Thermal Physics (2014), R. Chand & Co., New Delhi.

6.19 TERMINAL QUESTIONS

1. What are thermodynamic potentials? Why are they called potentials?
2. Write down the physical significance of thermodynamic potentials.
3. Deduce Maxwell's relations using thermodynamic potentials.
4. Prove that change in enthalpy in an isobaric process is equal to the heat transferred.
5. Prove that change (decrease) in the Helmholtz function in an isothermal process is equal to the work done by the system.
6. Prove that for a reversible isothermal and isobaric process, Gibbs function remain constant.
7. Show that one has to minimize Helmholtz function to find the equilibrium of a system at constant temperature and volume.
8. Show that Helmholtz free energy never increases in natural processes.

9.   What is adiabatic demagnetization? Explain how it could be utilized to achieve ultralow temperatures?

10.   Discuss the process of adiabatic cooling with the help of entropy-temperature behaviour of paramagnetic specimen.

11.   What is magneto-caloric effect?

12.   What is phase transition? Discuss the classification of phase transition with examples.

13.   Represent the behavior of specific Gibbs function, entropy, volume and heat capacity with temperature by drawing plots for first and second order phase transitions.

14.   Write down the significance of Clausius-Clapeyron heat equation.

15.   Give two examples of first and second order phase transition.

16.   Prove the thermodynamic relation

(a) $T.ds = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

(b) $T.ds = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

17.   Establish the following relation between enthalpy H, Helmholtz free energy F, and Gibbs free energy G,

$$G = H + T\left(\frac{dG}{dT}\right)_P$$

18.   Define the Helmholtz function and for an isochoric process establish the relation

$$U = F - T\left(\frac{dF}{dT}\right)_V$$

19.   Discuss the third law of thermodynamics

20.   Derive the relation of stretching of wire using Maxwell's relations.

21.   What is triple point and show that there is only one triple point.

22.   Establish the Clausius-Clapeyron's equation from Carnot's cycle

$$\frac{dP}{dT} = \frac{L}{[T(V)]_2 - V_1)}$$

and explain the effect of pressure on (i) boiling point of liquid and (ii) melting point of a solid.

24.   Calculate the depression of melting point of ice produced by one atmosphere increase of pressure. Given that latent heat of ice = 80 cal/gm and specific volume of ice and water at 0^0C are 1.091 cm^3 and 1.0 cm^3 respectively.

25.   Show that for a homogenous fluid $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

where C_P and C_V are the specific hats at constant pressure and volume respectively, and other symbols have their usual meaning.

(i) Also show that $C_P - C_V = TE\alpha^2 V$

where E is the bulk modulus of isothermal elasticity, and α the coefficient of volume expansion.

(ii) Hence prove that for a perfect gas $C_P - C_V = R$

(iii) Hence prove that for a real (van der Waals') gas $C_P - C_V = R\left(1 + \frac{2a}{VRT}\right)$

26.   Calculate the change in temperature of boiling water when the pressure is increased by 27.12 mm of Hg. The normal boiling point of water at atmospheric pressure is 100^0C.

Given: Latent heat of steam = 537 cal/gm and, specific volume of steam = 1674 cm^3.

27.   Calculate the pressure and temperature of the triple point water. Given that the lowering of melting point of ice per atmosphere increase of pressure is 0.0072^0C and the saturated vapour pressure at 0 ^{0}C = 4.60 m.m. while at 1^0C= 4.94 m.m.

28.   Calculate the specific heat of saturated steam at 100^0C from the following data:

                    L at 90^0 = 545.24 cal

                    L at 100^0C   = 539.30 cal

                    L at 110^0C   = 533.17 cal

Specific heat of water at 100^0C   = 1.013 cal/gm

29.   Objective Questions

(i) Four thermodynamic potentials are:

    (a) Pressure, Volume, Temperature and Internal energy function

    (b) Pressure, Volume, Internal Energy and Helmholtz function

    (c) Internal energy function, Helmholtz function, Enthalpy and Gibbs function

    (d) None of these.

(ii) Specific heat of saturated vapour pressure is:

    (a) zero   (b) positive

    (c) negative   (d) sometimes positive sometimes negative.

(iii) The Clausius-Clapeyron equation is:

(a) $\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$ (b) $\frac{dP}{dT} = \frac{T}{L(V_2-V_1)}$

(c) $\frac{dP}{dT} = TL(V_2 - V_1)$ (d) None of these.

(iv) Paraffin wax contracts on solidification. The melting point of wax will

    (a) increase with pressure   (b) decrease with pressure

    (c) no change with pressure   (d) decrease linearly with pressure.

(v) The number of thermodynamic function are:

    (a) 1   (b) 2

    (c) 3   (d) 4.

(vi) The change in each thermodynamic function:

    (a) depends on path between initial and final states

    (b) is independent of path between initial and final states

    (c) is always zero

    (d) none of above.

(vii) The internal energy of system is:

(a) a thermodynamic variable   (b) a thermodynamic function
(c) a universal constant   (d) always zero

(viii) In the presence of external magnetic field, the magnetic entropy of paramagnetic sample;

(a) increases   (b) decreases
(c) remains constant   (d) is always zero

UNIT-7   THEORY OF RADIATION - I

CONTENTS

7.1 INTRODUCTION

The subjects for consideration in this unit are black-body model (which is of primary importance in thermal radiation theory) and the fundamental laws of radiation. Natural and artificial objects which have close characteristics of black body are also discussed here. The notion of emissivity and absorptivity are also introduced. The Kirchhoff's law and its various corollaries are analyzed in detail.

Radiative transfer is the most common energy transport phenomenon that we feel around us every day. The Sun's energy travels to the earth in the form of electromagnetic waves, is selectively absorbed, and scattered as it goes through atmospheric layers.

Radiation allows us to see and sense everything in our surroundings as light or heat.

Heat may be propagated in a stationary medium by different ways, namely: conduction, convection and radiation. Conduction and convection of heat depends on the temperature gradient or temperature difference of the medium in which it takes place. Radiation of heat, however, is in itself entirely independent of the temperature of the medium through which it passes. Supported by a large number of experimental facts, the physical properties of heat rays are turned out to be identical with light or electromagnetic rays.

Have you ever thought what makes us see the objects? We see objects because of the reflections from the material. If we see green object, it is because of green wavelength that is reflected and all other wavelengths are absorbed by the material. So, if an object appears black then no wavelength will be reflected and every wavelength is absorbed. In turn, if we heat a black body, it emits radiations, called black body radiations. For example: Consider a black piece of iron, if we further heat it up or provide energy to it, it will start glowing with a red color. If we add more energy, the piece will become orange, yellow, white and finally bluish white.The color of light radiated can be correlated to the temperature of the object. This is called color temperature scale. The ideal scale uses the colors of an abstract object called Black Body Radiator, which absorbs and them radiates all the energy that reaches it.

But, why to use black body radiator as standard?

This is because black body radiation provides us a set of very precise working equation that relates temperature of an object to the light it emits. Planck's law gives the energy distribution across the spectrum for a given temperature, Stefan-Boltzmann law calculates total emitted power, the wavelength of peak emission or the color that dominates at particular temperature is provided by Wein's displacement law. Knowing the ideal case, the color scale can be applied to any source of light, using correction factors.

By knowing the wavelength of light coming from the star, scientists could know the exact temperature of the star.

7.2 OBJECTIVES

After studying this unit, you should be able to understand the following-

- Absorptivity and emissivity
- Properties of a black body
- Natural and artificial black body models
- Characteristics of black body radiation
- Black body radiation intensity versus wavelength curves: their shape and temperature dependence
- Energy distribution in black body radiation
- Kirchhoff's law

7.3 WHAT IS RADIATION?

The radiation is the energy travelling through space. It is there all around us; in fact you are currently being bombarded by radiation. It might be coming from the sun, various electronic devices you own etc. Weather a radiation can harm you or not, it depend on the type of radiation, the dosage and duration of exposure. Before proceeding to different types of radiations, you need to know what exactly radiation is in general.

Radiation can be defined as the emission or transmission of energy from a body in the form of waves or particles through space or through material medium. This can include anything from dangerous radiation created by a nuclear power plant to the harmless light created by a flashlight.

Sunshine is the most familiar kind of radiation. Microwaves are used for cooking foods. Radio waves transmit voices across the world into and out of our radios. The radiation used for cell phones falls somewhere in between radio and microwave spectrum and is used in similar fashion to radio waves. You might at some point have seen on television a police chase where a helicopter uses infrared radiation in a camera to see heat sources and spot a suspect in a dark. But, did you know your television remote is using the same infrared to communicate with the TV when you press buttons on it. The low energy ultraviolet radiations are used in tanning beds.

The ionizing radiation is far less commonly used, but it still has its place. One such use is for carbon dating. In every living thing, there are carbon-14 atoms, an unstable atom that experiences beta decay. While we live, the supply of this atomis replenished in our bodies, but when someone dies, the supply stops. Knowing how fast carbon-14 decays, archaeologists can check how much remains in a person, animal or plant to get an estimate how old it is.

7.3.1 TYPES AND ORIGIN / CAUSE OF RADIATION

Radiations are often categorized as either ionizing or non-ionizing depending on the energy. The radiations mainly include:

1. Electromagnetic radiations: radio waves, microwaves, visible, X-rays and gamma radiation

2. Particle radiation; alpha radiation, beta radiation and neutron radiation

3. Acoustic radiation: ultrasound, sound and seismic waves

4. Gravitational radiation

The word radiation has arisen from the phenomenon of radiating (i.e., travelling outward in all directions) from a source.

The electromagnetic radiations (EM) including gamma rays, x-rays, visible light and radio waves have energy 'packaged' in small units called 'photons' or 'quanta'. EM radiations have no mass, and is unaffected by either electrical or magnetic fields, and has a constant speed in a given medium. They travel in straight lines; however their trajectory can be altered when they interact with matter. The EM radiations are characterized by wavelength (λ), frequency (ν) and energy per photon (E). The EM radiation is transport of energy through space as combination of electric and magnetic fields. EM radiations are produced by a charge (charged particle) being accelerated. According to the classical theory EM radiations can be considered as the wave motion, however according to quantum theory EM radiation can also be considered as particles called photons.(The details about classical and quantum concepts will be discussed in Unit 13)

The particulate radiation consists of small particles of matter moving through space at very high velocity. The particle radiation differs from electromagnetic radiation in the sense that the particles consist of matter and have mass as in electron and alpha particles. The particle radiations re emitted by an unstable nucleus via radioactive decay or can be the product of some kind of nuclear reactions.

The acoustic radiations are a mode of coherent mechanical energy transfer, from a sound source to surrounding medium. The flared horn of a trumpet or a loudspeaker can be called acoustic source radiators. Unlike EM radiations the acoustic radiations travel at a much lower speed and mechanical motion of material medium is involved, and are also called pressure waves.

Gravitational radiations are produced by massive accelerating bodied, but they have a very feeble strength, it is entirely undetectable unless produced by intense astrophysical sources such as supernovae, collision of black holes etc.

7.3.2 THERMAL RADIATION

The thermal radiations or radiant heat are electromagnetic (EM) radiations that lie in the infrared region of the electromagnetic spectrum and are radiated by a hot body.

The word thermal means related to heat. The transference of heat from one point to another can take place by three modes namely conduction, convection and radiation. Conduction in propagation of heat through a material, from a region of higher temperature to a region of

lower temperature while the intermediate medium itself remains stationary. In convection, the heated material of the medium itself moves and carries the heat. The radiation is that mode of heat transfer where no material medium is required. Also, through radiation the heat transfer takes place without heating the intervening medium or space.

Supported by a large number of experimental facts, the physical properties of heat rays are turned out to be identical with light or electromagnetic rays i.e., they travel in straight line, obey laws of reflection and refraction and exhibit phenomena of interference, diffraction and polarization also.

William Herschel first noticed that thermal radiation fall in the infra-red region of the e.m. spectrum. The heat radiations have wavelengths ranging from 8×10^{-7} m to 4×10^{-4} m. They cannot be detected by the eye or photographic plates but they can be detected by the bolometer or by thermopile etc.

Thermal radiations are generated by the thermal motion of charged particle in matter. All matter at a temperature higher than absolute zero emits thermal radiation. When the temperature of any matter is above absolute zero, the atoms and molecules have random movement in the matter, and hence they interact/collide with each other, interatomic collisions cause the kinetic energy of atoms/molecules to change. These atoms and molecules are composed of charged particles, i.e. protons and electrons, and kinetic interaction among matter particles result in acceleration of charge and dipole oscillation. It leads to production of thermal (electromagnetic) radiation.

The characteristics of thermal radiation depend on various properties of the material it is emanating from, including its temperature, its absorptivity and emissive power.

Now we will briefly know about these terms.

7.4   *ABSOPTIVITY, REFLECTIVITY AND TRANSMISSIVITY*

Whenever a body is irradiated with radiation of any wavelength a fraction of the total incident radiation is absorbed, a part is reflected and the remaining is transmitted. If the amount of energy absorbed, reflected and transmitted when radiation strikes the surface are measured in percentage of the total energy in the incident electromagnetic waves then the total energy will be divided into three groups. They are called absorptivity (α), reflectivity (ρ) and transmissivity (t) is

$$\alpha + \rho + t = 1 \qquad\qquad\qquad\qquad (7.1)$$

Thus, Absorptivity is the fraction of radiation absorbed by a surface   Reflectivity is the fraction reflected by the surface. Transmitivissivity is the fraction transmitted by the surface.

The sum of all the three is always unity. The values of α, ρ and t vary depending on the nature of the surface or body.

A body for which α = 1 for all wavelengths is a black-body. A body for which α has the same value for all wavelengths, but less than the unity is a grey body.

Self Assessment Questions (SAQ)

1.   How thermal radiation is different from black body radiation?

2.   Why does SASA point spacecraft white?

7.5   SOME DEFINITIONS

7.5.1   Total energy density (u): Total energy density of radiations at any point is the total radiant energy per unit volume around that point for all the wavelengths taken together. It is generally expressed by u. Its SI unit is J/m^3 and in CGS erg/cm^3.

7.5.2   Spectral energy density (u$_\lambda$):   Spectral energy density for a particular wavelength is the energy per unit volume per unit range of wavelength. This is denoted by u$_\lambda$.

7.5.3   Total emissive power or Emissivity (E): The total emissive power of a body is the radiant energy emitted per unit time per unit surface area of the body for all wavelengths taken together. It is denoted by E.

7.5.4   Spectral emissive power (e$_\lambda$): 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. It is denoted by e$_\lambda$. For a perfectly black-body, e$_\lambda$ is maximum and is denoted by E$_\lambda$.

7.5.5   Absorptive power or Absorptivity (a$_\lambda$):   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$_\lambda$.

From the above definitions, we may write

$$u = \int_0^\infty u_\lambda d\lambda$$
(7.2)

$$E = \int_0^\infty E_\lambda d\lambda$$
(7.3)

 7.5.6 Relative emittance (e): The ratio of emittance of a surface to the emittance of a black-body is called relative emittance.

If E' is the emittance of a surface and E the emittance of a black-body, then relative emittance of the surface

$$e = \frac{E'}{E}$$

(7.4)

7.6   PREVOST'S THEORY OF HEAT EXCHANGE

Earlier the idea about radiant energy was quite confusing/People used to talk of hot radiations emitted by hot bodies and cold radiations emitted by cold bodies. Prevost for the first time pointed out that this notion was wrong and proved that thermal radiation was essentially an exchange process. The rise and fall of temperature observed in a body is due to an exchange of radiant energy between the body and its surroundings.

According to Prevost, everybody emits radiations continuously to its surroundings at a rate which depends only on the nature of its surface and temperature and at the same time it receives radiation from its surroundings at a rate depending on the surface and the temperature of surrounding.

If a body is at higher temperature than the surroundings, it radiates more quantity of heat per unit time to the surrounding than it receives from the surroundings. As a result, the temperature of the body will fall. When a body is at a temperature lower than that of surroundings it will radiate less heat and absorb more heat. Consequently the temperature of the body rises. When the body receives and radiates heat at the same rate, the temperature of the body remains constant and equal to the temperature of the surroundings. In this condition, we say that the body is in thermal equilibrium with the surroundings.

Thus all bodies at all temperatures are in a state of dynamical thermal-equilibrium when they are at the same temperature. The quantity of heat radiated by a body decreases with decrease in its temperature and at absolute zero temperature, itwill not radiate energy at all.

7.7 RADIATION PRESSURE

The thermal radiation possesses the properties of light. Like light it also exerts a small, but definite pressure on the surface on which it is incident. On the basis of electromagnetic theory Maxwell proved that the pressure is equal to the energy densities (i.e., the amount of radiationper unit volume) for the normal incidence on a surface.

Thus p = u for normal ncidence or beam radiation.

For isotropic or diffuse radiation, it is

$$p = \frac{1}{3}u \,.$$

Both the relations can be obtained on the basis of Quantum Theory.

7.8   BLACK BODY AND BLACK BODY RADIATION

A perfectly black-body is one which absorbs all the heat radiations of any wavelength incident on it. It neither reflects nor transmits any of the incident radiations and, therefore, appears black whatever be the colour (wavelength) "of incident radiation.

If a black-body is placed in an isothermal enclosure, the body will emit the full radiation of the enclosure after it is in thermal equilibrium with the enclosure. 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 an isothermal enclosure are known as black-body radiation.

In practice, no substance possesses strictly the properties of a black-body. Lamp-black and platinum black are very close to a black-body. However, the bodies showing close approximation to a perfectly black-body can be constructed. Ferry's black-body and Wien's black-body are two such examples. We will discuss about it in detail later on.

7.9   KIRCHHOFF'S LAW

Related to thermal radiation, it was already experimentally proven that a good absorber is a good emitter, and a poor absorber is a poor emitter.

Gustov Robert Kirchhoff recognised this fact and proposed a law named after him. According to this law For an arbitrary body emitting and absorbing thermal radiation in thermodynamic equilibrium the emissivity is equal to the absorptivity." It is also important that the thermodynamical equilibrium is an essential condition for it.

Statement: states that the ratio of the emissive power (e_λ) to the absorptive power (a_λ) 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 (E_λ) 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 λ and $\lambda + d\lambda$, incident on unit surace area per-second. If a_n is the absorptive power of the body for the wavelength λ and at the temperature of the enclosure, then the amount of radiant energy absorbed by unit surface area of the body per   second   will   be a_λ dQ. The remaining energy i.e. $(1 - a_\lambda)$ dQ will be reflected or transmitted.

If e_λ is the emissive power of the body for wavelength λ at the temperature of the enclosure, then the total radiations lying between wavelength λ and $\lambda + J\alpha$ emitted by unit surface area of the body per second is e_λ dλ 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 $\dfrac{e_\lambda}{a_\lambda} = \dfrac{dQ}{d\lambda}$ (7.5)

As $\dfrac{dQ}{d\lambda}$ depends only on temperature, therefore $\dfrac{e_\lambda}{a_\lambda}$ is the same for all substances at a given temperature. In other words, the ratio of emissive power to the absorptive power for radiation of given wavelength is same for all bodies at a given temperature.

If the body be perfectly black, the absorptive power $a_\lambda = 1$ for all wavelengths and e_λ has maximum value which we denote by E_λ Thus, for such a body, we have

$E_\lambda d\lambda = dQ$

or $E_\lambda = \dfrac{dQ}{d\lambda}$ (7.6)

Comparing eqn. (7.5) and (7.6), we have for any body

$\dfrac{e_\lambda}{a_\lambda} = E_\lambda$ (7.7)

i.e., the ratio of the emissive power to absorptive power of a body is equal to the emissive power of a perfectly black-body at a given temperature. This is Kirchhoff's law.

7.9.1 IMPORTANCE AND APPLICATIONS OF KIRCHHOFF'S LAW

(i) If emissive power e_λ of a body is greater, according to Kirchhoff's law the corresponding absorptive power a_λ must be greater, i.e., from Kirchhoff's law it follows that good absorbers of radiation are also good emitters of radiation.

(ii) This law established that the atoms of every element give a characteristic spectcum. Thus the presence of characteristic spectral lines in a spectrum indicates the presence of that element in the substance of which spectrum is taken.

(iii) When a polished metal ball having a black spot on its surface is heated to a high temperature, the black spot shines more brightly than the polished surface. This is due to the fact that the black spot is a better absorber of radiations and hence accordingly it will be a better emitter.

(iv) A piece of red glass glows with a green light when heated. Actually red glass appears red because it reflects red light and absorbs rest colours from the white light. The effect of visible spectrum minus red is green. Hence red glass emits green on heating which it has absorbed when it was cold. Similarly   green glass appears red on heating strongly.

(v) When sodium is heated, its vapour emits two yellow lines (D_1, and D_2) of wavelengths 5890 Å and 5896 Å. When white light is passed through a cooler sodium vapour, the continuous spectrum of white light shows two dark lines in exactly the positions of D_1 and D_2 lines of emission spectrum. It shows that sodium vapour which emits two yellow lines strongly at higher temperature, is also a good absorber of light of these two wavelengths at lower temperature.

(vi) The origin of Fraunhofer 's dark lines found in the continuous spectrum of the sun is the best example of Kirchhoff's law. The sun consists of a central glowing mass called photosphere which emits the continuous spectrum. When these radiations pass through the cooler surrounding atmosphere called the chromosphere, which contains various elements like hydrogen, nitrogen, sodium, copper etc. in the gaseous state, absorb those wavelengths which they emit at a higher temperature. As a result, these wavelengths are absent in the solar spectrum and we see dark lines in their places, which are known as Fraunhofer's lines.

7.10 ENERGY DISTRIBUTION IN BLACK BODY RADIATION

Black body radiation was a puzzle for several years. This section explains how this puzzle was solved and so that new laws of physics were discovered which are foundation of the quantum mechanics.

The first attempt was made by Lummer and Pringsheim in 1899. They plotted some curves between E_λ (spectral emissive power) and λ (wavelength) for various temperature as shown in Figure 7.1. These plots are known as spectral energy distribution curve of Black Body radiation. it is clear from the curves that the energy of black body radiation is not shared evenly by all wavelengths of light. The figure shows that some wavelengths get more energy than others.
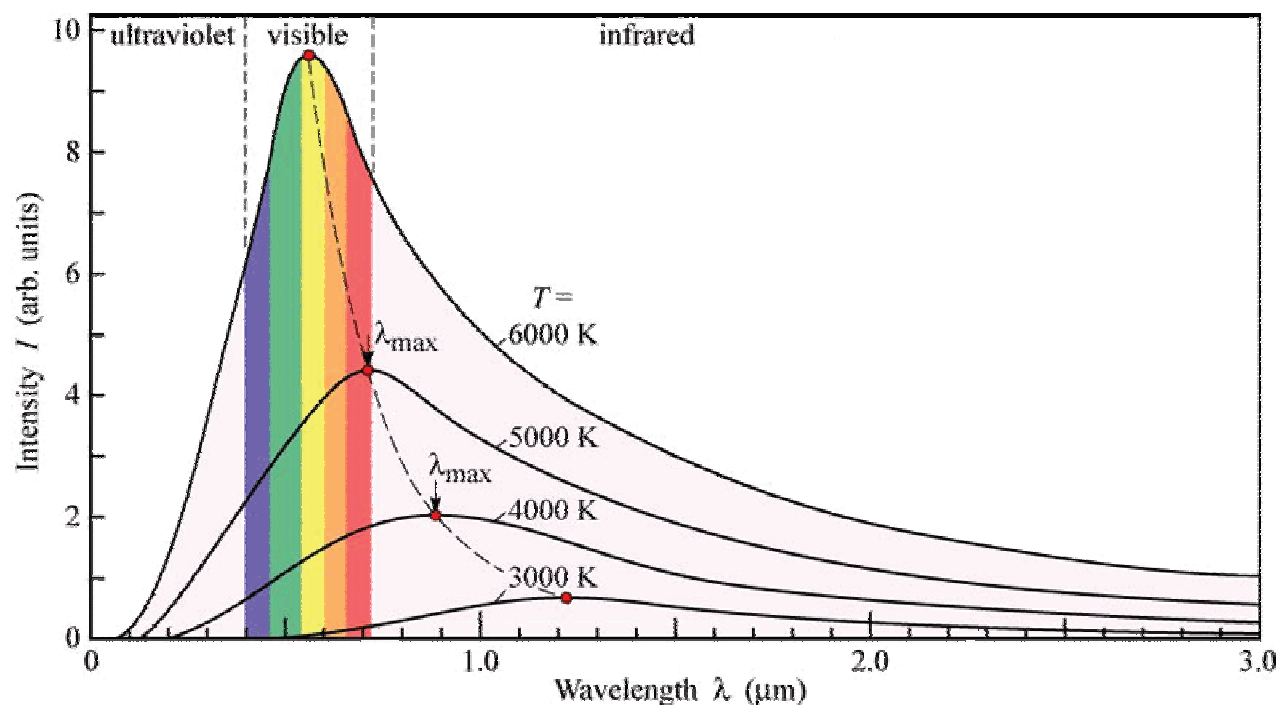

Fig. (7.1): spectral energy distribution of black-body radiation versus wavelength

7.10.1 EXPERIMENTAL OBSERVATIONS AND CHARACTERISTICS OF BLACK-BODY RADIATION

1. It is clear from the figure that the graph is continuous, which means that at every temperature radiation for all wavelengths are emitted but the spectral emissive power is different for different wavelengths. In other words the distribution of energy is not uniform in the radiation spectrum of a black-body.

2. The spectral energy density E_λ for each λ increases with temperature or as the temperature of the object increases, it emits more energy at all wavelengths.

3. For a particular temperature, firstly E_λ increases with λ but after reaching a certain maximum value it decrease. The highest value is denoted by $E_{\lambda m}$ and the wavelength at which E_λ is maximum is denoted by λ_m.

4. As seen from the graph, the wavelength (λ_m) corresponding to maximum emission, shifts towards lower wavelength with increase in temperature. It was Wein who first discovered mathematically that

$$\lambda_m \propto \frac{1}{T}$$

or $\qquad \lambda_m = \frac{b}{T}$

or $\qquad \lambda_m T = b$ (constant) $\hfill (7.8)$

Where b is a constant called Wein's constant and has a value of 2.968×10^{-3} meter kelvin.

The relation given by eq. (7.8) is known as wein's displacement law. This is an important law as it helps us to find the temperature of hot bodies at distance like stars.

Wein's displacement law can be expressed in terms of frequency as well which is

$$\nu_m = \frac{cT}{b}$$

5. It can also be seen from the graph that the value corresponding to peak of the curve increases rapidly with temperature. It was found that

$$E\lambda_m \propto T^5$$

6. The total energy emitted by the body at a particular temperature is represented by the area under the curve and mathematically the area under the curve at a particular temperature is given by

$$\int_0^\infty E_\lambda d\lambda \hfill (7.9)$$

This is the total emissive power of a Black Body. It was found that area under the curve is directly proportional to the fourth power of absolute temperature, hence

$$E \propto T^4$$

or, $E = \sigma T^4$ (7.10)

Where σ is Stephan's constant and has the value

$$\sigma = 5.67 \times 10^{-8} \text{ watt/m}^2/\text{K}^4$$

This law is known as Stephan-Boltzmann's law.

7. The black-body spectrum always become small at the left hand side (i.e., on shorter wavelength, or higher frequency side)
8. The black-body spectrum depends only on temperature of the body but not on its nature. An iron bar , a ceramic pot and a piece of charcoal all will emit the same black-body spectrum, if their temperatures are the same

7.10.2 LIMITATIONS OF CLASSICAL PHYSICS

Many attempts were made to explain the experimental curves of black body radiation. But they were not able to explain it completely (using classical physics). We will see in the next unit how these laws are unable to explain it completely. Further quantum physics was introduced and using it the curves were successfully explained.

7.11 BLACK BODY

When a smooth surface completely reflects all the incident rays, as is approximately the case with many metallic surfaces, it is termed 'reflecting'. When a rough surface reflects all incident rays completely and uniformly in all directions, it is called 'white'. A rough surface having the property of completely absorbing the incident radiation is described as 'black'.

In other words Kirchhoff defined black-body as a body having absorptivity and emissivity equal to one (a=e=1 where a and e are coefficients of absorption and emissivity respectively). Clearly for a black body $\gamma = t = 0$, i.e. there is no reflection and transmission.

As observed from the black body radiation spectrum, blackbodies have three important characteristics:

1. A black-body with a temperature higher than absolute zero emits some energy of all wavelengths extending to infinity (curves never meet x-axis)
2. A black-body at higher temperature emits more energy at all wavelengths than does a cooler one.
3. The higher the temperature, the shorter the wavelength at which the maximum energy is emitted.

7.11.1 PROPERTIES OF A BLACK BODY

A perfectly black-body is an idealized physical body which absorbs all the radiations that fall on it, irrespective of the wavelength or angle of incidence.

A black body in thermal equilibrium has two notable properties: It is an ideal emitter: at every frequency, it emits as much energy as or more energy than any other body at the same temperature. It is a diffuse emitter, the energy is radiated isotropically, independent of direction.

Let's discuss these properties in detail:

- **Perfect emitter**: Consider a black-body at a uniform temperature placed in vacuum within a perfectly insulated enclosure of arbitrary shape and whose walls are black-body. The black body and the enclosure attains a common uniform equilibrium temperature. In equilibrium condition, the black body must radiate exactly as much energy as it absorbs.

- **Radiation isotropy** (in a black enclosure): consider a black-body inside an isothermal enclosure with black walls and arbitrary shape. Move the black-body to another position or rotate it. Since enclosure remains isothermal the black-body must be at the same temperature. Thus, radiation received by the black-body is independent of the body's position or orientation throughout the enclosure.

- **Perfect emitter in each direction**: To maintain the thermal equilibrium and radiation isotropy throughout the enclosure the radiation emitted back in any incident direction must be equal to that received. Since the body is absorbing the maximum radiation from any direction, it must be emitting the maximum in any direction.

- **Perfect emitter at every wavelength**: Consider that the walls of the enclosure are so designed that they emit or absorb radiation in a very small intervals of dλ and λ. The black-body absorbs all the incident radiation in this wavelength interval. To maintain the thermal equilibrium of the enclosure, the black-body must reemit radiation in the same wavelength interval. Hence at every wavelength a black-body is a perfect emitter.

- **Radiation into vacuum is a function of temperature alone**: If the enclosure temperature is altered, the enclosed black-body temperature must adjust and become equal to the new enclose temperature so that the system is again isothermal. The absorbed energy and the emitted energy of the black-body will again be equal to each other. Hence the total radiant energy emitted by a black-body in vacuum is a function of its temperature only.

7.12 PRACTICAL EXAMPLES OF A BLACK BODY

A black body is a theoretical concept. It is defined as the body that absorbs 100% of the radiation that falls on it, irrespective of frequency or angle of incidence. Hence it reflects no radiation and appears perfectly black.

As you have already studied that according to G. Kirchhoff a perfect black-body is one which has the property to absorb all the incident radiations that fall on it. The statements is true for all incident wavelengths and all incident directions. There is no surface reflection and transmission. Therefore, for a given wavelength and in a given incident direction, no other body can absorbs more radiation than a black body.

In practice no material has been found to absorb all incoming radiations; however carbon in its graphite form absorbs 97% of incoming radiation. Platinum black and lamp black are the nearest example of a black body. Platinum black absorbs 98% of the visible light while lamp black absorbs 96%.An improvement on lamp-black is found in manufactured carbon nanotubes. Nano-porous materials can achieve average reflectance of 0.045% means absorbance of 99.955%.

SAQ 3. Give two examples of natural black body sources surrounding us.

SAQ 4 : Is the black body was to be necessarily black in colour?

However a body can be constructed which shows close approximations of a black body.

7.12.1 RADIATION WITHIN A CAVITY ENCLOSURE.

An approximate realization of a black body is a hole in the wall of a large enclosure. Any light entering the hole is reflected indefinitely or absorbed inside and is unlikely to re-emerge, making the hole a nearly perfect absorber.

The walls of the enclosure should be perfectly opaque to radiation. The incident radiations on the hole will pass into the cavity. If the cavity is large then entered ray is unlikely to be re-emitted (radiation gets absorbed by the inner walls of cavity after multiple reflections) Thus the hole acts act like a black-body. In a particular case if the wavelength of the incident radiation is longer than diameter of the hole, then incident radiation is partly reflected. Thus the box with a cavity is an approximation of the black-body.
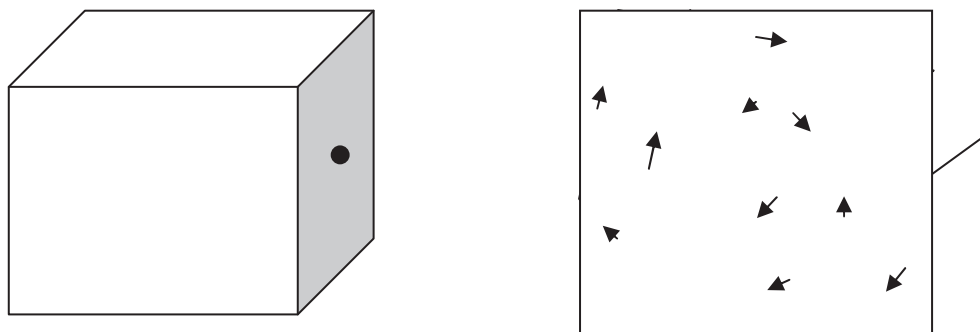

Fig. (7.2.) (a) A box with a hole simulating a black body. The walls are opaque to radiation (b) A ray entering the box get repeated reflections inside the box

The black body approximation is independent of the nature of walls of the enclosure. To prove this, consider two cavities at the same temperature. We'll suppose that the two cavities can be connected by a "door" that can be opened or closed to allow or to deny the passage of radiation between the cavities. We assume that the walls of one cavity are bright and shiny with an absorptance close to zero, and the walls of the other cavity are dull and black with an absorptance close to unity. Also suppose that, because of the difference in nature of the walls of the two cavities, the radiation density in one is greater than in the other. Let us open the door for a moment. Radiation will flow in both the directions, but there will be a net flow of radiation from the high-radiation-density cavity to the low-radiation-density cavity. As a consequence, the temperature of one cavity will rise and the temperature of the other will fall. Now the hotter cavity can be used as a source and the colder cavity can be used as a sink in order to operate a heat engine which will do an external work, such work, for example, to be used for repeatedly opening and closing the door separating the two cavities. We have thus constructed a perpetual motion machine that can continue to do work without the expenditure of additional energy. From this absurdity, we can conclude that despite the difference in nature of the walls of the two cavities (which were initially at the same temperature), the radiation densities within the two cavities must be equal. We thus deduce an important principle that the radiation density inside an enclosure is determined solely by the temperature and is independent of the nature of the walls of the enclosure.

7.12.2 FERRY'S BLACK BODY

Ferry designed a close approximation of a black body. The schematic diagrams of a black-body (Ferry's black-body), as an absorber and emitter, have been shown in the figure 7.3
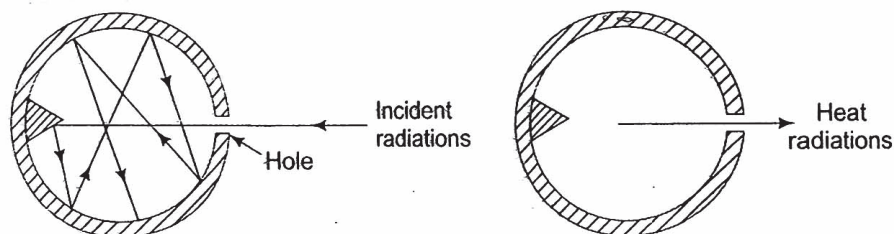
Fig. 7.3 : (a) Black-body absorber   (b) Black-body emitter

The Ferry's black-body consists of a hollow copper sphere blackened inside with a small fine hole 0 in the surface. When the radiations enter through the hole, they suffer a number of reflections at the inner walls of the sphere and finally they get trapped inside. To avoid direct reflection of the radiation from the inner surface, a pointed projection is made in front of the hole as shown in the figure. Thus the small hole acts as a black-body absorber. When this sphere is heated upto certain temperature, the heat radiations come out of the hole (Fig. 7.3b). It is to be noted that only the hole and not the walls of the sphere, acts as a black-body radiator.

7.12.3 Wein's Black Body

Fig. (7.4): Wein's Blackbody arrangement

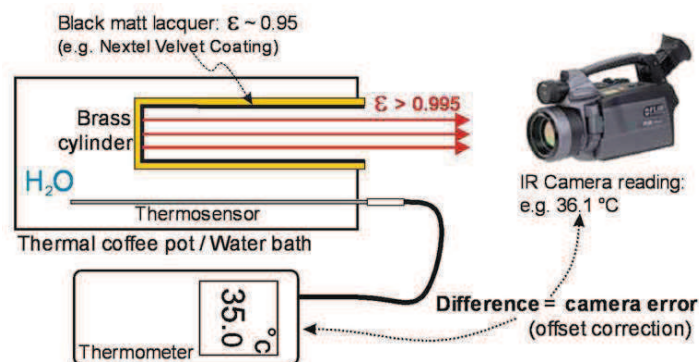Wein constructed a cylindrical black body. It consist of a hollow cylindrical chamber made of brass with heating coils of thin platinum wire wounded over it. The inner surface of the cylinder is painted black. On passing a suitable current through the wire the cylinder can be heated to a desired temperature and it can attain the equilibrium position in small time. The cylinder is isolated from the surroundings by a coaxial porcelain tube. The radiation from the cylinder emerges out of a hole and is limited by use of a blackened concave diaphragm. To measure temperature of the body a thermocouple is used. The hole acts as a black body radiator.

7.13 SUMMARY

The concept of an ideal black-body is important in studying thermal and electromagnetic radiation energy transfer in all wavelength bands. At a particular temperature a black body emits maximum amount of radiation as compared to any other body. Hence black body is used as a standard for comparison with radiation of real physical bodies. A black body is an ideal body which allows the whole of the incident radiation to be absorbed within itself as well as it is also an ideal emitter. A closed cavity with a hole is an approximation of black body. In an isothermal enclosure the radiation is constant both in quantity and spectral characteristics so that any energy absorbed is reradiated. The emission properties are independent of the nature of the walls of the enclosure. The energy of radiation emitted by a black body increases with rise in temperature and are isotropic in nature. Kirchhoff's law establishes the relation between the abilities of absorbing and emitting electromagnetic energy by any physical body. However, this law is not applicable in cases where thermodynamic equilibrium conditions are violated. The energy distribution in black body radiation is not uniform for all wavelengths but the intensity of emitted radiation becomes maximum for a particular wavelength. This wavelength varies with temperature and are correlated to each other by Wein's displacement law. The total energy emitted is given by Stefan-Boltzmann law. The study of black body radiation has enormous applications including estimating the temperature of far distant stars.

7.14 TERMINAL QUESTIONS

Objective type questions

1. Leaves are green because

    a. they only emit frequencies corresponding to green
    b. they only reflect frequencies corresponding to green
    c. they only transmit frequencies corresponding to green
    d. they only absorb frequencies corresponding to green

2. We can see any object when the electromagnetic waves in optical range

    a. is transmitted from the object
    b. is absorbed by the object
    c. is reflected from the object
    d. is scattered by the object

3. The thermal radiation is transmission of heat energy through space it,

    a. propagates only when a medium is present
    b. can propagate in vacuum
    c. does not require any medium to propagate
    d. is same as conduction

4. Heat rays are identical to

    a. Particle radiation
    b. Acoustic radiation
    c. Electromagnetic radiation
    d. Gavitational radiation

5. A black body radiation

    a. depends on the temperature of the medium
    b. is function of the temperature of the object
    c. is radiation emmitted by a black body at uniform temperature
    d.   all of the above

Long Answer type questions:

    1. State Korchoff's law of Black-body radiation.
    2. Define a black-body and write its properties.
    3. What is absorption, reflection and transmission?
    4. Discuss the intensity or energy distribution of black-body radiation.

5. Discuss variation of spectral intensity or spectral energy of the backbody radiation with temperature.
6. Give a practicel example of a black-body and dicuss it.

7.15 ANSWERS

SAQ answer 1. black-body radiation is defined as the radiations emitted by a black body held at a uniform temperature. These are electromagnetic radiation within or surrounding a body in thermodynamic equilibrium with its environment.

All matters emit electromagnetic radiation at all temperatures above absolute zero. The radiation represents a conversion of a body's thermal energy into electromagnetic energy, and is therefore called <u>thermal radiation</u>.

Conversely all normal matter absorbs electromagnetic radiation to some degree and reflects some wavelengths. An object that absorbs all radiations of all wavelengths falling on it, is called a black body. When a black body is at a uniform temperature, its emission has a characteristic spectrum for wavelength and intensity that depends only on the temperature of the enclosure and are independent of the nature of the substance, the walls of enclosure and the presence of any other body. These emitting radiations are called black-body radiation. A black body emission is diffuse in nature, i.e. it is independent of direction.

SAQ answer 2: white paint is for thermal protection of the space craft, it reflects all the incident radiations and prevent the heat transfer to the underlying structures.

SAQ answer 3. The biggest natural black body approximations are

(i)   Cosmic Microwave Background (CMB) of the universe: the electromagnetic radiation that fills the part of the universe, are nearly isotropic and are characterized by radiobrightness temperature of 2.73 K.
(ii)   The second source of black body radiation is the star nearest to the earth-the SUN. The direct radar experiments performed in 1950 and 1960 indicated complete absence of radio-echo. Detailed spectral studies of solar radiation in the optical and IR bands have indicated the presence of thermal black-body radiation with brightness temperature of 5800 K at the sun.
(iii)   The third space object is our home planet- The Earth which possesses radiation close to black-body radiation with thermodynamic temperature of 287 K.

SAQ answer 4. In physics, we refer to an object which radiates perfectly is a black body. Its colour not necessarily need to be black. Even a heated canon ball, or the surface of stars like sun are examples of black-body.

Answers to objective question:

     1. (b)

     2. (c)

     3.(b,c)

     4.(c)

     5.(b,c)

7.16 REFERENCES

1. Zemansky, M.W. &Dittman, R.H., *Heat and Thermodynamics*, 7th edition (McGraw-Hill)

2. Heat Thermodynamics and Statistical Physics, Brijlal, Dr. N. Subrahmanyam, P. S. Hemne, S. Chand & Co. New Delhi.

3. Statistical and Thermal physics an introduction, S. Lokanathan and R.S. Gambhir, PHI

4. Thermal Physics: With Kinetic theory, Thermodynamics and Statistical Mechanics, S. C. Garg, R. M. Bansal, C. K. Ghosh, Tata McGraw-Hill

5. Thermal Physics, Kumar. A. and Taneja S.P., R. Chand & Co., New Delhi

7.17 SUGGESTED READINGS

1.   Dr. Max Planck, *The Theory of Heat Radiation*, P. Balkiston's Son & Co.

2.   Robert Siegel and John R.Howell, *Thermal Radiation Heat Transfer*, 3rd ed., Hemisphere Publishing Corporation.

3.   C. Balaji, *Essentials of Radiation Heat Transfer*, Wiley (Ane Books Pvt. Ltd.)

7.18 GLOSSARY

Black body : A body that absorbs all the radiations falling on it.

Radiation : Form of heat transference that does not require any material medium.

Radiation: Enery travelling through space. An electromagentic wave.

Thermal radiation : Electromagnetic radiations that lie in the IR region of the EM spectrum and are emitted by a hot body.

Absorptivity : Fraction of the radiation falling on the body that is absorbed.

Reflectivity : Fraction of radiation falling on the body that is reflected.

Transmissivity : Fraction of the radiation falling on the body that gets transmitted.

Radiant heat : Thermal radiation.

UNIT 8   THEORY OF RADIATION-II

CONTENTS

8.1 INTRODUCTION

At the end of nineteenth century scientist felt that all the laws of physics (which were known at that time) are sufficient to explain all the phenomena that occur in nature. It was believed that there exists only two kinds of entities in nature, that is the one that are made up of particles and the others are radiations. All particles obey Newton's law of motion and radiations obey Maxwell's equations of electromagnetism. Now a days we call these laws as classical physics.

Fortunately at the same time some experiments were performed whose results could not be explained by the classical laws of physics. Some of them were blackbody radiation, photoelectric effect, Compton effect etc. In order to explain these effects, the classical physics was insufficient and some new laws of physics were developed which are known as quantum physics. Hence black body radiation is one of the great effects which led to the birth of Modern physics.

In this article we will see how classical physics failed to explain the black body radiation characteristics and how quantum principles could explain it.

8.2 OBJECTIVE

After studying this unit you will be able to understand the following:

- Limitation of Classical Physics and application of Quantum Physics.
- Wien's distribution law
- Rayleigh Jeans Law
- Stefan-Boltzmann law
- Wien's displacement law
- Ultraviolet catastrophe

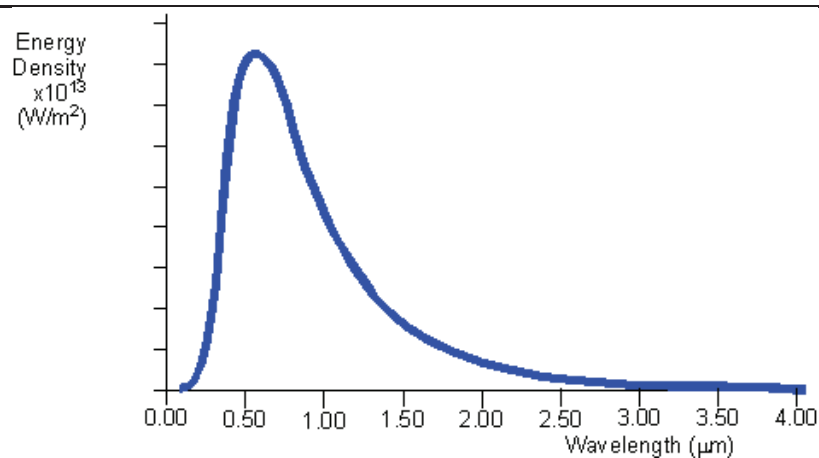## *8.3 EXPERIMENTAL FACTS ABOUT BLACK BODY RADIATION CURVE*

Fig (8.1): Theoretical curve for a black body at 5000K

The characteristics of black body radiation are exhibited by two graphs. The first graph (Fig.8.1) shows that

1. The black body does radiate energy at every wavelength. The curve gets infinitely close to the x-axis but never touches it, i.e., the curve touches the axis at infinite wavelength.
2. It also shows that there is a peak wavelength, at which most of the radiant energy is emitted. At 5000K the peak wavelength is about 5×10^{-7}m (500nm) which falls in the yellow-green section of the visible range of light.
3. At each temperature the black body emits certain amount of energy. This is represented by the area under the curve.
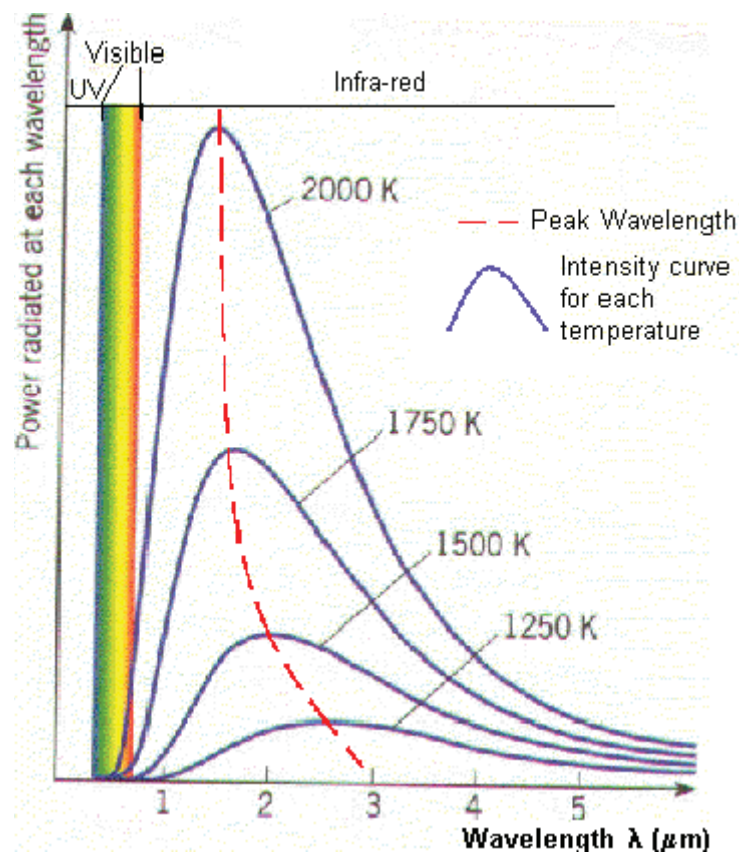
Fig (8.2): Black body radiation curves showing peak wavelengths at different temperatures.

The other graph (Fig.8.2) shows that

4. This graph shows how the black body radiation curves change at various temperatures. These all have their peak wavelengths in the infra-red part of the spectrum as they are at a lower temperature than the previous graph.
5. As the temperature increases, the peak wavelength emitted by the black body shifts towards lower value. It therefore begins to move from the infra-red to the visible part of the spectrum.
6. Again, none of the graphs touch the x-axis so they emit at all wavelengths. This means that some visible radiation is emitted even at these lower temperatures rather at any temperature above absolute zero, a black body will emit some visible light.

7. As temperature increases, the total energy emitted also increases, because the total area under the curve increases.
8. It also shows that the relationship is not linear as the area does not increase in even steps. The rate of increase of area, and therefore energy increases as the temperature increases.

8.3.1 THE EXPLANATION BY CLASSICAL PHYSICS

Light is an electromagnetic wave which is produced when an electric charge vibrates. (in true sense when it is accelerated. We know that heat is just the kinetic energy of random motion of molecules. In a hot object, electrons vibrate in random directions and produce light as a result. A hotter object means more energetic vibrations and so more light is emitted by a hotter object as a result it glows brighter, so far, so good. But classical physics could not explain the shape of the blackbody spectrum.

The electrons in a hot object can vibrate with a large range of frequencies, from a few to a very big number. In fact, there is no limit to how large the frequency value can be. Classical physics says that each frequency of vibration should have the same energy. Since there is no limit to how large the frequency can be, there is no limit to the energy of the vibrating electrons at high frequencies. Thus according to classical physics, there should be no limit to the energy of the light produced by the electrons vibrating at high frequencies. Experimentally, the blackbody spectrum always becomes small at the left-hand side (short wavelength and high frequency).

8.3.2 EXPLANATION BY QUANTUM PHYSICS

In 1900, Max Planck came up with his Quantum theory as a solution to the radiation problem. He proposed that the classical idea that each frequency of vibration should have the same energy must be wrong. Instead, he said that energy is not shared equally by electrons that vibrate with different frequencies. Planck said that energy is not continuous but comes in clumps. He called a clump of energy a **quantum**. The size of a clump of energy - a quantum depends on the frequency of vibration. Here is Planck's rule for the a quantum of energy for a vibrating electron:

energy of a quantum = (a calibration constant) x (frequency of vibration)

or $E = h\nu$ (8.1)

where ν is the frequency and h, the calibration constant, is called Planck's constant. Its value is 6.626×10^{-34}J–s, too small.

So how does this explain the spectrum of blackbody radiation? Planck said that an electron vibrating with a frequency ν could only have an energy of 1 $h\nu$, 2 $h\nu$, 3 $h\nu$, 4 $h\nu$, ... ; that is, the energy of vibrating electron is an integral multiple of $h\nu$

But an electron has to have *at least* one quantum of energy if it is going to vibrate. If it doesn't have at least an energy of 1$h\nu$, it will not vibrate at all and can't produce any light. At high frequencies the amount of energy in a quantum, $h\nu$, is so large that the high-frequency

vibrations can never occur. This is why the blackbody spectrum always becomes small at the left-hand side.

We will study these facts of quantum physics in unit 13 in detail.

Let's now study step by step, the attempts made by scientists to explain the blackbody radiation curves.

8.4 ATTEMPTS TO DESCRIBE THE BLACK BODY SPECTRUM

Several theoretical attempts were made to explain the observed spectrum using the thermo dynamical laws. The Stefan-Boltzmann law derived a relationship between total energy emitted in the whole wavelength range and the temperature of the blackbody, but it failed to explain actual distribution of energy in different parts of the spectrum. There were still many questions not answered like- how the spectral intensity (I_λ) or spectral energy (E_λ) vary with wavelength ? For a given wavelength how does spectral intensity vary with temperature ? In the early twentieth century, before Planck, several works were proposed within classical framework to describe wavelength dependency of spectral energy or intensity. These are *Wien's distribution* and *Rayleigh-Jeans distribution*, collectively called blackbody distribution function.

8.4.1 WIEN'S DISTRIBUTION LAW

The first noticeable success was achieved by Wilhelm Wien in 1896.
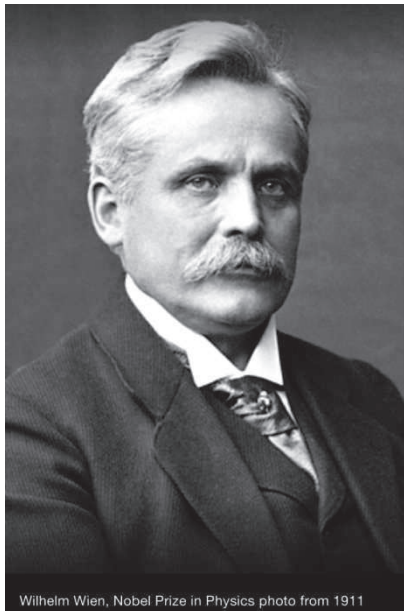
Wilhelm Wien, Nobel Prize in Physics photo from 1911

Wilhelm Wiens, who in 1893 came up with Wiens displacement law

Wilhelm Wiens was a German physicist who, in 1893,used theories about heat and electromagnetism to deduce Wien's displacement law, which calculates the emissionof a blackbody at any temperature from the emission at any one reference temperature.

In 1896 Wien empirically determined a distribution law of blackbody radiation. Wien received the 1911 Nobel Prize for his work on heat radiation.

By 1896 Wien had come up with a theory to explain the shape of the spectrum (even though the shape in the infrared was not fully known at that time). In what we now call *'Wien's distribution law'* or *'Wien's approximation'*, he tried to explain the blackbody spectrum using thermodynamic arguments, and assuming that the gas molecules obeyed the Maxwell-Boltzmann speed distribution for molecules (or atoms) in a gas.

He treated Blackbody radiation as a collection of molecules with Maxwellian distribution of speeds and assumed that these speeds are determined by the frequency of light emitted. Wien suggested that the energy of a black body in the wavelength interval $d\lambda$ could be given by

$$E_\lambda d\lambda = \tfrac{A}{\lambda^5} f(\lambda T) d\lambda$$

Wien found, using the Maxwell-Boltzmann distribution law for the speed of atoms (or molecules) in a gas, that the form of the function $f(\lambda T)$ was

$$f(\lambda T) = e^{-a/\lambda T}$$

or,
$$E_\lambda d\lambda = \frac{A}{\lambda^5} e^{-a/\lambda T} d\lambda \tag{8.2}$$

where, A and a were constants having values as   A = 8πhc and a = hc/K, K is another constant.

If we wish to express this in terms of frequency ν instead of wavelength λthen from the wave equation, $c = \nu\lambda$ and so $\lambda = c/\nu$. But, we also need to rewrite $d\lambda$ in terms of $d\nu$ and to do this we write

$$\nu = \tfrac{c}{\lambda} \rightarrow d\lambda = \tfrac{-c}{\nu^2} \, d\nu \tag{8.3}$$

We can ignore the minus sign as it just indicates us that as the frequency increases the wavelength decreases, and so substituting for λ and $d\lambda$ we can write that the energy in the *frequency* interval $d\nu$ is given by

$$E_\nu d\nu = \tfrac{A\nu^5}{c^5} e^{-a\nu/cT} \tfrac{c}{\nu^2} d\nu$$

$$E_\nu d\nu = A'\nu^3 e^{-a'\nu/T} d\nu \tag{8.4}$$

where A' and a' are also constants to be determined.

Thus Wien derived a formula, providing a relation between the intensity of radiation between λ and λ+dλ, as a function of the temperature T of the source and the wavelength λ.

The expression given by eq. (8.4) is **Wien's law of energy distribution**

8.4.2 WIEN'S LAW BREAKS DOWN

Wiens formula fits the experimental data collected prior to 1900 very well and was hence gave good agreement with the blackbody curve on the short-wavelength side of the peak (what we now call the '*Wien-side*' of the peak). But, the experimental results on the longer-wavelength side did not match well with the theoretical result as predicted by this law.

Thus, Wien's law holds good only in the region of shorter wavelengths at lower temperatures, but not found in accordance with the experimental curves at longer wavelengths and at higher temperatures.

8.4.3 RAYLEIGH-JEANS LAW

This law was derived by Lord Rayleigh in 1900 and then more rigorously by Rayleigh and Sir James Jeans working together, in 1905.

Rayleigh found some shortcomings in Wien's law. Lord Rayleigh and Sir J. Jeans alternatively applied the thermodynamic principle of equipartition of energy. According to them the radiation spectrum could be explained by considering the set of modes of the oscillating electromagnetic field within the blackbody. By the law of equipartition of energy, no mode is preferred over other, so energy is evenly distributed among all modes.

They found that the energy density (energy per unit volume) of the radiation coming from a black body varies as the square of the frequency of the radiation. This is the Rayleigh-Jeans law, and mathematically we can write this as

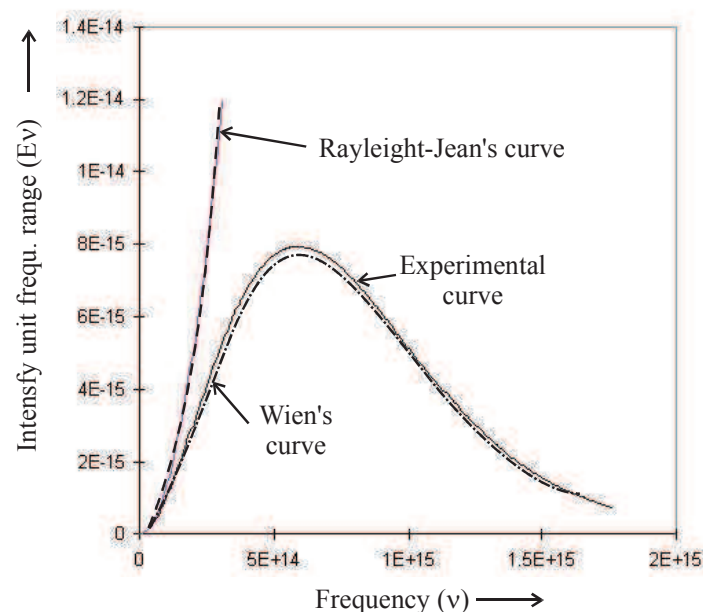$$u(v) \propto v^2 \tag{8.5}$$

Figure (8.3): Spectrum of radiations as a function of frequency.

This law led to what is known as *the ultraviolet catastrophe*, as it predicted that blackbodies would get brighter and brighter at higher frequencies of radiation, and that the total power radiated per unit area of the blackbody would be infinite. It was in trying to resolve this absurdity in 1900 that Max Planck came up with the idea of the quantisation of energy, which was the first step in what would later become quantum mechanics, an entirely new description of the sub-atomic world. But how was the Rayleigh-Jeans law derived? In order to understand what Planck did in 1900, we first of all need to properly understand what Rayleigh and Jeans derived using *classical physics*.

Rayleigh and Jeans considered *the radiation in a box* with perfectly reflective walls in thermal equilibrium as an idealized *cavity* to derive their eponymous law. For simplicity consider the cube of side length L
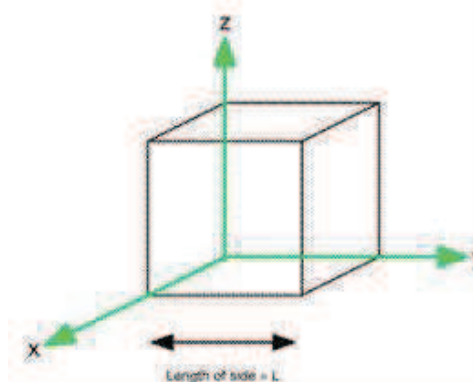
Fig. (8.4): Radiations in a cubical box of length L in thermal equilibrium

The 3-dimensional wave equation for an electromagnetic (EM) wave can be written (ignoring the magnetic component $\vec{B}$ as it is much smaller than the electric component $\vec{E}$) as

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + \frac{\partial^2 E}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2} \qquad (8.6)$$

For EM waves in a cubic cavity with sides of length L, the only modes which can exist have to satisfy the equation that electric field needs to be zero at the walls. If $\vec{E}$ needs to be zero this means E_x, E_y and E_z also needs to be zero at the walls. After solving equation (8.6) we get

$$n_x^2 + n_y^2 + n_z^2 = \frac{4L^2}{\lambda^2} \qquad (8.7)$$

Where n_x, n_y and n_z are related to number of waves between the wall in x, y and z direction, in other words number of modes allowed in the cavity in x,y and z directions.
This is the so-called *"standing wave solution to the wave equation for a cubical cavity with sides of length L".*

The total number of modes in cubic cavity

In order to calculate the total number of allowed modes N in cubic cavity, we need to sum over all possible values of n_x, n_y and n_z. To do this we use a mathematical tool of working in *"n-space"*, that is to say we determine the volume of a sphere where the x-axis is given by n_x, the y-axis by n_y and the z-axis by n_z. The value of $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$.

We can determine the value of N by considering the volume of a sphere with radius n, which is of course just

$$N = \frac{4\pi}{3}n^3 \qquad\qquad (8.6)$$

But, as we can see in the diagram below, if we sum over n for an entire sphere we will be including negative values of $n_x, n_y \ and \ n_z$ whereas we only have positive values of each.
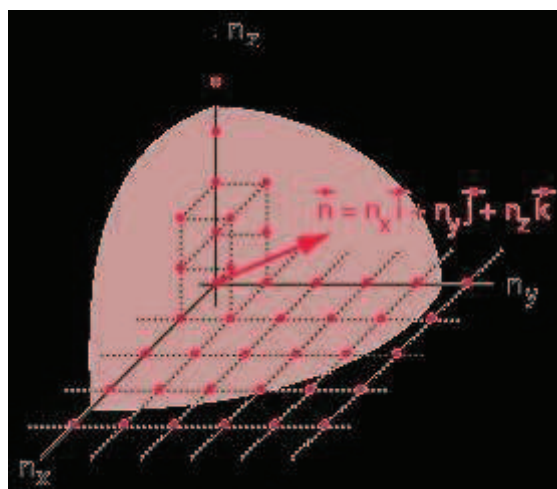
Figure 8.5. Allowed normal modes in the cavity

In order to correct this, we consider the positive values of $n_x, n_y \ and \ n_z$ only and thus we just need to divide the volume by 8, as the part of a sphere in the positive part of the diagram is one eighth of the total volume. There is one more correction: Light can exist independently in two different polarisations at right angles to each other, so we need to double the number of solutions to our standing wave equation to account for this .We, therefore, can write

$$N = \frac{4\pi}{3}n^3 \left(\frac{1}{8}\right)(2) \qquad\qquad (8.9)$$

$$= \frac{\pi}{3}n^3$$

$$= \frac{\pi}{3}\left(n_x^2 + n_y^2 + n_z^2\right)^{3/2}$$

$$= \frac{\pi}{3}\left(\frac{4L^2}{\lambda^3}\right)^{3/2}$$

Which gives the number of modes in the cavity as

$$N = \frac{8\pi L^3}{3\lambda^3} \qquad\qquad (8.10)$$

The number of modes per unit wavelength

The expression (8.10) gives is the total number of modes in the cavity summed over all wavelengths. The number of modes per unit wavelength can be found out by differentiating this expression with respect to λ, i.e., we find $\frac{dN}{d\lambda}$.

$$\frac{dN}{d\lambda} = \frac{d}{dx}\left(\frac{8\pi L^3}{3\lambda^3}\right) = -\frac{8\pi L^3}{\lambda^4} \qquad\qquad (8.11)$$

The minus sign implies that the number of modes decreases with increasing wavelength. The number of modes per unit wavelength per unit volume in the cavity

$$\frac{total\ number\ of\ modes\ per\ unit\ wavelength}{cavity\ volume} = \frac{1}{L^3}\frac{dN}{d\lambda}$$

$$= -\frac{1}{L^3}\left(\frac{8\pi L^3}{\lambda^4}\right) = -\frac{8\pi}{\lambda^4} \qquad\qquad (8.12)$$

The energy per unit volume per unit wavelength and per unit frequency

Because the matter and radiation are in thermal equilibrium with each other, we can say that the energy of each mode of the EM radiation is $E=kT$, where k is Boltzmann's constant and T is the temperature of radiation in kelvin. This comes from the principle of the *Equipartition of Energy*. We write the energy per unit volume (also called the *energy density*) with the symbol u so that we have the energy per unit volume per unit wavelength given by

$$\frac{du}{d\lambda} = \frac{1}{L^3}\frac{dE}{d\lambda} = \frac{1}{L^3}\left(\frac{dN}{d\lambda}\right)kT = \frac{8\pi kT}{\lambda^4} \qquad\qquad (8.13)$$

In terms of frequency it can be written as

$$\frac{du}{dv} = \left(\frac{8\pi kT}{c^3}\right)v^2 \qquad\qquad (8.14)$$

This is the *Rayleigh-Jeans law*.

8.5.4 Rayleigh Jeans law fails for shorter frequencies

So, using *Classical Physics*, we find that the energy density is proportional to the square of the frequency, which means the energy density plotted as a function of frequency should look like that shown in the figure (8.3).

It has already been shown that the energy density of blackbodies follows the continuous curve (Fig. 8.3). If it were to follow the dashed curve (the Rayleigh-Jeans law) the blackbody would get brighter and brighter at shorter and shorter wavelengths, resulting the so-called **ultraviolet catastrophe**.
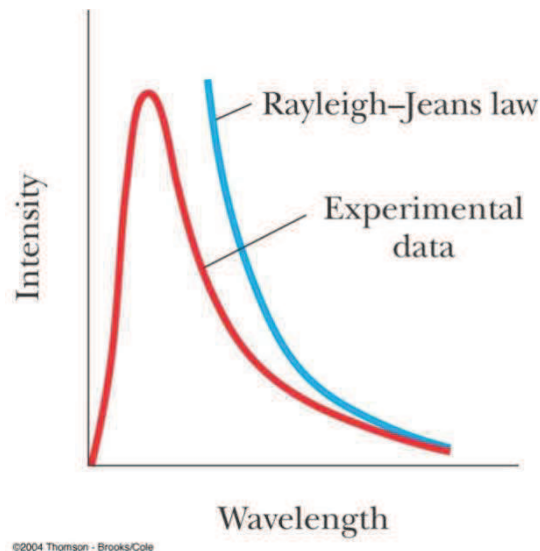
Fig. 8.6.Rayleigh Jeans Law curve (dashed) and experimentally observed curve (continuous)

Like Wiens law, Rayleigh law also found not to be in accordance with the experimental curves of blackbody radiation. The Rayleigh-Jeans law was found to be in agreement with experimental curves at longer wavelengths (shorter frequencies) and at higher temperature but fails for shorter wavelengths.

Thus, both Rayleigh-Jeans law and Wien's law do not agree precisely with experimental curves throughout.

8.5 THE STEFAN-BOLTZMANN LAW

The black body radiation emitted in any direction is measured in terms of radiation intensity. Based on the thermodynamic properties and considering the simplicity of the system, we can easily find the total emissive power ($E_b(T)$), Radiation Pressure (P) and radiation energy density (u) of the blackbody in terms of total radiation intensity ($\mathbf{I_b}$, that includes intensity of all the wavelengths) as

Emissive Power: $$E_b(T) = \pi\, I_b(T)$$ …………(i)

Radiation Pressure: $$P(T) = \frac{4\pi\, I_b(T)}{3c}$$ …………(ii)

Energy Density: $$u(T) = \frac{4\pi\, I_b(T)}{c}$$ …………(iii)

From equation (ii) and (iii) we get

$$P = \frac{u}{3} \qquad\qquad\qquad ....(iv)$$

The total internal energy U is equal to the product of the specific internal energy and the volume. The specific internal energy is defined as energy per unit volume. From TdS relation in thermodynamics we have,

$$TdS = dU + PdV$$

$$= d(uV) + PdV$$

$$= udV + Vdu + PdV$$

$$= udV + Vdu + \left(\frac{u}{3}\right)dV$$

$$= Vdu + \left(\frac{4u}{3}\right)dV$$

$$\therefore \qquad dS = \left(\frac{V}{T}\right)du + \left(\frac{4u}{3T}\right)dV$$

$$= \frac{V}{T}\frac{\partial u}{\partial T}dT + \frac{4u}{3T}dV$$

For any function $\qquad\qquad Z = f(x,y)$

and differential $\qquad\qquad dZ = Mdx + Ndy$

fordZ to be an exact differential

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

For dS to be exact differential, we have

$$\frac{\partial}{\partial V}\left\{\frac{V}{T}\frac{\partial u}{\partial T}\right\} = \frac{\partial}{\partial T}\left(\frac{4u}{3T}\right)$$

or $\qquad\qquad \frac{1}{T}\frac{du}{dT} = \frac{4}{3T}\frac{du}{dT} - \frac{4u}{3T^2}$

or $\qquad\qquad \frac{4}{3}\frac{u}{T^2} = \frac{1}{3T}\frac{du}{dT}$

or $\qquad \frac{du}{u} = 4\frac{dT}{T}$

Integrating this equation we get

$$u = aT^4 \qquad\qquad\qquad (8.15)$$

Substituting above expression in equation (iii) we get

$$\frac{4\pi I_b(T)}{c} = aT^4$$

$$I_b(T) = \frac{ac}{4\pi}T^4$$

or

For a black body the emissive power is

$$E_b = \pi I_b = \frac{ac}{4}T^4 \tag{8.16}$$

where c is the speed of light in vacuum. Determining the value of a from experiment, we get

$$\frac{ac}{4} = 5.67 \times 10^{-8}\,\frac{W}{m^2 K^4} = \sigma \tag{8.17}$$

or $$E_b = \sigma\,T^4 \tag{8.18}$$

Here, σ is known as Stefan-Boltzmann constant and eq. (8.18) as Stefan-Boltzman Law or T^4-law.

Josef Stefan (1835 - 1896) and Ludwig Boltzmann (1844 - 1906) were the two physicists behind this equation. Stefan was an Austrian Professor and Boltzmann's research supervisor. It is worth noting that Boltzmann got his PhD at the age of 22 and at the age of 25, he was appointed full professor in mathematical physics at the University of Graz!

The Stefan-Boltzmann law relates the heat flow rate emitted or absorbed from an object to its temperature
The Stefan-Boltzmann law is also known as Stefan's law. It states that the rate of emission of radiant energy by unit area of a perfectly blackbody is directly proportional to the fourth power of its absolute temperature.

In other words it states that the total energy radiated per unit surface area of a black-body in unit time (known as the blackbody irradiance, energy flux density, radiant flux or emissive power), E is directly proportional to the fourth power of the blackbody's thermodynamic temperature T (also called absolute temperature)

Hence $E = \sigma T^4$

The constant of proportionality σ is called the Stefan-Boltzmann constant or Stefan's constant. It is not a fundamental constant, in the sense that it can be derived from other known constants of nature. The value of the constant is 5.6704×10^{-8} Js^{-1}m^{-2}K^{-4}.

Above law refers only to emission of heat radiation and not to the net loss of heat radiations by the body after exchange with the surroundings.

Self Assessent Questons (SAQ)

SAQ 1. Is the black body has to be necessarily black in colour?

SAQ 2. A black surface is radiating with a total emissive power of $20 \, kW/m^2$. What is its surface temperature? At what wavelength is its maximum spectral emissive power?

SAQ 3. An electric flat-plate heater is squre with a $0.1 \, m$ edge length is radiating $10^2 W$ from each side. If the heater can be considered black what is its temperature?

When an iron piece (rod) is heated it starts changing its colour. With rise in temperature it first appears dark red, then yellowish white, white and then bluish white. Hence, the emitted colour from a hot body has relation with its temperature.

8.6 WIEN'S DISPLACEMENT LAW

Wien's displacement law relates the wavelength corresponding to maximum energy of the thermal radiation emitted by an object to its absolute temperature. First derived by the German physicist Wilhelm Wien in 1893 using thermodynamic principles.

In section 8.4.1 we have studied a relation for the spectral energy of radiation between λ and λ+dλ, as a function of temperature T of the source and the wavelength λ as

$$E_\lambda d\lambda = k\lambda^{-5}e^{-a/\lambda T}d\lambda$$

So that

$$E_\lambda = k\lambda^{-5}e^{-a/\lambda T} \qquad (8.19)$$

Differentiating above expression w.r.t. λ

$$\frac{dE_\lambda}{d\lambda} = -5 \, k \, \lambda^{-6}e^{-a/\lambda T} + k \, \lambda^{-5}e^{-a/\lambda T}\left(-\frac{a}{T}\right)\left(-\frac{1}{\lambda^2}\right)$$

For maximum energy radiation, the corresponding wavelength $\lambda \to \lambda_{max}$ and $\frac{dE_\lambda}{d\lambda} = 0$

or, $-5 \, \lambda_{max}^{-6} + \lambda_{max}^{-7}\frac{a}{T} = 0$

or, $-5 + \lambda_{max}^{-1}\frac{a}{T} = 0$

$$\boldsymbol{\lambda_{max} \, T = b} \qquad (8.20)$$

Where b is the constant of proportionality called Wien's displacement constant and equals $2.8978 \times 10^{-3} \, mK$.

In other words Wien's displacement law states that the hotter the object is, the shorter the wavelength at which it will emit most of its radiation. Thus, there is an inverse relationship between the wavelength of the peak of maximum emission λ_{max} of a blackbody and its absolute temperature T, i.e.,

$$\lambda_{max} \propto \frac{1}{T}$$

or, $\lambda_{max}T = b$

where λ_{max} is the wavelength in m and T is the temperature of the black body in K

Due to this reason most of the radiation coming form the sun (at about 6000 K) are of shorter wavelengths, whereas radiations emitted by warm earth surface or other bodies are in infrared region (longer wavelength). The Green House effect is an illustration of Wien's displacement law.

Example: Find the peak wavelength of the blackbody radiation emited by (A) a body at 2000 K

(B) the tungsten filament of a lightbulb at 3000 K

Solution:

(A) the sun (2000 K)

By Wien's displacement law, $\lambda_{max} = 2.898 \times 10^{-3}$ m.K/2000K

= 1.4 μ

(1.4 μm corresponds to infrared range)

(B) the tungsten filament of a light bulb at 3000 K

$$\lambda_{max} = 2.898 \times 10^{-3} \text{ m.K/5800 K}$$

= 0.5 μm

(visible light range, yellow-green)

SAQ 4: The sun's surface temperature is at 6000 K. What is the wavelength at which maximum solar energy is emitted?

8.7 ULTRAVIOLET CATASTROPHE

The ultraviolet catastrophe is also known as Rayleigh Jeans catastrophe. The Rayleigh-Jeans law was in significant disagreement with the experimental results near the maximum of the curve   and at higher frequencies.   The word "ultraviolet" signifies that the law is in disagreement in the short wavelength (high frequency) region of the spectrum. The glaring errors in the law were as follows:

Rayleigh formula was derived from a model of a blackbody cavity with a hole, having electromagnetic waves bouncing around in it. The electromagnetic radiations are compared to standing waves, hence solution of wave equation also applies to EM waves. The standing waves have vibration zero at two fixed ends. If distance between two ends is L then the possible wavelengths which could be produced in the cavity are such that

$$L = \frac{n\lambda}{2} \qquad\qquad (1) \qquad\qquad \text{where n = 1,2,3,4 .....etc.}$$

In other words the EM wave will have complete number of half cycles within the box. These allowed vibrations are called modes.

Considering the physical situation, it is clear that 'nodes' will be formed at the two extreme ends of the cavity i.e., opposite walls. As a result, the first possible mode inside will have half wave only. Subsequently, thereafter one, one and half, two .... waves thereby giving increasing number of frequencies.

The number of modes for a frequency range ω and ω+dω was found to be

$$N(\nu)d(\nu) \propto \nu^2 d\nu \qquad \text{(ii)}$$

Above result was obtained with an assumption of considering vibrations of EM field like of an harmonic oscillator

According to equipartition theorem, each allowed mode will have energy

$$E = \frac{1}{2}kT \qquad \text{(iii)}$$

where k is Boltzmann constant. There was an attempt to apply equipartition law to EM radiation as they were thought of like waves.

Thus energy density for an interval ν and ν+dν will be

$$\in(\nu) \propto \nu^2 kTd\nu \qquad \text{(iv)}$$

This is Rayleigh Jeans law. According to classical physics all the modes have equal chance to be produced, and the number of modes goes up proportional to square of the frequency. Hence according to this law there should be continous increase in radiated energy with increase in frequency and approaches infinity when frequency approaches infinity. But it was not observed experimentally. The situation has been shown by the Rayleight-Jeans curve in Fig. 8.3

The classical theory (the Rayleigh-Jeans law) predicts that there will be an *infinite* number of modes allowed in the cavity as we go to higher and higher frequency, so more and more energy exists in each frequency interval as we go to higher and higher frequencies (shorter and shorter wavelengths). The total area under the curve, the power per unit area, of the blackbody would be infinite and it would be infinitely bright at ultraviolet wavelengths (high frequencies) which *clearly* doesn't happen, the theory had completely failed. This disagreement of the observed behaviour with the prediction of the Rayleigh-Jeans law came to be known as the *ultraviolet catastrophe.*

Thus, the error in Rayleigh –Jeans law at shorter wavelengths that an ideal black body at thermal equilibrium will emit radiation with infinite power is called ultraviolet catastrophe. This catastrophe was a fatal failure of classical physics

8.8 SUMMARY

A black body is an idealized object which absorbs and emits radiations of all frequencies. The total radiant energy emitted from a surface was found to be proportional to the fourth power of its absolute temperature called Stefan –Boltzmann law. A relationship between wavelength λ_{max} (at which energy of emitted radiation is maximum) to the temperature of the body was given by Wien's displacement law. As temperature of blackbody increases the overall radiant energy increases (Stefan law) and the peak of radiation curve shifts towards shorter wavelengths that is λ_{max} is inversely proportional to temperature (Wien's displacement law). It is useful in determining the temperature of hot radiant objects such as stars. Further Wien derived a distribution law of radiation. However this law was valid at high frequencies and broke down completely at low frequencies resulting a situation called infrared catastrophe. Classical Physics was used to derive equation which describes intensity of black body radiation as a function of frequency for a fixed temperature. The result was known as Rayleigh-Jeans law. Although it works for low frequencies, and diverges as v^2; this divergence for high frequency will result into a situation which is called ultraviolet catastrophe.

8.9 TERMINAL QUESTIONS

Objective Question

1. The blackbody radiation is
   a. longitudinal wave
   b. electromagnetic wave
   c. sound wave
   d. transverse wave
2. The energy emitted by an object held at constant temperature and having capacity to absorb all the light falling on it is known as
   a. blackbody radiation
   b. conduction
   c. convection
   d. thermal radiation
3. The energy radiated by a blackbody comprises
   a. all wavelength range.
   b. only radio waves.
   c. only visible wavelength range.
   d. ultravoilet, Infra-red and x-rays
4. As the temperature of blackbody increases the wavelength at which it emits maximum energy
   a. increases
   b. decreases
   c. same for all temperature
   d. zero

5. The area under the intensity curve of blackbody radiation
   a. increases with decrease in blackbody temperature.
   b. increases with increase in blackbody temperature.
   c. represents total energy density emitted by the blackbody.
   d. proportional to fourth power of the blackbody temperature.
6. The mathematical description of blackbody intensity curve is given by
   a. Wien's law
   b. Planck's law
   c. Rayleigh-Jeans law
   d. Stefan-Boltzmann law
7. Any differential $dZ = Mdx + Ndy$ is said to be exact when
   a. $\frac{\partial M}{\partial x} = \frac{\partial N}{\partial y}$
   b. $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$
   c. $\frac{\partial Z}{\partial y} = \frac{\partial Z}{\partial x}$
   d. $\frac{\partial y}{\partial M} = \frac{\partial x}{\partial N}$

Numerical Questions

1. Consider a blackbody at a temperature of 6000K. Find the total emissive power.
2. Assuming the Earth is a black body and has a temperature of 300 K, how much energy is it emitting?
3. Assuming that a beaker of water is boiling and has a emissivity of 0.95. How much energy is it emitting? What is the peak energy emission wavelength? What part of the electromagnetic spectrum is this in?

Short Questions

1. What is Stefan-Boltzmann law?
2. What is the wavelength region in which Wien's distribution formula is valid?
3. What is the limitation of Rayleigh-Jeans Law?
4. What is spectral energy density?
5. State Kirchoff's radiation law?

Long Answer Questions

1. Discuss the experimental curve of blackbody radiation.
2. Derive the expression of Stefan-Boltzmann law using first law of thermodynamics.
3. Explain what is ultraviolet catastrophe.
4. Derive the expression of Wien's displacement law

8.10 ANSWERS

Answer to Self assessment questions

Answer SAQ: 1.In Physics, we refer to an object which radiates perfectly as a *blackbody*. The name is a little misleading, as there is nothing about a black body which is black in colour. An example of a blackbody is a heated canon ball, or the surface of stars like the Sun. It has been known since time that if you heat a metal object, such as a canon ball, it will start to glow; it actually starts giving off its own *visible* light rather than just reflecting light.

Answer SAQ 2. *From Stefan-Boltzmann law, the temperature of the blackbody is* $T = \left(\frac{E_b}{\sigma}\right)^{\frac{1}{4}}$

$$T = \left(\frac{20000}{5.67051 \times 10^{-8}}\right)^{\frac{1}{4}} = 770.6 \ K$$

From Wien's displacement law $\lambda_{max} = \frac{b}{T}$

$$\lambda_{max} = \frac{2898}{770.6} = 3.76 \ \mu m$$

Answer SAQ 3. Using Stefan-Boltzmann law

$$T = \left(\frac{Q}{A\sigma}\right)^{\frac{1}{4}} = \left[\frac{10^2 W}{(0.1 \ m)^2 \ 5.67051 \times 10^{-8} W/(m^2 K^4)}\right]^{\frac{1}{4}} = 648 \ K$$

Answer SAQ 4. From Wien's displacement law $\lambda_{max} T = 2898 \ \mu mK$

$$\lambda_{max} = \frac{2898}{6000} = 0.483 \ \mu m.$$

This lies in the visible portion of the spectrum, which is $0.4 - 0.7 \ \mu m$ and that is why we have daylight and Earth is so habitable.

Answers to Objective type questions

1. (b),(d)

2. (a)

3. (a)

4.(d)

5.(b),(c),(d)

6.(b)

7.(b)

Answers to Numerical questions

Answer 1. The total emissive power is given by Stefan-Boltzmann law: $E_b = \sigma\, T^4$.

$$E_b = 5.67 \times 10^{-8} \frac{W}{m^2 K^4} \times (6000K)^4 = 7.35 \times 10^7 W/m^2$$

Answer 2. $E_b = 5.67 \times 10^{-8} \frac{W}{m^2 K^4} \times (300K)^4 = 459\; W/m^2$

Answer 3. Emissivity (ϵ)is a measure of how efficiently a surface emits thermal energy (i.e. material's radiating efficiency), can have a value from 0 (shiny mirror) to 1.0 (blackbody).

Energy emitted by boiling water is $= \epsilon\, \sigma\, T^4$

$$= 0.95 \times 5.67 \times 10^{-8} \frac{W}{m^2 K^4} \times (100K + 273K)^4$$
$$= 1042\; W/m^2$$

$$\lambda_{max} = \frac{2898}{373} = 7.77\; \mu m. \textit{This is in infra-red part of the spectrum.}$$

Answers to Short question

Answer 1. The Stefan–Boltzmann law states that the total energy radiated per unit surface area of a black body across all wavelengths per unit time (also known as the black-body radiant emittance) is directly proportional to the fourth power of the black body's thermodynamic temperature T i.e.

$$E_b = \sigma\, T^4$$

Answer 2. Wien's distribution law gave good (but not perfect) agreement with the blackbody curve in region of shorter wavelengths at lower temperatures, but not found in accordance with experimental curves at longer wavelengths. According to wien'spostulates $E_\lambda = k\lambda^{-5}e^{-a/\lambda T}$. At large wavelengths the spectral energy decreases much rapidly than the observed curve.

Answer 3. The Rayleigh-Jeans prediction suggested that the energy density (energy per unit volume) of the radiation coming from an ideal blackbody varies as the square of the frequency of the radiation, $u(\nu) \propto \nu^2$. So the amount of energy radiated simply gets greater and greater at higher and higher frequencies. The total energy would become infinite which violets the law of conservation of energy. The name Ultraviolet Catastrophe was used to describe this failure of theory because UV light has a higher frequency than visible light.

Answer 4. Spectral energy density is defined for a particular wavelength. It is the energy per unit volume per unit range of wavelength. The spectral energy density describes how electromagnetic energy is distributed with wavelength or frequency.

Answer 5. Kirchhoff 's radiation law states that the ratio of emissive power to absorptive power $e_\lambda/a_\lambda = f(\lambda, T)$, a universal function of wavelength and temperature, independent of the nature or shape of the cavity. This law accounts for the fact that good absorbers are also good emitters.

UNIT-9   THEORY OF RADIATION-III

CONTENTS

9.1 INTRODUCTION

The key points understood from previous units are

- A black body in thermal equilibrium emits electromagnetic radiation called Black body radiations.

- The black body radiations have specific spectrum and intensity that depends only on temperature of the body

- Predictions based on classical theories failed to explain the black body spectra observed experimentally.

- Based on the application of Wein and Rayleigh's explanations, the energy spectrum of blackbody radiation can be explained partly. By considering the utility of the above two laws, Paschen concluded that the classical theory, that is the continuous emission of radiation, failed to explain the above phenomenon.

Classical physics cannot explain the experimentally observed spectra of radiation. Classical physics assumed that radiation is emitted continuously by the matter with smooth continuous spectrum of all possible energy levels. The classical theory of radiation was based on Maxwell's equations. According to this theory oscillating charges are responsible for emission/absorption of electromagnetic radiation. The frequency of radiation is equal to frequency of charge oscillation. The emission/absorption of radiation takes place continuously at a rate determined by the parameters of the oscillating system. However new phenomenon like Compton effect, Photoelectric effect, Zeemann effect, emission of light, absorption of light etc. cannot be explained on the basis of classical theory. The failure of these theories to explain new phenomenon led to the discovery of a new concept namely the **quantum theory of radiation.** In 1900 Max Planck postulated that the electromagnetic energy is emitted not continuously (like by vibrating oscillators), but in discrete packets of energy called quanta. This was the birth of Quantum Physics.

According to Quantum theory the energy of electromagnetic waves is *quantized* rather than continuous. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). This quantum of radiation is called photon.

The quantum theory gave a simple and straightforward explanation of these phenomena. On the basis of quantum theory, the satisfactory explanation of black body radiation was given by Planck which is popularly known as Planck's radiation law. We will find that this law can satisfactorily explain several physical phenomena and laws of radiation.

9.2 OBJECTIVES

After reading this unit you will be able to understand the following:

- Assumptions made by Max Planck to describe electromagnetic radiation emitted by a black body.

- Quantization of energy and Planck's hypothesis.

- Derivation of Planck's law.

- Deduction of Weins law, Rayleigh-Jeans law and Wein's displacement law from Planck's law.

9.3 QUANTUM THEORY OF RADIATION

Max Planck in 1901 proposed quantum theory of radiation. His theory says:

1. The radiation energy is always in the form of tiny bundles of energy called quanta, i.e., energy is absorbed or emitted discontinuously.

2. Each quantum has some definite energy, which depends upon the frequency of the radiation, given by the relation

$$E = h\nu \qquad\qquad (9.1)$$

Here E is the energy of each quantum in joules, and the frequency of radiation in s^{-1} and h is Planck constant, $h = 6.626 \times 10^{-34}$ J-s

also $E = hc\omega$ (9.2)

where ω is known as wave number ($\omega = 1/\lambda$ m^{-1})

from above two equations it is evident that

$$\nu = c/\lambda = c\omega \qquad\qquad (9.3)$$

3. The energy emitted or absorbed by a body is always a whole multiple of a quantum that is a body cannot absorb or emit energy in fractions of quantum. This concept is known as quantization of energy.

The Nobel Prize in Physics 1918 was awarded to Max Planck "in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta".The importance of the discovery, with its far-reaching effect on classical physics, was not appreciated at first. However the evidence for its validity gradually became overwhelming as its application accounted for many discrepancies between observed phenomena and classical theory.

9.4 PLANCK'S HYPOTHESIS

In order to develop a theory/ law which can satisfactorily explain the distribution of energy in a black body radiation, Planck proposed the following hypothesis:

1. A blackbody radiation chamber is made up of a number of oscillating particles (of molecular dimensions) called harmonic oscillators or resonators (energy emitters), known as Planck's oscillators or Planck's resonators.

2. An oscillator emits radiation of frequency ν when it drops from one energy state to the next lower one, and it jumps to the next higher state when it absorbs radiation of frequency ν. Each discrete bundle has energy hν or multiples of hν. It is given by

    $$\varepsilon_n = nh\nu \qquad\qquad (9.4)$$

    where, n = 0,1,2,3, ….
    and h (Planck's constant) = 6.6 x 10^{-34} J-s
    Hence the energy of radiation is not continuous, but discrete in nature. The values of the energy of oscillators are therefore like 0, hν, 2hν, 3hν, 4hν………., nhν

3. The oscillating particles cannot radiate or emit energy continuously. They will radiate energy only in the form of a discrete packet of energy that is a small unit called quanta or photon.

In other words, the exchange of energy between radiation and matter is quantized that is exchange of energy takes place in multiples of the fundamental energy unit (hν) of the resonator called **quantum.**

Example 1 The Planck's constant h has the dimensions equal to
a) M L ^{2} T $^{-1}$
b) M L T $^{-1}$
c) M L T $^{-2}$

d) M L T

Answer: a

Explanation: It has unit J s and its value is 6.626×10^{-34}.

Example 2 Calculate the energy of one mole of photons of radiation whose frequency is 5.00×10^{14} Hz.

Solution: Formula used is E=nhν where:

E is the energy, n is the number of photons of light and h is [Planck's constant]

By inserting the values in the formula.

1 mol of photons = 6.022×10^{23} photons.

E=nhν = $6.022 \times 10^{23} \times 6.626 \times 10^{-34}$ J·s $\times 5.00 \times 10^{14}$ s^{-1} = 2.00×10^{5} J = 2.00×10^{2} kJ

The energy is 2.00×10^{2} kJ.

Self-assessment question 1

Ques1. The energy of vibrating molecules involved in blackbody radiation existed only in

y Multiples of certain fixed amount of energy

y Constant energy

y Continuous energy

y Amount of energy which is never consistent

9.5 DERIVATION OF PLANCK'S RADIATION LAW

Assume that the number of vibrating particles (Planck's resonator) in the body as N_0, N_1, N_2, N_3, ……..N_n. According to planck's hypothesis, the energy of the above particles can be written as 0, ε, 2ε, 3ε, 4ε,……..nε

Thus total number of vibrating particles are

$$N=N_0+N_1+N_2+N_3+…..N_n \tag{9.5}$$

Similarly total energy of the body

$$E=0+ε+2ε+ 3ε+4ε+……..nε \tag{9.6}$$

Therefore, average energy of a particle is given by

$$\bar{\varepsilon} = \frac{E}{N} \tag{9.7}$$

According to Maxwell's distribution law, the number of particles in the nth oscillating system can be written as

$$N_n = N_0 e^{-\frac{n\varepsilon}{kT}} \tag{9.8}$$

where ε is the average energy per oscillator k the Boltzmann constant and the absolute temperature.

Extending Maxwell distribution formula to the present system, the total number of particles can be written as

$$N = N_0 + N_0 e^{-\frac{\varepsilon}{kT}} + N_0 e^{-\frac{2\varepsilon}{kT}} + N_0 e^{-\frac{3\varepsilon}{kT}} + \cdots \ldots \ldots$$

or $\quad N = N_0 \left[1 + e^{-\frac{\varepsilon}{kT}} + e^{-\frac{2\varepsilon}{kT}} + e^{-\frac{3\varepsilon}{kT}} + \cdots \ldots \ldots \right]. \tag{9.9}$

Using the mathematical expression

$$1 + x + x^2 + x^3 + \cdots \ldots \ldots = \frac{1}{1-x}$$

and putting $x = e^{-\frac{\varepsilon}{kT}}$, we can rewrite the above equation (9.9) as

$$N = \frac{N_0}{1 - e^{-\frac{\varepsilon}{kT}}} \tag{9.10}$$

Similarly total energy of the body can be written as

$$E = 0 + \varepsilon. N_0 e^{-\frac{\varepsilon}{kT}} + 2\varepsilon. N_0 e^{-\frac{2\varepsilon}{kT}} + 3\varepsilon. N_0 e^{-\frac{3\varepsilon}{kT}} + \cdots$$

$$E = N_0 \varepsilon e^{-\frac{\varepsilon}{kT}} \left[1 + 2e^{-\frac{\varepsilon}{kT}} + 3e^{-\frac{2\varepsilon}{kT}} + 4e^{-\frac{3\varepsilon}{kT}} + \cdots \ldots \ldots \right]. \tag{9.11}$$

Using the mathematical expression

$$1 + 2x + 3x^2 + 4x^3 + \cdots \ldots + n. x^{n-1} = \frac{1}{(1-x)^2}$$

Above equation (9.11) can be written as

$$E = \frac{N_0 \varepsilon e^{-\frac{\varepsilon}{kT}}}{\left(1 - e^{-\frac{\varepsilon}{kT}} \right)^2} \tag{9.12}$$

Thus we have got expressions for total energy (eq. 9.12) and total number of particles (eq. 9.10). Substituting these in the expression of average energy(eq. 9.7) we get

$$\bar{\varepsilon} = \frac{\dfrac{N_0 \varepsilon e^{-\frac{\varepsilon}{kT}}}{\left(1 - e^{-\frac{\varepsilon}{kT}} \right)^2}}{\dfrac{N_0}{\left(1 - e^{-\frac{\varepsilon}{kT}} \right)}} \tag{9.13}$$

or, $$\bar{\varepsilon} = \frac{\varepsilon e^{-\frac{\varepsilon}{kT}}}{\left(1-e^{-\frac{\varepsilon}{kT}}\right)}$$

$$= \frac{\varepsilon}{\left(e^{\frac{\varepsilon}{kT}}-1\right)} \tag{9.13}$$

$$= \frac{h\nu}{\left(e^{\frac{h\nu}{kT}}-1\right)} \tag{9.14}$$

Eq. (9.14) gives the average energy of oscillator.

Note: the average energy obtained from quantum physics is different from that obtained from the classical physics where average energy per mode is kT

In the frequency range ν and ν+dν the energy density (total energy per unit volume for a particular frequency range) can be obtained by multiplying the number of Planck's oscillators lying in that particular range multiplied with the average energy of the Planck's oscillator. So we need to calculate the number of oscillators per unit volume lying in the frequency range ν and ν+dν.

Here we can clearly see that the average energy per mode is kT as suggested by Rayleigh Jeans law.

whereas the Planck's quantum radiation law suggests its value equal to $h\nu/(e^{h\nu/kT}-1)$.

9.5.1 NUMBER OF OSCILLATORS PER UNIT VOLUME LYING IN THE FREQUENCY RANGE N AND N+DN.

Consider a Blackbody in the form of a hollow cubical box. The radiations inside the box consist of a number of waves travelling in all possible diractions. The waves suffer multiple reflection from the walls of the encloser. As a result of interference between incident and reflected waves a stationary or standing wave pattern is formed. This is also called resonant mode of the cavity. The radiated energy from the blackbody can be considered to be produced by the resonant modes of the cavity.

A mode for an electromagnetic wave in a cavity must satisfy the condition of zero electric field at the walls as shown in the figure 9.1
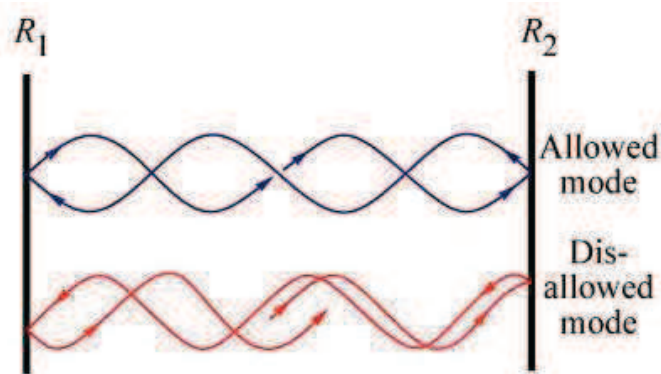
Figure 9.1 Number of modes in the cavity be such that Electric field becomes zero at the walls of cavity

Through analysis by Rayleigh and Jeans it was shown that number of modes was proportional to the square of frequency as shown in figure 9.2.
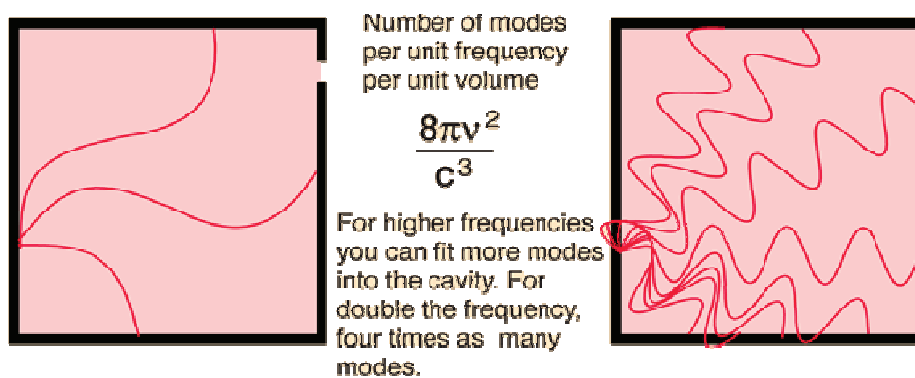
Figure 9.2.Number of modes in a cavity are proportional to square of frequency

If l be the length of the box then allowed wavelengths or frequencies are given by

$$\lambda = \frac{2l}{n} \qquad \text{where, } n = 1,2,3,4 \dots \dots, \infty \ \text{(Fig. 9.3)} \qquad (9.15)$$

$$v = \frac{c}{\lambda} = \frac{nc}{2l} \quad \text{where } n = 1,2,3,4 \dots \dots \infty \qquad (9.16)$$

The allowed frequency is called mode of vibration
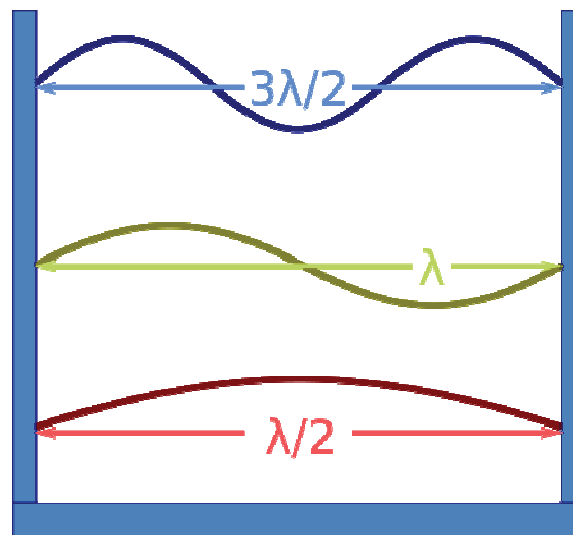
Figure 9.3: If l is length of the box then allowed wavelength must follow l =nλ/2

The allowed mode of vibrations in the cavity can be calculated as follows:

Let each side of the cubical cavity is of length l and three intersecting edges of the cavity are the X, Y and Z directions of the Cartesian co-ordinate system. Let the wave is propagating in any random direction then l cos α, l cos β and l cos γ will be the projections of the edges of the cube on the direction of propogation of the wave (where cos α, cos β and cos γ are the direction cosines of the direction of propagation of a particular wave). According to electromagnetic theory the allowed waves are those which have nodal points at the faces of cube. Thus the allowed wavelength must satisfy the following conditions

$$\lambda = \frac{2l\cos\alpha}{n_1}, \frac{2l\cos\beta}{n_2} \text{ and } \frac{2l\cos\gamma}{n_3} \qquad (9.17)$$

where n_1, n_2 and n_3 are positive integer.

By trignnometric condition of direction cosines, we know that

$$cos^2\alpha + cos^2\beta + cos^2\gamma = 1$$

From equation (9.17), put the values of cos α, cos β and cos γ in above equation we get

$$\frac{n_1^2\lambda^2}{4l^2} + \frac{n_2^2\lambda^2}{4l^2} + \frac{n_3^2\lambda^2}{4l^2} = 1$$

Rearranging the above relation we get

$$n_1^2 + n_2^2 + n_3^2 = \frac{4l^2}{\lambda^2} = \left(\frac{2l}{\lambda}\right)^2 = \left(\frac{2l\nu}{c}\right)^2 \qquad (9.18)$$

The above equation gives the allowed modes of vibration (allowed frequencies) inside the cavity and the total number of possible sets (n_1,n_2,n_3) gives the total number of modes of vibrations.

Within the frequency interval ν and ν + dν the number of modes of vibration can be found out with the help of equation (9.18)

Two – Dimensional Resonators

In order to simplify the problem of counting the number of modes in a particular frequency interval, let us consider a similar two dimensional problem. An equivalent two dimensional equation will be

$$n_1^2 + n_2^2 = \left(\frac{2l\nu}{c}\right)^2 \tag{9.19}$$

If we plot a graph with n_1 along x-axis and n_2 along y-axis then equation (9.19) represents a circle of radius $\left(\frac{2l\nu}{c}\right)$ as shown in the figure (9.4).
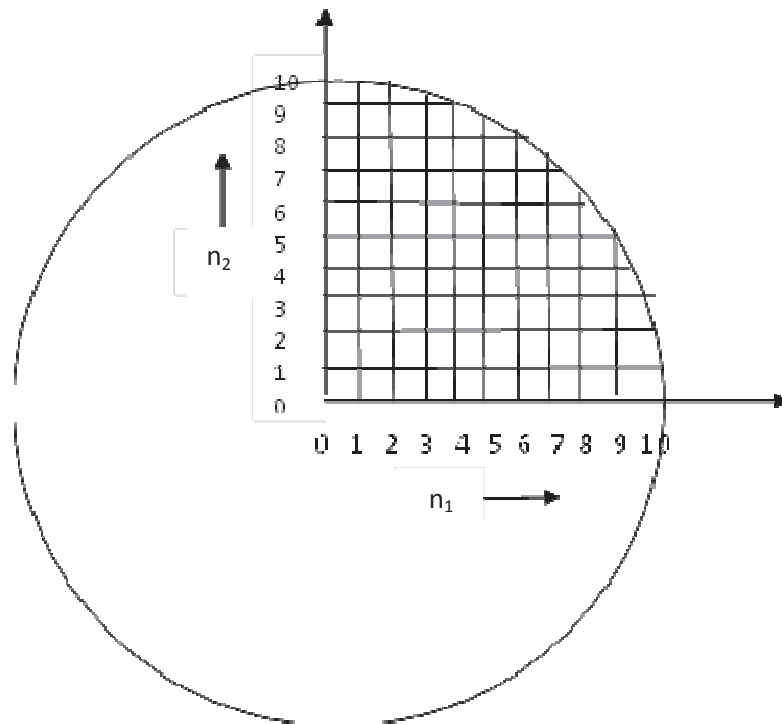
Figure 9.4. Number of modes in a 2-dimensional cavity

Figure 9.4 shows

- All possible values of n_1 and n_2 upto 10
- The points lying on the circle corresponds to frequency ν, while inside the circle corresponds to frequency less than ν, and outside the circle corresponds to frequency greater than ν.
- The area under the first positive quadrant is divided into number of unit squares by the lines drawn through n_1 and n_2 axes.
- The point of intersection of two lines through n_1 and n_2 axes represents a possible mode of vibration. Each point can be associated by a unit square.
- Since area of each square is unity thus number of squares will be equal to the area under the quadrant.

Hence number of modes of vibration within frequency interval v and $v+dv$ will be equal to the area under the positive quadrant lying between two circles of radii $\frac{2lv}{c}$ and $\frac{2l(v+dv)}{c}$

Thus the area is $= \frac{1}{4}\pi \left[\left(\frac{2l(v+dv)}{c} \right)^2 - \left(\frac{2lv}{c} \right)^2 \right]$

$$= \frac{\pi}{4} \times \frac{8l^2 v dv}{c^2}$$

$$= \frac{2\pi l^2 v}{c^2} dv \tag{9.20}$$

The above calculations can be extended to three dimensions also.

In 3-dimensions, the number of modes of vibration in the frequency interval v and $v+dv$ is given by the $\left(\frac{1}{8}\right)^{th}$ of the volume of the spherical shell within radii $\frac{2lv}{c}$ and $\frac{2l(v+dv)}{c}$

This volume of spherical shell is given by $= \frac{1}{8}\left\{ \frac{4}{3}\pi \left(\frac{2lv}{c} \right)^3 - \frac{4}{3}\pi \left(\frac{2l(v+dv)}{c} \right)^3 \right\}$

$$= \frac{1}{8} \times \frac{4}{3}\pi \times \frac{8l^3}{c^3} \times 3v^2 dv$$

Putting $l^3 = V$, where V is the volume of the cube (blackbody endoser), the number of modes of vibration inside the blackbody enclosure within the frequency range v and $v+dv$ is given by

$$= \frac{4\pi V v^2}{c^3} dv \tag{9.21}$$

The number of modes per unit volume within the frequency range v and $v+dv$ will be

$$= \frac{4\pi v^2}{c^3} dv \tag{9.22}$$

Three-Dimensional Resonator:
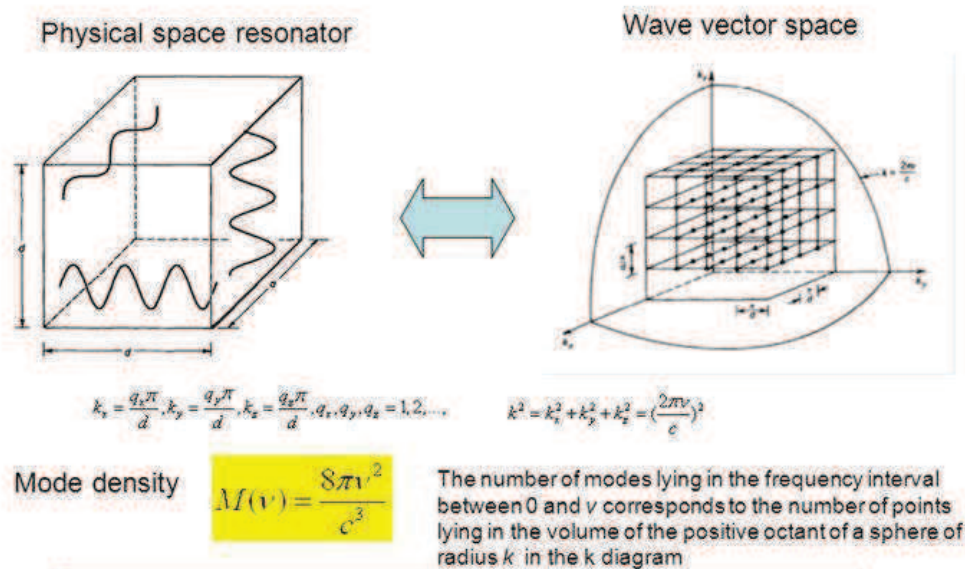
Fig. 9.5 : Number of modes in 3-dimensional cavity resonator

The blackbody radiations (electromagnetic wave) travel with velocity of light and are transverse in nature, hence the number of modes of vibration will be double as that for longitudinal waves.

Thus number of modes per unit volume within the frequency range ν and $\nu + d\nu$ for the blackbody radiation will be

$$= \frac{8\pi\nu^2}{c^3} d\nu \tag{9.22a}$$

Hence, energy density in the interval ν and $\nu + d\nu$ can now be calculated by multiplying the average energy of the Planck's oscillator by the number of oscillators per unit volume in the frequency range ν and $\nu + d\nu$. Thus,

$$E_\nu d\nu = \left(\frac{8\pi\nu^2}{c^3} d\nu\right)\left(\frac{h\nu}{e^{h\nu/kT}-1}\right)$$

$$= \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT}-1} \cdot d\nu \tag{9.23}$$

Equation (9.23) is famous Planck's radiation law. It gives the energy density that is energy per unit volume in the frequency range ν and $\nu + d\nu$

Planck's radiation law in terms of wavelength can be obtained by applying the relation $\nu = \frac{c}{\lambda}$ and $|d\nu| = \left|-\frac{c}{\lambda^2} d\lambda\right|$

Self-assessment Question 2 : Calculate the number of modes in a chamber of volume 100 cm^3 in the frequency range 4 x 10^{14} Hz to 4.01 x 10^{14} Hz

9.6   DEDUCTION OF WEIN'S LAW FROM PLANCK'S LAW

Planck's radiation law is

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{he/\lambda kT} - 1}$$

For small temperature, λT is small and for shorter wavelength $e^{hc/\lambda kT}$ becomes large compared to unity and hence Planck's law reduces to

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{he/\lambda kT}}$$

or it can be written as

$$E_\lambda \, d\lambda = \frac{8\pi hc}{\lambda^5} . e^{-hc/\lambda kT}. \, d\lambda \qquad\qquad (9.24)$$

This is the required Wein's law, hence Planck's law reduces to Wein's law for shorter wavelengths.

9.7 DEDUCTION OF RAYLEIGH-JEANS LAW FROM PLANCK'S LAW

Planck's radiation law is

$$E_\lambda = \frac{8\pi hc}{\lambda^5} . \frac{d\lambda}{e^{hc/\lambda kT} - 1}$$

For large temperature, λT is large and also for longer wavelengths $e^{hc/\lambda kT}$ can be approximated as $\left(1 + \frac{hc}{\lambda kT}\right)$ (the first two terms of Taylor series expansion $e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots, -\infty < x < \infty$)

i.e. $e^{he/\lambda kT} = 1 + \frac{he}{\lambda kT} + \left(\frac{hc}{\lambda kT}\right)^2 \frac{1}{2!} + \ldots = 1 + \frac{hc}{\lambda kT}$

Hence Planck's law reduces to

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} . \frac{d\lambda}{(1 + \frac{hc}{\lambda kT} - 1)}$$

$$= \frac{8\pi hc}{\lambda^5} \frac{\lambda kT}{hc} d\lambda$$

$$= \frac{8\pi kT}{\lambda^4} d\lambda \qquad\qquad (9.25)$$

This is required Rayleigh-Jeans law. Hence for longer wavelengths the Planck's law reduces to Rayleigh-Jeans law.

Hence it can be concluded that both Wein's law and Rayleigh Jeans law are incorporated in Planck's law.

9.8 DEDUCTION OF WEIN'S DISPLACEMENT LAW FROM PLANCK'S LAW

Planck's radiation law is

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda kT} - 1}$$

When the above relation (Planck's law) is differentiated w.r.t. λ and equated to zero, the Wien's displacement law (λT = constant) is obtained for wavelength which corresponds to maximum energy emission for a given value of T. That is

$$\frac{dE_\lambda}{d\lambda} = \frac{1}{e^{hc/\lambda kT} - 1} \times \frac{-5(8\pi hc)}{\lambda^6} + \frac{(8\pi hc)}{\lambda^5} \times \frac{\frac{hc}{\lambda^2 kT} e^{hc/\lambda kT}}{\left(e^{hc/\lambda kT} - 1\right)^2}$$

$$= \frac{1}{e^{hc/\lambda kT} - 1} \times \frac{-40\pi hc}{\lambda^6} + \frac{(8\pi hc)}{\lambda^5} \times \frac{hc}{\lambda^2 kT} \times \frac{e^{hc/\lambda kT}}{\left(e^{hc/\lambda kT} - 1\right)^2}$$

For E_λ to be maximum the value of its first derivative should be zero. Hence,

$$\frac{1}{e^{hc/\lambda kT} - 1} \times \frac{-40\pi hc}{\lambda^6} + \frac{(8\pi hc)}{\lambda^5} \times \frac{hc}{\lambda^2 kT} \times \frac{e^{hc/\lambda kT}}{\left(e^{hc/\lambda kT} - 1\right)^2} = 0$$

or,

$$\frac{8\pi hc}{(e^{hc/\lambda kT} - 1)\lambda^6} \left[-5 + \frac{hc}{\lambda kT} \cdot \frac{e^{hc/\lambda kT}}{(e^{hc/\lambda kT} - 1)}\right] = 0$$

or

$$\left[-5 + \frac{hc}{\lambda kT} \frac{e^{hc/\lambda kT}}{(e^{hc/\lambda kT} - 1)}\right] = 0$$

{∵ terms out side the large bracket cannot be equal to zero}

Substitute $\frac{hc}{\lambda kT}$ = y in above equation, we get

$$\left[-5 + y\frac{e^y}{(e^y - 1)}\right] = 0$$

Solving above equation for y we get y=4.965

$$\Rightarrow y = \frac{hc}{\lambda kT} = 4.965$$

λ in the above equation represents the wavelength at which the energy emission is maximum. So let this value be represented by λ_m

Rewriting above equation we get

$$\frac{hc}{\lambda_m kT} = 4.965$$

or $\qquad \lambda_m T = \frac{hc}{4.965 k} = constant$ $\hfill$ (9.26)

This is Wein's displacement law.

9.9 DEDUCTION OF STEFAN'S LAW FROM PLANCK'S LAW

Planck's radiation law in terms of frequency is given by

$$E_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{d\nu}{e^{h\nu/kT} - 1}$$

This is energy radiated in the frequency range ν and $\nu+d\nu$. To calculate total radiant energy over the entire frequency range that is from 0 to ∞, integration needs to be performed in the frequency range from 0 to ∞ i.e.,

$$E = \int_0^\infty E_\nu \, d\nu = \frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/kT}-1} \qquad (9.27)$$

Substitute $\frac{h\nu}{kT} = x$ hence $d\nu = \frac{kT}{h} dx$

Substituting in equation (9.27), we get

$$E = \frac{8\pi k^4 T^4}{c^3 h^3} \int_0^\infty \frac{x^3 dx}{e^x-1} \qquad (9.28)$$

The value of the integral $\int_0^\infty \frac{x^3 dx}{e^x-1} = \frac{\pi^4}{15}$

Hence, $\qquad E = \frac{8\pi^5 k^4 T^4}{15 \, c^3 h^3}$ $\hfill$ (9.29)

or $\qquad E = \sigma T^4$ $\hfill$ (9.30)

where

$$\sigma = \frac{8\pi^5 k^4}{15 \, c^3 h^3}$$

This is Stefan's law or T^4 law.

The above relation completely agrees with the experimental curves.

Self-assessment question 3 The sun emits maximum radiation of 0.52 micron meter. Assuming the sun to be a black body, calculate the emissive ability of the sun's surface at that temperature

a) 3.47×10^{7} W/m^2

b) 4.47×10^{7} W/m^2

c) 5.47×10^{7} W/m^2

d) 6.47×10^{7} W/m^2

9.10 SUMMARY

Planck's radiation law, a Quantum theory based mathematical relationship was formulated in 1900 by German physicist Max Planck to explain the spectral-energy distribution of radiation emitted by a blackbody (a hypothetical body that completely absorbs all radiant energy falling upon it, reaches some equilibrium temperature, and then reemits that energy as quickly as it absorbs it). Planck assumed that the sources of radiation are atoms in a state of oscillation and that the vibrational energy of each oscillator may have any of a series of discrete values but never any value between. Planck further assumed that when an oscillator changes from a state of energy E_1 to a state of lower energy E_2, the discrete amount of energy $E_1 - E_2$, or quantum of radiation, is equal to the product of the frequency of the radiation, symbolized by the Greek letter ν and a constant h, now called Planck's constant, that he determined from blackbody radiation data; i.e., $E_1 - E_2 = h\nu$. Planck's law accurately describes the complete spectrum of thermal radiation. The Wien approximation may be derived from Planck's law by assuming $(h\nu \gg kT)$ so Planck's law approximately equals the Wien approximation at high frequencies. Unlike Rayleigh law the Planck's law does not suffer from an ultraviolet catastrophe, and agrees well with the experimental data. In the limit of high temperatures or long wavelengths the exponential is well approximated with the Taylor polynomial's first-order term. Hence it results in Planck's blackbody formula reducing to the formula which was identical to the classically derived Rayleigh–Jeans expression. Thus, in the limit of small frequencies, that is $(h\nu \ll kT)$ Planck's law reduces to Rayleigh-Jeans law.

9.11 TERMINAL QUESTIONS

Objective Question

8. In Planck's resonators particles can vibrate with
   a. only one frequency.
   b. frequency of red light.
   c. frequencies lies in sound wave range.
   d. all frequencies of electromagnetic wave spectrum following quantization of energy.
9. The vibrating particles radiates
   a. energy continuously.

b. no energy
c. discrete packet of energy.
d. same energy.

10. In Maxwell's distribution law, the number of particles in the nth oscillating system is given by

   a. $N = N_o e^{-\frac{n\varepsilon}{KT}}$

   b. $N = N_o e^{-\frac{1}{KT}}$

   c. $N = N_o e^{-\frac{hv}{KT}}$

   d. $N = N_o (e^{-\frac{hv}{kT}} - 1)$

11. The quanta of energy in quantum mechanics
   a. is hv
   b. does not depend on frequency
   c. is $h\omega$
   d. is hk

12. Which of the following is (are) explained by quantum mechanics
   a. Photoelectric effect
   b. Compton effect.
   c. Zeemann effect.
   d. Phenomena of absorption of light.

13. According to Planck's assumption, the energy radiated from a black body can be considered to be produced by
   a. stationary wave condition inside the cavity.
   b. resonant modes of cavity.
   c. multiple reflections from walls of cavity.
   d. transmission through the wall of cavity.

14. The value of Planck's constant is
   a. $1.6 \times 10^{-27} kg$
   b. $1.38 \times 10^{-23} m^2 kg\ s^{-2} K^{-1}$
   c. $6.626 \times 10^{-34} Js$
   d. $9.1 \times 10^{-31} kg$

15. The average energy of a Planck's oscillator is

   a. $-hv/(1 - e^{\frac{hv}{kT}})$

   b. $hk/(e^{\frac{hv}{kT}} - 1)$

   c. $hv/(e^{\frac{1}{kT}} - 1)$

   d. $hv/(1 - e^{\frac{hv}{kT}})$

16. The difference in light emitted from the candle, an incandescent light bulb, and the sun are basically differences in (emissivity less than 1)
   a. Energy sources
   b. Materials
   c. Temperatures

       d.   Phases of matter

Short Questions

6. What is quantum theory?
7. What is meant by the term quantum?
8. How does particle radiates energy?
9. What are Planck resonators?
10. How resonant mode is achieved inside a blackbody cavity?
11. What is the condition on the resonent mode for an electromagnetic wave in a cavity?

Long Answer Questions

1. What are the hypothesis of Planck's law?
2. Derive Planck's radiation law.
3. Derive Stefan-Boltzmann law from Planck's law.
4. Derive Wien's distribution law from Planck's law.
5. Derive Rayleigh-Jeans law from Planck's law.
6. Derive the expression of Wien's displacement law from Planck's law.

9.12 ANSWERS

Self assessment questions

Answer 1 Multiples of certain fixed amounts

Answer 2 Solution

(a) The total number of modes in the frequency range ν and ν+dν isgiven by

$$N_\nu d\nu = \frac{8\pi\nu^2 V}{c^3} d\nu$$

Here V= 100 cm^3 = 10^{-4} m^3

$\nu = 4\text{x}10^{14}$ Hz, c= 3x 10^8 m/s.

$N_\nu d\nu$ = 8 x 3.14x (4x 10^{14})^{2}x (10^{-4}) x (0.01 x 10^{14})/(3 x10^8)^3

= 1.49 x 10^{13}

Answer 3: c
Explanation: E = σT^4 = 5.47 * 10 ^{7} W/m^2.

Terminal questions Answers

Objective type

   1. (d), 2. (c)   3. (a)   4.(a)   5.(a), (b), (c), (d)   6.(a), (b) 7. (c) 8.(a)   9.(c)

Short question

1. Quantum theory is the theoretical basis of modern physics that explains the nature and behavior of **matter** and energy on the atomic and subatomic level. The nature and behavior of **matter** and energy at that level is sometimes referred to as quantum physics and quantum mechanics.

2. **Quantum** is the Latin **word** for amount and, in modern understanding, **means** the smallest possible discrete unit of any physical property, such as energy or matter. **Quantum** came into the latter usage in 1900, when the physicist Max Planck used it in a presentation to the German Physical Society.

3. The vibrating particles can radiate energy when the oscillators move from one state to another state. The radiation of energy is not continuous, but discrete in nature.

4. Planck assumed that the Blackbody radiation chamber is made up of a number of oscillating particles (of molecular dimensions) called harmonic oscillators/resonators (energy emitters), known as Planck's oscillators or Planck's resonators.

5. Consider a Blackbody in the form of a hollow cubical box . The radiations inside the box consist of a number of waves travelling in all possible directions. The waves suffer multiple reflections from the walls of the encloser. As a result of interference between incident and reflected waves a stationary wave pattern is formed also called standing wave or resonant mode of the cavity.

6. A resonant mode for an electromagnetic wave in a cavity must satisfy the condition of zero electric field at the walls. If the mode is of shorter wavelength there are more number of ways by which they can be fitted in the cavity to meet the condition of zero electric field at the walls.

9.13 REFERENCES

1) Statistical And Thermal Physics by S. Loknathan and Gambhir
2) Concept of Modern physics by Arthur Beiser
3) Thermal and Statistical physics by Garg Bansal Ghosh
4) (http://motls.blogspot.in/2010/04/on-importance-of-blackbodies.html)
5) Paul A. Tipler. College Physics. Worth Publishers Inc., 1987, section29.1.
6) Richard P. Feynman, Robert B. Leighton and Matthew Sands.
Lectures on Physics. The Definitive Edition, Volume III, Addison–
Wesley, 2006, section 4-5.
7) Heat, Thermodynamics and Statistical Physics, Brijlal, Dr. N. Subrahmanyam, P. S. Hemne, S. Chand

8) Thermal Physics, A. Kumar and S. P. Taneja, R. Chand & Co. New Delhi

9.14 SUGGESTED READINGS

1) Dr. Max Planck, The Theory of Heat Radiation, P. Balkiston's Son & Co.
2) Robert Siegel and John R. Howell, Thermal Radiation Heat Transfer, 3rd ed., Hemisphere Publishing Corporation.
3) C. Balaji, Essentials of Radiation Heat Transfer, Wiley (Ane Books Pvt. Ltd.)

UNIT -10   STATISTICAL MECHANICS : BASIC CONCEPTS

CONTENTS

10.1 INTRODUCTION

Statistical physics gives a clear understanding of Thermodynamics in terms of microscopic particles and their interactions. It allows calculation of macroscopic properties of the systems from microscopic considerations. The tools and methods developed in statistical physics are widely used in latest research areas to understand the characteristics of large systems. Statistical mechanics is the way of relating the microscopic laws of physics to a description of nature on a macroscopic scale. Statistical systems are complex systems due to containing large no of particles. We do not know all the information that is needed to characterize the systems completely. For example, 1 liter of gas may contain 10^{23} atoms at NTP. To completely describe such a dynamic system we need to know the three components of the velocity for each atom and the three components of the position for each atoms i.e.6 components when solved one equation of motion. It is impossible to obtain 6×10^{23} real numbers to completely characterize the gas. However, it is not necessary to know all the information to develop a theory of the gas by calculating theoretically some average properties like the pressure, volume, temperature (macroscopic parameters). Those properties do not depend on every little detail of each atom. Not knowing everything about the atoms does not prevent us from calculating those properties. In statistical physics we try to understand the properties of a complex system without knowing all the information of the systems. This is possible since the properties we are interested in do not depend on the details of the system.

For describing the macroscopic state of a gas, characterized by pressure, volume, temperature (macro-parameter), we do not need information on every microscopic detail. A large number of microstates may correspond to the same, single macrostate. Suppose we are interested in knowing the pressure of the gas, we should not bother about what a particular atom of the gas is doing at every instance. In other words, we only need some average macroscopic quantities and not every microscopic detail. So as thermodynamics is concerned about heat and the direction of heat flow, statistical mechanics   gives a microscopic perspective of heat in terms of the structure of matter and provides a way of evaluating the thermal properties of matter, for e.g., energy, pressure, heat capacity, entropy, free energies or thermodynamic potentials, etc. Before the development of quantum theory, laws of classical(Newtonian) mechanics were applied in association with the statistics to study the behavior of large number particle systems. It applies to systems which are sufficiently large that microscopic fluctuations can be ignored, and it does not assume that there is an underlying atomic structure to matter. These methods are called classical statistics or Maxwell-Boltzmann statistics, due to the great contribution of Maxwell and Boltzmann in development of the kinetic theory of gases. Later on this work extended and improved by some physicist like Gibbs etc. The **kinetic theory of gases** tries to determine the properties of gases by considering probability distributions associated with the motions of individual molecules. The recognition that atoms and molecules exist led to the development of **statistical mechanics**. this approach begins with trying to describe the individual microscopic states of a system and then uses statistical methods to derive the macroscopic properties from them instead of starting with descriptions of macroscopic properties (as in thermodynamics).

.This approach gets an additional motivation with the development of **quantum theory** which showed clearly how to describe the microscopic quantum states of different systems. The thermodynamic behavior of a system is then asymptotically approximated by the results of statistical mechanics in the thermodynamic limit, i.e. as the number of particles tends to infinity (with intensive quantities such as pressure and density remaining finite).The classical statistics is very successful theory to explain the phenomenon like energy, temperature, entropy etc., but fails to explain some other physical phenomena like black body radiation, variations of specific heat and electrical conductivity with temperature, behavior of gases under high pressure and low temperature, electrical properties of metals and semiconductors etc. By using the Planck's hypothesis of discrete exchange of energy between systems, Bose, Einstein , Fermi and Dirac introduced a new statistics called quantum statistics, that can explain those phenomena's very well which cannot be explained by classical statistics. Quantum statistics is further subdivided into two branches: Bose- Einstein statistics and Fermi- Dirac statistics. You will study quantum statistics in unit 13.

10.2 OBJECTIVES

After going through this unit, you will be able to:
- Understand the need of statistical mechanics and its classification
- Know the theory of probability.
- Understand continuous and discrete distributions.
- Derive Binomial, Poisson and Gaussian distribution functions.
- Understand the concept of phase space.
- Know division of phase space into cells.
- Understand the density of states
- Understand thermodynamical probability.
- Differentiate thermodynamical probability for classical and quantum systems.

10.3 PROBABILITY

Statistical mechanics applies on large and complex systems, where we cannot predict an exact behavior of the individual constituent of the system. We predict only average behavior of the system theoretically which can be verified by experimental observations. To develop the mathematical theory of statistical mechanics we exploit probabilistic approach of mathematics. Since the basis of Statistical mechanics is theory of probability. So it is necessary to grasp some fundamental concepts of the theory of probability before the study of Statistical mechanics. It is important to keep in mind that whenever it is desired to describe a situation from a statistical point of view (i.e., in terms of probabilities), it is always necessary to consider an assembly (ensemble) consisting of a very large number of similar prepared systems. Ensembles are statistical model to study any physical system. The probability of occurrence of an event is defined as follows: The probability of occurrence of a particular event is the ratio of number of cases in which that event occurs to the total number of possible events.

The probability of an event $= \dfrac{\text{numberof cases in which the event occours}}{\text{total number of possible events}}$

If an experiment is repeated N time in which a certain event A occurs n_A times then the probability of occurrence of an event A is

$$P_A = n_A / N \qquad\qquad\qquad ……… (10.1)$$

This formula is applicable when N is very large i.e. N→ ∞.So more correctly

$$P_A = \lim_{N\to\infty} n_A / N \qquad\qquad ……. (10.2)$$

In other words if an event can happen in n_A ways and fails to happen in n_B ways ,then the probability of occurrence of that event is $P_A = n_A/ n_{A+}n_B$ and probability of non-occurrence of an event is $P_B = n_B/ n_{A+}n_B$. Here $N = n_{A+}n_B$ is the total number of equally likely possible events. The value of P_A lies between 0 to 1 i.e. $0< P < 1$. P=1 implies 100% chance of occurrence of that event i.e. event is definite and P = 0 expresses the impossibility of occurrence of that event i.e. the event will never take place. The total probability is always 1 ($P_A + P_A$ =1) since the event may either occur or fail.

10.3.1 ADDITIVE LAW OF PROBABILITY

Consider two separate possible events, X and Y, of an observation made on the system S, with probabilities of occurrence P(X) and P(Y), respectively. Let us determine the probability of obtaining the outcome X or Y, which we shall denote, P(X or Y). From the basic definition of probability

$$P(X \text{ or } Y) = n(X \text{ or } Y)/N \qquad\qquad ………. (10.3)$$

where n (X or Y) is the number of events in the system which exhibit either the event X or the event Y. It is clear that

$$n(X \text{ or } Y) = n(X) + n(Y) \ (2.3) \qquad\qquad ……… (10.4)$$

If the events X and Y are mutually exclusive (if they are two distinct outcomes). Thus,

$$P(X \text{ or } Y) = P(X) + P(Y). \ (2.4) \qquad\qquad …………….. (10.5)$$

So, the probability of the occurrence of event X or the event Y is just the sum of the individual probabilities of these events X and Y. For instance, with a six sided die the probability of throwing any particular number (one to six) is 1/6, because all of the possible outcomes are considered to be equally likely or equally probable. It follows from what has just been said that the probability of throwing either a one

or a two is simply 1/6 + 1/6 which equals 1/3.
Let us denote all possible events of an observation made on the system S by Xi, where i run from 1 to m. Let us determine the probability of obtaining any of these events.

$$P = n(x_1)/N + n(x_2)/N+………+n(x_m)/N \qquad\qquad (10.6)$$

So

$$P(x_1) + P(x_2) + \ldots\ldots\ldots + P(x_m)$$

$$= \sum_{i=0}^{m} P(xi) = 1 \tag{10.7}$$

This number is clearly unity, from the basic definition of probability, because every one of the systems in the collection must exhibit one of the possible events. But, this quantity is also equal to the sum of the probabilities of all the individual events, by eq. (10.5), so we conclude that this sum is equal to unity. Thus, it is called the normalization condition. it is a necessary condition that must be satisfied by any complete set of probabilities. This condition is equivalent to the self-evident statement that an observation of a system must definitely result in one of its possible outcomes.

10.3.2 MULTIPLICATION RULE OF PROBABILITY

There is another way in which we can combine probabilities. Suppose that we make an observation on a state picked at random from the collection and then pick a second state completely independently and make another observation. We are assuming here that the first observation does not influence the second observation in any way. So two observations are statistically independent events. Let us determine the probability of obtaining the event X in the first state and the event Y in the second state, which is denoted by P(X and Y). In order to determine this probability, we have to form a collection of all of the possible pairs of states which we could choose from the collection N (X and Y). Let us denote this n(X and Y). It is obvious that the number of pairs of states in this new collection is just the square of the number of states in the original collection, so

$$N(X \text{ and } Y) = N(X).N(Y) \tag{10.8}$$

It is also obvious that the number of pairs of states in the collection which exhibit the event X in the first state and Y in the second state is just the product of the number of states which exhibit the event X and the number of states which exhibit the event Y in the original collection, so

$$n(X \text{ and } Y) = n(X).n(Y). \ (2.7) \tag{10.9}$$

It follows from the basic definition of probability that

$$P(X \text{ and } Y) = n(X \text{ and } Y)/ N(X \text{ and } Y) = P(X) P(Y) \tag{10.10}$$

Thus, the probability of obtaining the events X and Y in two statistically independent observations is just the product of the individual probabilities of X and Y.

For example, the probability of throwing a one and then a two on a six sided die is $1/6 \times 1/6$, which equals 1/36.

10.3.3 CONDITIONAL PROBABILITY

The probability for an event X to occur the condition that event Y has already occurred is called conditional probability. Written as P(X/Y), means the probability of X given Y. If

events X and Y are independent (where event Y has no effect on the probability of event X) ,the conditional probability of event X given event Y is simply the probability of event X, that is P(X). If events X and Y are not independent, then the probability that both event occur is defined as P(X and Y) = P(Y).P(X/Y). Let us understand it by an example. Suppose a box contains 7 white and 4 black balls. We want to know the probability of getting 2 white balls, if balls are drawn successively .Since we have 7 white balls out of total 11 balls. In first draw the probability of outcome white ball, event Y will be P(Y) = $\frac{7}{11}$. Now the condition is that second ball also must be white. Since 6 white balls remained out of total 10 balls. So in second draw , the probability of outcome white ball, event X, when event Y has already occurred is P(X/Y) = $\frac{6}{10}$. Since events are not independent, the probability of getting both balls is black

$$P(X \text{ and } Y) = P(Y).P(X/Y) = \frac{7}{11} \times \frac{6}{10} = \frac{21}{55}$$

Example 01

Two dices are thrown randomly, the outcome (upward face) of first dice be 'A' and the outcome of second dice be 'B' .calculate :(a) The probability of outcome A = 3(b) What is the probability to obtain a total of score 6 or less?(c) What is the probability that A = 3 and A+B ≤**6.**

Solution

(a)The outcome A may come in six ways 1, 2, 3, 4, 5, or6. Similarly six possibilities of outcome B. Total possible outcomes are 6x6 = 36, all 36 outcomes shown in sample space, table (10.1). Now A = 3 , comes in exactly six ways (bold- shaded numbers) (A, B) = (3,1) ,(3,2), (3,3) ,(3,4) (3,5), (3,6) .

	+	1	2	3	4	5	6
				B			
	1	2	3	4	5	6	7
	2	3	4	5	6	7	8
	3	**4**	**5**	**6**	**7**	**8**	**9**
A	4	5	6	7	8	9	10
	5	6	7	8	9	10	11
	6	7	8	9	10	11	12

Table (10.1)

Hence, the probability of outcome A = 3

P (A=3) = $\frac{6}{36}$ = $\frac{1}{6}$

(b) The outcome (upward face) of first dice is A and the outcome of second dice is B. condition is A+B ≤ 6.

	+	1	2	3	4	5	6
				B			
	1	**2**	**3**	**4**	**5**	**6**	7
	2	**3**	**4**	**5**	**6**	7	8

A	3	**4**	**5**	**6**	7	8	9
	4	**5**	**6**	7	8	9	10
	5	**6**	7	8	9	10	11
	6	7	8	9	10	11	12

Table (10.2)

Table(10.2) shows all possible outcomes (bold shaded numbers)subject to condition $A+B \leq 6$,are exactly15.

Hence P $(A+B \leq 6) = \frac{15}{36} = \frac{5}{12}$

(c) Now the probability that A = 3 and $A+B \leq 6$. Both conditions are fulfilled in 3 ways   (dark shaded numbers) out of 15(light shaded numbers).

	+				B		
		1	2	3	4	5	6
	1	**2**	**3**	**4**	**5**	**6**	7
	2	**3**	**4**	**5**	**6**	7	8
A	3	*4*	*5*	*6*	7	8	9
	4	**5**	**6**	7	8	9	10
	5	**6**	7	8	9	10	11
	6	7	8	9	10	11	12

Table (10.3)

Thus conditional probability P $(A=3|A+B \leq 6) = \frac{3}{15} = \frac{1}{5}$

10.4 THE TWO STATE SYSTEMS

The simplest system which we can study using probability theory is one for which there are only two possible outcomes (events). Let us suppose that there are two possible outcomes to an observation made on some system. Let us denote these outcomes 1 and 2, and let their probabilities of occurrence be

P (1) = p

P (2) = q

It follows immediately from the normalization condition that

p + q = 1

So   q = 1 − p.

The best known example of a two-state system is a tossed coin. The two outcomes are "heads" and "tails," each with equal probabilities 1/2. So,

p = q = 1/2 for this system.

Suppose that we make N statistically independent observations of a system. Let us determine the probability of n occurrences of the outcome 1 and N − n occurrences of the outcome 2, without taking care of the order of these occurrences. Denoting the probability by $P_N(n)$, let

us consider a case in which there are only three observations. Suppose we have three coins. Let us try to calculate the probability of two occurrences of the outcome heads(H) and one occurrence of the outcome tail (T). There are three different ways of getting this result. We could get the outcome heads (H)   on the first two observations and the outcome tail (T) on the third (H,H, and T). Or, we could get the outcome tail (T) on the first observation and the outcome head (H) on the latter two observations, (T,H, and H). Or, we could get the outcome head (H) on the first and last observations and the outcome tail (T) on the middle observation (H,T, and H).

Let the probability of outcome head(H) is denoted by p=½ and the probability of outcome tail(T) is denoted by q=½ by applying (multiplicative rule of probability)

$$P(X \text{ and } Y) = P(X)\ P(Y) \tag{10.11}$$

the probability of getting (H,H,T) =p.p.q, similarly for (T,H,H) = q.p.p and for (H,T,H) = p.q.p .
Now applying (additive rule of probability)

$$P(X \text{ or } Y) = P(X) + P(Y) \tag{10.12}$$

The probability of two occurrences of the outcome heads(H) and one occurrence of the outcome tail (T) will be

$$P\ (2H,1T) = p\ p\ q + q\ p\ p + p\ q\ p = 3\ p^2\ q$$

It is3rd term of the binomial expansion of $(p + q)^3 = q^3 + 3pq^2 + 3p^2\ q + p^3$

By generalizing it, the probability of obtaining n occurrences of a particular outcome in N observations is given by

$$P_N(n) = C_n^N p^n\ q^{N-n} = \frac{N!}{n!(N-n)}\ p^n\ q^{N-n} \tag{10.13}$$

This probability function is called the binomial distribution function. The reason for this is clear if we tabulate the probabilities for the first few possible values of N; see Table (10.4), shows binomial probability distribution.

		n				
		0	1	2	3	4
N	1	q	p			
	2	q^2	$2pq$	p^2		
	3	q^3	$3pq^2$	$3p^2q$	p^3	
	4	q^4	$4pq^3$	$6p^2q^2$	$4p^3q$	p^4

Table (10.4)

Of course, we immediately identify these expressions, they appear in the standard algebraic expansions of $(p + q)$, $(p + q)^2$, $(p + q)^3$, and $(p+q)^4$, respectively. In algebra, the expansion of $(p+q)^N$ is called the binomial expansion. In eq. (10.13) $C_n^N p^n\ q^{N-n}$ is the (n+1) th term of the Binomial expansion of $(p + q)^N$, represents the number of ways of arranging two distinct sets of n andN – ndistinguishable objects. Thus the probability of getting two occurrencesof the outcome heads(H) and one occurrence of the outcome tail(T) was obtained by writingout all

of the possible arrangements of two p' s (the probability of outcome H) and one q (the probability of outcome T), and then added them all together.

So now $\sum_{n=0}^{N} P(n, N-n) = \sum_{n=0}^{N} \cdot \frac{N!}{n!(N-n)!} p^n q^{N-n}$ (10.14)

$$= \sum_{n=0}^{N} (p+q)^N = 1 \quad \text{since} \quad p+q=1$$

or simply $\sum P(n)=1$

Example 02

Explain two state paramagnet systems .

Solution

Consider a system having N number of non-interacting magnetic dipoles. These dipoles may point in one of only two ways: up or down. If an external uniform magnetic field is applied, say in the up direction, each dipole will experience a torque tending to rotate it to the up direction also. The energy of the system depends on the number of dipoles aligned with the external field, say q. But, we don't care which q dipoles out of the N total are in the up state. Having q dipoles up specifies the energy macrostate, which may be realized by the selection of any q dipoles out of N to be up. The number of microstates for each macrostate is just the number of combinations, the number of ways of choosing q objects from a collection of N objects.

$$\Omega(q, N-q) = \left({}^{N}C_q \right) = \frac{N!}{q!(N-q)!}$$
                    (10.15)

Assuming every microstate is equally likely, the probability of occurrence of this macrostate

$$P(q) = \frac{\Omega(q, N-q)}{\Omega(\text{all})} .$$
                    (10.16)

Notice that the total multiplicity is $\Omega(\text{all}) = 2^N$ because each dipole has only two possible states.

*The terms macrostate and microstate are discussed in detail, in the next unit.

10.4.1 MEAN VALUE IN BINOMIAL DISTRIBUTION

The mean value of the variable n is

$$<\text{n}> = \sum_{n=0}^{N} n. P(n)$$
                    (10.17)

Substituting the value of P (n) from eq. (10.13)

$$<n> = \sum_{n=0}^{N} \cdot \frac{n.N!}{n!(N-n)!} \, p^n \, q^{N-n}$$

which can be written as

$$= \sum_{n=0}^{N} \cdot \frac{n.N!}{n!(N-n)!} p(\, dp^n/dp).q^{N-n}$$

$$= \; p\frac{\partial}{\partial p}(\sum_{n=0}^{N} \cdot \frac{N!}{n!(N-n)!} \, p^n q^{N-n} \,)$$

$$= p\frac{\partial}{\partial p} \sum_{n=0}^{N} P(n)$$

$$= \; p\frac{\partial}{\partial p} \sum\nolimits_{\cdot} (p + q)^N$$

So $<n>$ = p.N(p+q)^N = pN   (10.18)

Thus, the mean value of the variable in Binomial distribution is probability of occurrence of event p multiplied by the total number of trials N.

Binomial distribution is again sub divided into two category viz. Poisson distribution and Gaussian distribution, depending on the condition of applicability.

10.4.2 POISSION DISTRIBUTION

The binomial distribution is good for any finite number of repeated trials. In statistical thermodynamics, systems containing large numbers of particles, i.e. N is very large imply $N\rightarrow\infty$. For such conditions, the binomial distribution can be simplified to two more familiar distributions, one is discrete and the other is continuous. When p is very small and N is very large the process with these conditions, the distribution is named Poisson distribution. This distribution is particularly applicable to photon-counting processes, in which the total numbers of photons counted, $N\rightarrow\infty$, while the possibility of observing any single photon, $p\rightarrow$ 0. Thus the conditions of applicability of Poisson distribution is

(i)   N is very large, $N\rightarrow\infty$

(ii)   p is very small, $p\rightarrow 0$

(iii)   n is very small n<<N

 Under these conditions the approximate value of the factor $\frac{N!}{(N-n)!}$, which appears in Binomial distribution $\frac{N!}{(N-n)!}$ = N (N-1) (N-2)….. (N-n+1)

$$\approx \;\; N^n \quad \text{[Applying conditions (i) and (iii) both]}$$

Since q = 1-p

$$\ln q = \ln (1- p)$$

Expanding ln(1− p) by Taylor's theorem and taking only first term due to condition (ii)

$$\ln q = -p \text{ gives } q = e^{-p}$$

so $\qquad q^{N-n} = e^{-p(N-n)} \approx e^{-pN}$

Applying these approximations in Binomial distribution function

$$P(n) = \frac{1}{n!} N^n p^n e^{-pN}$$

$$= \frac{1}{n!} (pN)^n e^{-pN} \qquad\qquad (10.19)$$

This is Poisson distribution. Hence, for $N \to \infty$ and $p \to 0$, the binomial distribution becomes the discrete Poisson distribution. This can be written in standard form as

$$P(n) = \frac{1}{n!} (<n>)^n e^{-<n>} \qquad\qquad (10.20)$$

Again $\sum P(n) = \sum \frac{1}{n!} (<n>)^n e^{-<n>} = e^{<n>} e^{-<n>} = 1$, fulfills the condition of normalization.

Now the mean value of variable in this distribution is

$$<n> = \sum_{n=0}^{N} n.P(n)$$

Substituting the value of P (n) from eq. (10.20)

$$<n> = \sum_{n=0}^{N} n \frac{1}{n!} (<n>)^n e^{-<n>}$$

$$= <n> e^{-<n>} \sum_{n=0}^{N} \frac{1}{n-1!} (<n>)^{n-1}$$

$$= <n> e^{<n>} e^{-<n>} = <n> = pN \qquad\qquad (10.21)$$

This is same as Binomial distribution.

10.4.3 GAUSSIAN DISTRIBUTION

When the number N is large i.e. $N \to \infty$, but p is not small, the binomial distribution becomes the continuous Gaussian distribution. Gaussian distribution is applicable when N and n both are large but n is not too close to N. The Gaussian distribution is particularly applicable to various diffusive processes for which the total number of molecules $N \to \infty$. Now the binomial distribution function

$$P(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$$

Taking logarithm of both side, we have

$$\ln P_N(n) = \ln \frac{N!}{n!(N-n)} p^n q^{N-n}$$

$$= \ln N! - \ln n! - \ln(N-n)! + n\ln p + (N-n)\ln q \qquad (10.22)$$

Using Stirling's approximation ($\ln N! \approx N \ln N - N$ for large value of N). Macroscopic systems contain multiples of Avogadro's number, 6.02×10^{23} perhaps many, many multiples. The factorials of such large numbers are even larger numbers. We'll use Stirling's approximation to evaluate the factorials:

$$N! \approx N^N e^{-N} \sqrt{2\pi N}.$$

Ultimately, we want to find the logarithm of $N!$: $\ln N! \approx N \ln N - N$.

lnP(n) = N lnN – N - n ln n + n – (N-n)ln(N-n) + N-n + n ln p + (N-n)ln q

   = N lnN – n ln n – (N-n) ln(N-n) + n ln p + (N-n) ln q   (10.23)

To find the condition for which this function gives maximum value, differentiating eq. (10.23) with respect to n

$$\frac{d}{dn}\ln P(n) = -\ln n - 1 + \ln(N\text{-}n) + 1 + \ln p + \ln q$$

$$= \ln\frac{(N-n)p}{nq} \qquad\qquad\qquad\qquad (10.24)$$

Imposing the condition of maxima i.e., $\frac{d}{dn}$ ln P(n) = 0

so $\ln\frac{(N-n)p}{nq}$ = 0, implies $\frac{(N-n)p}{nq}$ = 1, putting q = 1-p

we get   n = pN   (10.25)

This shows that the function P(n) will be maximum at   <n> = n = pN and have large value in the neighborhood of n = <n> but becomes negligible far from <n>. So the region for which <n> - n is small, is the region of prime interest. For this region we have to calculate distribution function. Assuming   <n> - n is very small, expending lnP(n) about <n> by applying Taylor's theorem

 lnP(n) = lnP{ <n> +(n -<n>) }

   = lnP<n> + { $\frac{d}{dn}$ ln P<n>} (n - <n>) +$\frac{1}{2!}$[d²/dn²(lnP<n>)](n - <n>)² +   (10.26)

From equation (10.26) at n = <n>, $\frac{d}{dn}$ ln P(n) = 0

Differentiating eq. (10.24) again, d²/dn²(lnP(n)) = -$\frac{1}{Npq}$, putting these in eq. (10.26) we have

    lnP(n) = lnP <n>(- (n - <n>)²/2Npq)   (10.27)

So

    P(n) = lnP <n>. $e^{-(n-<n>)2/2Npq}$

To calculating ln P <n>, applying the condition of normalization

$$\sum P(n) = \sum P<n>.e^{-(n-<n>)2/2Npq} = 1$$

Taking x = n -<n>) and replacing summation by integration

$$\sum P(n) = \int_{-\infty}^{\infty} \left(P<n>.e^{\frac{(x)^2}{2Npq}} \right)$$

(10.28)

Let y = x/√2Npq

Therefore, $\sum P(n) = P<n> \int_{-\infty}^{-\infty} e^{-y2}.\sqrt{2Npq} = 1$

$P<n>.\sqrt{2Npq}.\sqrt{\pi} = 1$ so $P<n> = 1/\sqrt{2\pi Npq}$

and, $P(n) = (1/\sqrt{2\pi Npq})\, e^{-(n-Np)^2/2Npq}$ (10.29)

10.4.4 VARIANCE

We now know how to calculate the average of a set of values, but what about the spread in the values? The first idea one might have to quantify the spread of values in a distribution is to consider the **deviation** from the mean for a particular value of x. This is defined by

x −<x>   (10.30)

This quantity tells you by how much a particular value is above or below the mean value. So the average of the deviation (averaging over all values of x) follows:

$<x-<x>> = 0$ (10.31)

Thus the average deviation is not going to be a very useable term. The problem with it is that the deviation is sometimes positive and sometimes negative, and the positive and negative deviations cancel out. Another approach is to use another quantity which is always positive, the square of the deviation, $(x-<x>)^2$. This quantity is what we need: always positive and easy to apply. Hence, its average is called the **variance**. Consequently, the variance of x, written as σ^2_x or σ^2, is defined as the mean squared deviation:

$$\sigma^2_x = <(x-<x>)^2>$$ (10.32)

And σ_x as the square root of the variance: $\sigma_x = \sqrt{<(x-<x>)^2>}$ defined as the **standard deviation**. The standard deviation represents the 'root mean square' (known as the 'r.m.s.') spread in the data.   .
The following identity is very useful:

Mean squared deviation, $\sigma^2_x = <(x-<x>)^2>$

$$= <x^2 - 2x<x> + <x>^2>$$

$$= <x^2> - <x>^2$$ (10.33)

10.5 PHASE SPACE

To determine the state of a many particle system like a gas having N particles enclosed in a container, let us consider the system consists of a single spin less particles moving classically in one dimension. Assuming that we know the particle's equation of motion, the state of the system is fully specified once we simultaneously measure the particle's position q and momentum p. If we know q and p then we can calculate the state of the system at any time using the equation of motion. The coordinates p_i and q_i(conjugate coordinates) are governed by the canonical Hamilton's equation of motion

$$\dot{q}_{i=}\frac{\partial H}{\partial pi} \quad , \quad \dot{p}_{i=}-\frac{\partial H}{\partial qi} \qquad\qquad (10.34)$$

In practice, it is impossible to specify q and p exactly, because there is always a natural uncertainty (Heisenberg uncertainty $dq.dp \geq \hbar$) in any experimental measurement.
The time evolution of q and p can be visualized by plotting the point (q, p) in the q-p plane. This plane is generally known as phase-space. In general, the point (q, p) will trace out some very complicated pattern in phase space and is called phase trajectory. Suppose that we divide phase-space into rectangular cells of uniform dimensions dq and dp. Here, dq is the uncertainty in the position measurement, and dp the uncertainty in the momentum measurement. The "area" of each cell is dqdp.

And from Uncertainty principle, dq. dp = $\hbar$

Where h is a small constant having the dimensions of angular momentum. The coordinates q and p can now be conveniently specified by indicating the cell in phase-space into which they plot at any given time. In other words, the uncertainty principle sets a lower limit on how finely we can split up classical phase-space.
Let us now consider a single spin less particle moving in three dimensions. In order to specify the state of the system we need to know three q-p pairs: i.e., $q_x - p_x$, q_y - p_y, and q_z - p_z. Obviously the number of q-p pairs needed to specify the state of the system is usually called the number of degrees of freedom of the system. Thus, a single particle moving in one dimension constitutes a one degree of freedom system, whereas a single particle moving in three dimensions constitutes a three degree of freedom system.

Consider the time evolution of q and p, where q = (q_x , q_y, q_z), etc. This can be visualized by plotting the point (q, p) in the six dimensional q-p phase-space. This space is called μ space.Suppose that we divide the q_x –p_x plane into rectangular cells of uniform dimensions dq and dp, and do likewise for the q_y-p_y, and q_z-p_z planes. This is equivalent to dividing phase-space up into regular six dimensional cells each having volume h^3 . The coordinates q and p can now be conveniently specified by indicating the cell in phase-space into which they plot at any given time.   .
Now, let us consider a system consisting of N classical particles moving in three dimensions. In order to specify the state of the system, we need to specify a large number of q-p pairs. The required number is simply the number of degrees of freedom, f. For N particle system f = 3N. Thus, phase-space (i.e., the space of all the q-p pairs) will be 2 f = 6N dimensional, called Γ space. Consider a particular pair of conjugate coordinates, qi and pi. As before, we divide the qi-pi plane into rectangular cells of uniform dimensions dq and dp. This is equivalent to dividing phase-space into regular 2f dimensional cells of volume h^f . The state of the system is specified by indicating which cell it occupies in phase-space at any given time. As we

know that classical particles are distinguishable. If the position and momentum of two particles are exchanged, the new state will be represented by a different point (phase cell) in phase space. This single point will represent a microstate. In principle, we can specify the state of the system to arbitrary accuracy by taking the limit h → 0. In reality, we know from quantum mechanics that it is impossible to simultaneously measure a coordinate qi and its conjugate momentum pi to greater accuracy than dqi .dpi = ħ = h/2π, here h is Planck's constant. This implies that, classical h≥ ħ .

10.5.1 DIVISION OF PHASE SPACE INTO CELLS

For a single particle having 2f dimensional space be represented by $q_1,q_2,q_3.....q_f$ position coordinates and $p_1,p_2,p_3.......p_f$ momentum coordinates. the volume of an element in phase space will be $dq_1dq_2dq_3.....dq_f.dp_1.dp_2.dp_3....dp_f$.

Or $d\tau = dq_1.dp_1.....dq_i.dp_i...dp_fdp_f$

$$= \prod_{i=1}^{f} dq_i.dp_i \tag{10.35}$$

The dimension of this volume element will be (length x momentum)^f and the unit will be (joule x second)^f .We divide this volume element into cells of finite size. Let the volume of each cell be h^f .where h is some arbitrary quantity having the dimension of action (length x momentum) or (energy x time). i.e. h = dq.dp

So the number of cells in the volume element $d\tau$ will be

$$d\Omega = \frac{d\tau}{(h)}f \tag{10.36}$$

Thus for a single point particle or monoatomic molecule the volume of one cell will be h^3 because a single point particle has f = 3, translational degrees of freedom only.

The same expression can be generalized for many particle systems. Suppose a system consists of N particles each having f degrees of freedom .to represent the present state of the system we need Nf coordinate of the position and Nf coordinates for the momentum, i.e., the phase space will be 2fN dimensional.The volume of one cell will be h^{Nf}

So the volume element in Γ space is

$$d\Gamma = dq_1.dq_2....dq_{fN}.dp_1.dp_2...dp_{fN}$$

$$= \prod_{i=1}^{fN} dq_i.dp_i \tag{10.37}$$

And, $$d\Omega = \frac{d\Gamma}{(h)}fN$$

$$= \prod_{i=1}^{fN} dq_i.dp_i / h^{fN} \tag{10.38}$$

10.5.2 HARMONIC OSCILLATOR IN PHASE SPACE

Let us consider a one dimensional harmonic oscillator of mass m and force constant k oscillating along x axis with frequency ν. At any instant the total energy of the oscillator is sum of the kinetic energy to potential energy.

E = P.E + K.E

$$E = \frac{1}{2}kx^2 + \frac{p_x^2}{2m} \tag{10.39}$$

Dividing both sides by E and rearranging, we get

$$1 = \frac{x^2}{2E/k} + \frac{p_x^2}{2mE}$$

or,

$$\frac{x^2}{\left(\sqrt{2E/k}\right)^2} + \frac{p_x^2}{\left(\sqrt{2mE}\right)^2} = 1$$

We can compare it with equation of ellipse $\dfrac{x^2}{(a)^2} + \dfrac{y^2}{(b)^2} = 1$, so it is an ellipse in x-$p_x$plane

with semi-major axis a = $\sqrt{2E/k}$ and semi minor axis b = $\sqrt{2mE}$, fig.(10.5).
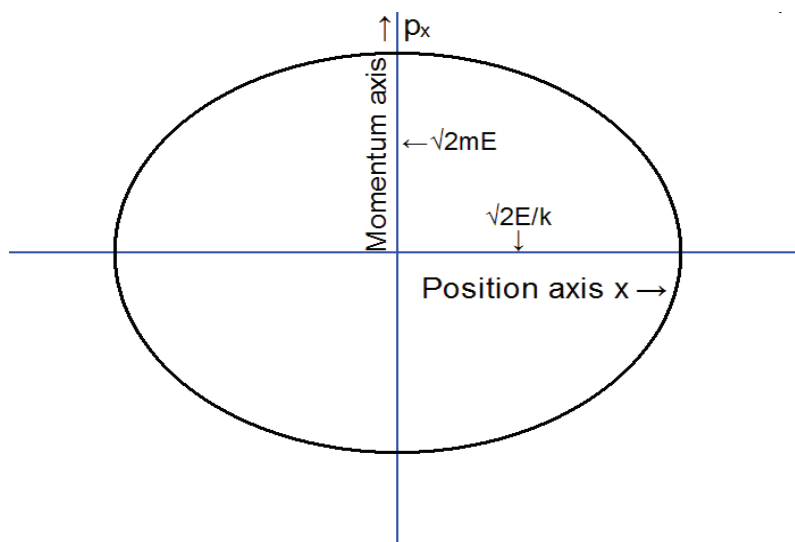
Fig (10.5): Harmonic oscilator in Phase space (x − p_x)

So a one dimensional harmonic oscillator which executes to and fro motion along x axis in static space , will have elliptical trajectory in phase space . The total energy of oscillator along the ellipse will remain constant. The area of this ellipse gives the phase area available from energy range 0 to E. So number of phase cells available in energy range 0 to E will be

$$\phi(E) = \frac{\text{Total phase area}}{\text{Phase cell area}}$$

Since the total phase area of ellipse = $\pi ab = \pi \sqrt{2E/k} . \sqrt{2mE}$
and the area of one phase cell is dx.dp_x = h.

So the number of phase cells,

$$\phi(E) = \frac{2\pi E}{h}\left(\frac{m}{k}\right)^{1/2} \tag{10.40}$$

Since frequency $v = \dfrac{1}{2\pi}\sqrt{\dfrac{m}{k}}$

Therefore, $\phi(E) = \dfrac{E}{hv}$ or E = $hv . \phi(E)$ $\qquad\qquad$ (10.41)

If $\phi(E)$ is discrete or quantize, i.e. $\phi(E) = 0, 1, 2…., n$, then $E = nh\nu$ .the energy of a harmonic oscillator will be in multiples of $h\nu$.

10.5.3 THE DENSITY OF STATES

A macroscopic system is one which has many degrees of freedom denoting the energy of the system by E. Let $\Omega(E)$ represents the number of states whose energy lies between E and E+dE in a system. Let $\phi(E)$ is the total number of possible discrete states(accessible or allowed states) of the system which are characterized by energies less than E. Clearly $\phi(E)$ increases when E increases. The number of states $\Omega(E)$ in the range between E and E+ dE is then

$$\Omega(E) = \varphi(E + \delta E) - \varphi(E) = \frac{\partial \varphi}{\partial E} \delta E = \rho(E)\delta E$$

The term ρ(E) gives number of energy states in unit energy interval; hence it is called density of states. Let us calculate the number of phase cells available in energy range 0 to E for a single particle of mass m in volume V.

The phase space volume is

$$V_{ph} = \iiint dq_x.dq_y.dq_z.\iiint dp_x.dp_y.dp_z$$

$$= V \iiint dp_x.dp_y.dp_z \qquad (10.42)$$

In momentum space $p^2 = p_x^2 + p_y^2 + p_z^2 = 2mE$, so volume of that space is

$$\iiint dp_x.dp_y.dp_z = \frac{4\pi}{3} p^3 = \frac{4\pi}{3}(2mE)^{3/2}$$

$$\therefore V_{ph} = \frac{4\pi}{3} V(2mE)^{3/2} \qquad (10.43)$$

And hence, the number of phase cells available in energy range 0 to E will be

$$\phi(E) = \frac{\text{phase space volume}}{\text{Phase cell volume}}$$

The number of accessible or allowed states

$$\varphi(E) = \frac{V_{ph}}{h^3} = \frac{4\pi}{3h^3} V(2mE)^{3/2} \qquad (10.44)$$

So the accessible states in the energy range E to E + dE is

$$\Omega(E) = \frac{\partial \varphi}{\partial E} \delta E = \rho(E)\delta E \ ,$$

Differentiating eq. (10.44) and rearranging, we get

$$\Omega(E) = \frac{2\pi}{h^3} V(2m)^{3/2} E^{1/2} dE \qquad (10.45)$$

and the density of states $\rho(E) = \frac{2\pi}{h^3} V(2m)^{3/2} E^{1/2}$. $\qquad (10.46)$

This term has great importance in many statistical calculations; it is also called degeneracy of states g_i.

10.6 THERMODYNAMICAL PROBABILITY

Suppose we want to determine the number of ways that N objects (molecules) can be placed in M containers (energy states) on a single compartment (energy level). Before making such *combinatorial* calculations, we must know whether the objects (molecules) are distinguishable or indistinguishable and the restrictions on the population of objects within each energy state. You must know that some atomic or molecular particles having half integral spin (Fermions) are occupy   one particle per energy state. Other particles having integral spin (Bosons) have no limit on their occupancy in single state. For proper statistical calculations, we must account for both of these cases, as well as for objects that can be either distinguishable or indistinguishable.

10.6.1 DISTINGUSHABLE OBJECT

Combinatorial analysis for distinguishable objects is divided in three cases, depending on to different constraints. These are as follows:

CASE1. In how many ways may N identical, distinguishable objects be placed in M different containers with a limit of one object per container?

The limitation of one object per container requires $N \leq M$. The first object may be placed in any of M available containers, the second in $(M- 1)$ available containers, and so on. Hence the number of ways for this case becomes

$$\Omega = M(M- 1)(M- 2) \cdot \cdot \cdot (M- N + 1)$$

or

$$\Omega = \frac{M!}{(M-N)!} \qquad\qquad (10.47)$$

CASE 2. In how many ways may N identical, distinguishable objects be placed in M different containers such that the ith container holds exactly N_i objects?

The total number of permutations for N objects is $N!$ However, within each container, permutations are irrelevant as we are concerned only with their number rather than their identity. Hence, the number of permutations, $N!$ over counts the number of ways by the number of permutations, $N_i !$, for each container. Therefore, the number of ways is

$$\Omega = \frac{N!}{N1!N2!...Nm!}$$

or

$$\Omega_i (N_1,N_2…,N_M) = \frac{(N)!}{\prod_{i=1}^{M} Ni!} \qquad\qquad 10.48)$$

Here Ω gives the number of microstates in a particular macrostate for distinguishable particles system (classical system). The total number of microstates, Ω, corresponding to particular macrostate is called the *thermodynamic probability.*

CASE 3. In how many ways may N identical, distinguishable objects be placed in M different containers with no limitation on the number per container?

Because no limit exists, each object can be placed in any of the containers. Therefore,

$$\Omega = M^N \qquad\qquad (10.49)$$

It gives total number of microstates in a distinguishable particles system (classical system). Hence the probability of occurrence of a particular distribution $(N_1,N_2..,N_M)$ will be

$$P_i(N_1, N_2 \ldots, N_M) = \frac{\Omega i\ (N1, N2\ldots, NM)}{\Omega} \qquad (10.50)$$

i.e., $Pi = \dfrac{\text{Thermodynamical Probability of ith distribution}}{\text{total number of possible microstates}}$

10.6.2 INDISTINGUISHABLE OBJECT

Combinatorial analysis for indistinguishable objects divided into two cases following

CASE 4. In how many ways may N identical, indistinguishable objects be placed in M different containers?

A similar restriction for distinguishable objects gives Eq. (10.47). For indistinguishable objects, however, any rearrangement among the No objects is unrecognizable. Hence, Ω given by eq. (10.47) over counts the number of ways for indistinguishable objects by a factor of N! Therefore,

$$\Omega = \frac{M!}{N!(M-N)!} \qquad (10.51)$$

CASE 5. In how many ways may N identical, indistinguishable objects be placed in M different containers with no limitation on the number per container?

This is fully unconstrained case (indistinguishable objects, no limitation). We begin by initially assuming distinguishable objects labeled $1, 2, 3, N$. Let us now arrange these N objects in a row, with the M containers identified and separated by partitions. As an example,
$$1, 2, 3 \mid 4, 5 \mid 6 \mid \ldots \mid N-1, N$$
Specifies that objects 1, 2, and 3 are in the first container, objects 4 and 5 are in the second container, and object 6 is in the third container, and so on. Now, regardless of their actual arrangement, the maximum number of rearrangements among the N objects and $M-1$ partitions is $(N + M-1)!$ However, interchanging the partitions produces no new arrangements; thus, we have over counted by a factor of $(M-1)!$ Similarly, because the N objects are actually indistinguishable, we have again over counted by a factor of $N!$, as in case 4. Therefore, the number of ways for this case becomes

$$\Omega = \frac{(N+M-1)!}{N!(M-1)!} \qquad (10.52)$$

Cases 3–5 are important to us in view of statistical mechanics. As we will see in the later course, Eq. (10.49) is related to M-B statistics(See unit III), Eq. (10.51) is related to Fermi–Dirac statistics, and Eq. (10.52) is related to Bose–Einstein statistics(See unit 17).

10.7 CONCLUSIONS

This unit of the course has devoted to a brief and simple introduction to a branch of mathematics the probability theory, then phase space and thermodynamical probability. The essential element of statistical mechanics is the probability distribution, so Binomial, Poisson and Gaussian distribution are explained in detail. The probabilistic 'calculation' which we apply to develop this subject is very simple. You do not need deep understanding of probability theory in order to understand statistical thermodynamics. This material is

sufficient to understand the fundamental concept of thermodynamical probability, the concept of classical phase space and density of states.

10.8 SUMMARY

1. The probability of an event $=\dfrac{\text{numberof cases in which the event occours}}{\text{total number of possible events}}$

or $\qquad$ $P_A = \lim\limits_{N\to\infty} n_A / N$

2. The probability of obtaining n occurrences of a particular outcome in N observations is

given by $\quad P_N(n) = C_n^N p^n q^{N-n} = \dfrac{N!}{n!(N-n)} p^n q^{N-n}$

This probability function is called the Binomial distribution function.

3. The mean value of the variable in Binomial distribution is probability of occurrence of

event p multiplied by total the number of trials N. $\quad <n> = \sum_{n=0}^{N} n.P(n) =$pN

4. Binomial distribution Becomes Poisson distribution when N is very large, $N\to\infty$, p is very

small, $p\to 0$ and n is very small i.e., n<<N

5. Poisson distribution function is $P(n) = \dfrac{1}{n!}(<n>)^n e^{-<n>}$, here $<n>=$ pN

6. When the number N is large i.e.$N\to\infty$, but p is not small, the Binomial distribution

becomes the continuous Gaussian distribution .Gaussian distribution is applicable when N

and n both are large but n is not too close to N .

7. Gaussian distribution is, $P(n) = (1 /\sqrt{2} \pi Npq).e^{-(n-Np)2/2Npq}$.

8. A single particle having 2f dimensional space, occupies the phase space volume,
$d\tau = \prod_{i=1}^{f} dq_i.dp_i.$ The volume of each cell is h^f, the number of cells in the volume
element $d\tau$ will be$d\Omega = \dfrac{d\tau}{(h)}f$

9. Density of states in phase space $\phi(E) = \dfrac{\text{phase space volume}}{\text{Phase cell volume}}$

10. For a free single particle of mass m having energy E, enclosed in volume V, the density
of states is, $\rho(E) = \dfrac{2\pi}{h^3} V (2m)^{3/2} E^{1/2}$

11. The probability of occurrence of a particular distribution $(N_1,N_2..,N_M)$ will be
$P_i(N_1,N_2...,N_M) = \dfrac{\Omega i\ (N1,N2...,NM)}{\Omega}$

or Pi $= \dfrac{\text{Thermodynamical probability of ith distribution}}{\text{total number of possible microstates}}$

10.9 REFERENCES

1.   Reif, F. Fundamentals of Statistical and Thermal Physics. New York, NY: McGraw-Hill, June 1, 1965. ISBN: 0070518009.
2.   Hemne, P.S,Subrahmanyam N.,Brijlal .Heat and Thermodynamics. S Chand pub. New Delhi, 2014. ISBN 81-219-2813-3.
3.   Laud, B.B. Fundamentals of Statistical Mechanics. 2nd edition 2012 ISBN 978-81-224-3278-7
4.   Satya Prakash, Statistical Mechanics. edition 2014 (Kedar Nath Ram Nath pub, Delhi).
5.   Beiser, A., Mahajan S., S.RaiChoudhary. Concepts of Modern Physics. 6th edition 2009
6.   Gupta and Kumar, Elementary statistical mechanics. 21 edition 2006. ISBN 81-7556-988

10.10 SUGGESTED READINGS

1.   Huang, Kerson, Statistical Mechanics, 2nd ed., John Wiley & Sons, Inc., 1987, ISBN 0-471-81518-7.
2.   L. D. Landau and E. M. Lifshitz, Statistical Physics, 3rd Edition, Part I (Butterworth-Heinemann, Oxford, 1980) ISBN 0-7506-3372-7.
3.   Pathria, R. K., Statistical Mechanics, 2nd ed., Butterworth-Heinemann, Burlington, MA, 1996, ISBN 0 -7506-2469-8.
4.   Zemansky, M., and R. Dittman. Heat and thermodynamics: an intermediate textbook. 7th Ed. New York, NY: McGraw-Hill Companies, 1997. ISBN: 0070170592
5.   Carter, Ashley, Classical and Statistical Thermodynamics, Prentice-Hall, Upper Saddle River, NJ, 2001, ISBN 0-13-779208-5.
6.   http://www.jamia-physics.net/lecnotes/statmech/
7.   http://www.jamia-physics.net/lecnotes/statmech/
8.   Kumar, A. and Taneja, S.P., Thermal Physics and Statistical Mechanics, R. Chand and CO., New Delhi, 2017.

10.9 TERMINAL QUESTIONS

1.   What is classical statistics? Discuss its importance and limitations.
2.   Define probability and discuss its importance in statistical mechanics.
3.   Discuss additive and multiplicative laws of probability.
4.   What is conditional probability, explain with an example?
5.   Explain two state systems with an example
6.   Calculate the probability of drawing two aces in succession from a well shuffled pack of 52 cards(Ans. 1/121)
7.   What is the probability of throwing 3 dice to obtain a total of score of 6 or less? (Ans.0.093)
8.   Calculate the probability of getting 3 'heads' and only 2 'tails' in an experiment where a coin is tossed 5 times, or where 5 coins are tossed simultaneously. (Ans.5/6)

9. What is the Binomial distribution ? Explain with suitable example
10. Explain the difference between discrete and continuous distributions.
11. Prove that, the mean value of the variable in Binomial distribution is probability of
    occurrence of event multiplied by the total   number of trials.
12. Prove that for a system N→∞ and $p→ 0$, the Binomial distribution becomes the
    discrete Poisson distribution.
13. What is the Gaussian distribution? Prove its distribution function.
14. Explain the terms variance and standard deviation.
15. Define phase space .What is the volume of one phase cell for a system of N
    monoatomic particles?
16. What is the minimum size of phase cell in classical and quantum mechanics?
17. Differentiate μ space to Γspace.
18. Discuss one dimensional harmonic oscillator. Prove that the trajectory of oscillator is
    and ellipse.
19. What is density of states?
20. A free particle of mass m is enclosed in volume V .Calculate the number of accessible
    states in the energy range E and E+dE.
21. What is Thermodynamical probability? How does it differ from mathematical
    probability?
22. A fairly-weighted coin is tossed 20 times.
    a. Prove that the probability for a specific number of heads is given by the binomial
    distribution.
    b. Calculate the probabilities for each of the possible numbers of heads.
    c. Recalculate the probabilities in part (b) by invoking a Gaussian distribution.
    d. Display your results from parts (b) and (c) on a single plot. Discuss the implications of
    your comparison
23. Determine the number of ways of placing three balls in three numbered boxes for each
    of the following cases.
    a. The balls are distinguishable with a limit of one ball per box.
    b. The balls are distinguishable with no limit on the number per box.
    c. The balls are indistinguishable with a limit of one ball per box.
    d. The balls are indistinguishable with no limit on the number per box.
    Construct four tables showing all possible distributions for each case.

Unit 11   STATISTICAL THERMODYNAMICS

CONTENTS

11.1 OBJECTIVES

After going through this unit, you will be able to:
- Define the fundamental postulates of statistical mechanics.
- Make the distinction between microstates and macrostates.
- Tabulate the distributions and microstates of a system.
- Understand the most probable macrostate and its importance.
- Equilibrium between two macroscopic systems in thermal contact.
- Derive the relation between entropy and probability.
- Understand second and third law of thermodynamics in terms of entropy.
- Know the condition for equilibrium.
- Know thermal equilibrium, mechanical equilibrium and particle equilibrium.
- Derive the connections between statistical and thermodynamical quantities.
- Apply statistical mechanics in analysis of an ideal gas.
- Derive the relation for the statistical entropy of ideal gas.

11.2 POSTULATES OF STATISTICAL MECHANICS

The fundamental postulates of statistical mechanics are as follows:
1. Any system may be considered to be composed of very small point like particles in motion and interact elastically.
2. Total number of particle and total energy of the system is constant.
3. All the cells in the phase space are of equal size.
4. All accessible microstates corresponding to possible macrostate are equally probable.
5. The equilibrium state of a system corresponds to the macrostate of maximum probability.
Now let us understand these postulates in detail.
An ideal classical system to apply M–B statistics is an isolated system of independent (non-interacting) particles. For an isolated system, the total number of particles and energy of the system must remain constant. Hence, we have two system constraints that can be expressed as

$$\sum_i n_i = N$$

$$\sum_i \varepsilon_i n_i = E$$

Where n_i is the number of independent particles occupying the ith energy level with energy ε_i. Expressing the total number of particles N, and the total energy E, in terms of summations over all possible energy levels .We also note that the total system energy E, must, of course, be equivalent to the macroscopic internal energy, $U \equiv E$. The description of the number of particles N_i, within each energy level with its respective energy ε_i, is called the *particle distribution*. The ratio, N_i/N, indicates either (1) the fraction of total particles in the ith energy level or (2) the probability that a single particle will be in the ith energy level. Many distributions are possible, and these distributions vary continuously with time because of particle interactions. For such large number of possible distributions, averaging over all of them would be a vast task. Fortunately, we know from classical thermodynamics that properties such as the internal energy have a well-defined value for an isolated system, thus suggesting that a most probable distribution might define the equilibrium state for a system

containing a large number of atoms or molecules. So our prime object is to search the most probable distribution.

11.2.1 MACROSTATE AND MICROSTATE

Consider a system of three distinguishable coins. Let us make all possibilities of heads facing up when these coins are thrown. There are four such possibilities, named 0 (outcome with no head), 1(outcome with one head), 2(outcome with two heads), & 3 (outcome with all heads). This arrangement is called the *macrostate* of this system. We might even call these energy levels 0, 1, 2, & 3. The orientation of each individual coin will be a *microstate*. We can list the microstates, using H for heads and T for tails: TTT, HTT, THT, TTH, HHT, HTH, THH, and HHH. Now, we write the microstates into different macrostateor energy levels.

energy level	microstates	multiplicity, Ω
0	TTT	1
1	HTT, THT, TTH	3
2	HHT, HTH, THH	3
3	HHH	1

Table (11.1)

The *multiplicity* is the number of distinct microstates in a specified macrostate. From table (11.1) it is clear that, the number of microstates in a macrostate with one head and two tails are three. So the *multiplicity* of this macrostate (one H, two T) is $\Omega(1,2)=3$.   The total multiplicity of the system is the total of all the possible microstates. For these three coins, that is $\Omega(all)=8$.

A macrostate specifies a system in terms of quantities that "average" over the microscopic constituents of the system. Examples of such quantities include the pressure, volume and temperature of a gas. Such quantities only make sense when considered in a system composed of very large numbers of particles: it makes no sense to talk of the pressure or temperature of a single molecule.

A microstate specifies a system in terms of the properties of each of the constituent particles; for example, the position and momentum of each of the molecules in a sample of gas.

We have seen that a particle distribution is ordinarily specified by the number of particles in each *energy level*, $N_i(\varepsilon_i)$. This energy *level* wise particle distribution is called a *macrostate*. We can, consider more directly the influence of degeneracy and specify instead the number of distinct particles in each *energy state*, $N_i(\varepsilon_i)$. This more deep distribution is called a *microstate*. A **microstate** is a single state of a system, including the exact states of all the system's constituent particles. A classical microstate includes each particle's position and momentum. A microstate cannot be observed or determined in a laboratory. However, the knowledge of microstates from physical theories is essential to applying Statistical Mechanics to predict observable phenomena. Clearly, for each separate macrostate, there are many possible microstates having high values of the degeneracy, g_i. Hence, the most probable distribution of particles over energy levels should correspond to that macrostate associated with the greatest number of microstates. Based on the above concepts of microstate and macrostate, we may state the two basic postulates of statistical thermodynamics, suitable for application to the M– B statistics. Therefore, for an isolated system of independent particles, we have two basic postulates of statistical thermodynamics that can be stated as follows:

1. The time average for a thermodynamic variable is equivalent to its average over all possible microstates.
2. All microstates are equally probable; hence, the relative probability of each macrostate is given by its number of microstates. The second statement is called the *postulate of equal a priori probability*.

11.2.1.1 ERGODIC HYPOTHISIS:

In statistical physics , the **Ergodic hypothesis** says that, over long periods of time, the time spent by a system in some region of the phase space of microstates with the same energy is proportional to the volume of this region, i.e., all accessible microstates are equiprobable over a long period of time.Similarly, if each system quantum state is equally likely, then every microstate must also be equally likely. As a result, the most probable macrostate must be that having the largest number of microstates.

Example 1

Problem : Consider an isolated system of independent particles with the following allowed energy levels and associated degeneracies: $\varepsilon_0 = 0$, $g_0 = 1$; $\varepsilon_1 = 1$, $g_1 = 2$; $\varepsilon_2 = 2$, $g_2 = 3$. If the system consist of two particles and the total energy should be two units, determine: .

(a) The number of macrostates (b) The number of microstates for distinguishable particles (c) The number of microstates for indistinguishable particles. Assuming, no limit on the number of particles per energy state.

Solution : (a) We have two distinguishable particles ⊛, ⊙. They must be distributed among the three allowed energy levels either with one particle at $\varepsilon_0 = 0$ and the other at $\varepsilon_2 = 2$ or with both at $\varepsilon_2 = 1$, *so that* the total energy be two units. Therefore, this system contains only two macrostates.(b) The following table shows the possible microstates for each macrostate when the particles are distinguishable. Macrostate #1 has six microstates (columns) and macrostate #2 has four microstates Table (11.2). Hence, the total number of microstates is 10. In this case, macrostate #1 is the most probable macrostate.

	macrostate #1						macrostate #2			
$\epsilon_2 = 2$ $g_2 = 3$	⊙			⊛						
		⊙			⊛					
			⊙			⊛				
$\epsilon_1 = 1$ $g_1 = 2$							⊙	⊛	⊛⊙	
							⊛	⊙		⊛⊙
$\epsilon_0 = 0$ $g_0 = 1$	⊛	⊛	⊛	⊙	⊙	⊙				

Table (11.2)

(c) For indistinguishable particles, the distinguishable open and closed circles are irrelevant. Hence, the number of microstates in both macrostate #1 and macrostate #2 is three, for a total of six microstates.

11.2.2 THE MOST PROBABLE MACROSTATE

The thermodynamic properties of a system can be estimated by considering only the most probable macrostate, i.e., the most probable distribution of particles over energy levels. We can easily   show that a large majority of all possible microstates is associated with the most probable macrostate.

To show the significance of the most probable macrostate, we shall study two cases, by identifying each possible macrostate and then determining the associated number of microstates per macrostate. We assume particles are distinguishable with no limit on the number of particles per energy state. In case 1 we choose $N = 6$ particles distributed into $M = 2$ non degenerate energy levels. In case 2, to investigate the influence of large numbers, we will consider $N = 10^{23}$ particles system.

We begin by determining the number of possible particle distributions or macrostates Ω_m, which is equivalent to the number of ways that N indistinguishable objects can be placed in M different containers with no limitation on the number of objects per container. Indistinguishability is temporarily presumed here because we are only concerned with the number of objects in each container and not their order of placement. We thus have, from Eq. (10.52) of unit (10),

$$\Omega = \frac{(N+M-1)!}{N!(M-1)!}$$

so that, for $M = 2$, $\Omega_m = N + 1$

Hence, for given $N = 6$, we find that $\Omega_m = 7$; these seven macrostates of six particles distributed between two energy levels are as follows: $\{0, 6\}, \{1, 5\}, \{2, 4\}, \{3, 3\}, \{4, 2\}, \{5, 1\}$, and $\{6, 0\}$.

 Next, we determine the number of possible arrangements for a given particle distribution, or the number of microstates per macrostate, Ω_i, which is equivalent to the number of ways that N distinguishable objects can be placed in M different containers such that Ni objects occupy the ith container. Employing Eq. (10.48) of section 10.6.1, we have

$$\Omega_i \quad = \quad \frac{(N)!}{\prod_{i=1}^{M} Ni!} \tag{11.2}$$

So that, for each of the above macrostates, we obtain $\Omega_i \{0, 6\} = \Omega_i \{6, 0\} = 1$, $\Omega_i \{1, 5\} = \Omega_i \{5, 1\} = 6, \Omega_i \{2, 4\} = \Omega_i \{4, 2\} = 15$, and $\Omega_i \{3, 3\} = 20$. Hence, we find that the number of microstates associated with the most probable macrostate Ωmp, is 20. Similarly, the total number of microstates, Ω, is given by $2(1 + 6 + 15) + 20 = 64$.

We can independently determine the total number of possible arrangements or microstates because this tally is equivalent to the number of ways N distinguishable objects can be placed in M different containers with no limitation on the number per container.

Hence, from Eq. (10.49), the total number of microstates is

$$\Omega = M^N$$

so that $\Omega = 2^6 = 64$, is in agreement with our previous calculation. In summary, we find that for $\Omega = 64$, $\Omega_{mp} = 20$, and thus that mean number of microstates $\overline{\Omega} = \Omega/\Omega_m = 9$.

Consequently, comparing these three statistics, we may write the expected result for any $N > M$; i.e.

$$\Omega > \Omega mp > \overline{\Omega}. \tag{11.3}$$

Let us now consider a very large number of particles, say $N = 10^{23}$. For $M = 2$, the total number of microstates and the mean number of microstates can be expressed as

$$\Omega = M^N \quad \text{and} \quad \overline{\Omega} = \Omega/\Omega_m = \frac{2^N}{N+1}$$

Where we have employed Eqs. (11.1) and (11.2). Therefore,

$$\ln\Omega = N\ln 2 \approx 7.0 \times 10^{22}$$
$$\ln\overline{\Omega} = N\ln 2 - \ln(N + 1) \approx 7.0 \times 10^{22} - 53.$$

It is clear from this analysis, when N is large, almost no difference arises between $\ln\Omega$ and $\ln\overline{\Omega}$. Consequently, using Eq. (10.49), we have for a very large number of particles

$$\ln\Omega \approx \quad \ln\Omega_{mp} \approx \ln\overline{\Omega}, \qquad\qquad (11.4)$$

So that

$$\lim_{N\to\infty} \frac{\Omega_{mp}}{\Omega} = 1 \qquad\qquad (11.5)$$

Equation (11.5) indicates that for large macroscopic systems almost all microstates are associated with the most probable macrostate. Hence, the knowledge of most probable macrostate is sufficient to study large systems. The significant conclusion is that utilizing the most probable distribution of particles over energy levels is essentially equivalent to averaging over all microstates because those microstates associated with the most probable macrostate invariably account for nearly all possible microstates. Therefore, from the viewpoint of classical thermodynamics, *the most probable particle distribution must represent the equilibrium particle distribution.*

11.2.3 LIFE TIME OF MICROSTATE

In order to estimate the time taken in observing all the possible microstates, let us consider a case, say a paramagnetic system (where the atomic spins interact with the external magnetic field- Zeeman Effect).   The   particles inside   this system ($N \sim 10^{23}$)   are assumed   to be non-interacting,   and each electron has a spin of $\pm \frac{1}{2}$. We also fix E and T for a fixed macrostate i.e. n_i. Note that it is a Quantum Mechanical system,   so the energy of the system will be quantized. The total energy of the paramagnetic system having k quantized energy states is given by

$$E = \sum_k \mu_k.B$$

How   many microstates   does the system   transit   during the time of observation? The change   in microstates   will mean   that the spin energy   of the electron   is exchanged between   neighboring atoms   so the atoms   interchange   energy levels. The   typical time for spin flip (spin change from one state to another) is 10^{-12}s. So for a system of 10^{23} electrons: So the number of microstates transited or covered by the system in one second, or the transition speed $10^{12} \times 10^{23} = 10^{35}$ per-sec

Now,   the number of microstates $\Omega = \exp(N \ln N) > e^{10^{35}} >>> 10^{35}$
 Since the time of any observation or experiment is too small, so it is impossible to observe each microstate.

11.3 MACROSCOPIC SYSTEMS IN THERMAL CONTACT

Let us consider   two macroscopic systems, A and A′, having energy E and E' respectively, are in thermal contact with each other by a conducting interface fig. (11.3). suppose the interaction is purely thermal i.e., all other external parameters are constant. Whole system is thermally isolated from their surroundings.
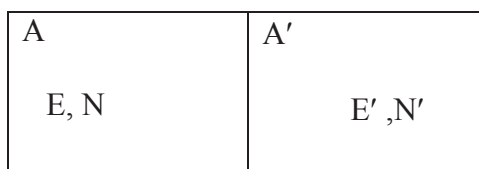
A	A′
E, N	E′ ,N′

Fig. (11.3)

Since the external parameters are constant, so that A and A′ cannot do work on one another and the systems are thermally in contact so they will exchange heat. Considering the energy range from E to E+δE, let us see the temperature at equilibrium and the entropy of the system at equilibrium.

Let the number of microstates of A, related with a macrostate in which the energy lies in the range E to E + δE is denoted Ω(E). Likewise, the number of microstates of A′, related with a macrostate in which the energy lies between E′ and E′ + δE is denoted Ω(E′).
The combined system A$^{(0)}$ = A + A′ is assumed to be isolated (i.e., it neither does work on nor exchanges heat with its surroundings). Let the number of accessible microstates to the entire system A^{0}is denoted by Ω^0(E) when A^0 has energy between E and E+dE. When systems A and A' are in equilibrium, the whole system can be in any one of Ω (E).Ω (E′) microstates, the probability of the system A and A′ possessing energies E and E′ respectively, will be maximum. Then the probability that A has energy equal to E, by using the postulate of statistical mechanics.

$$P\,(E) = C\ \Omega\,(E) \tag{11.6}$$

Similarly the probability that A' has energy equal to E′ will be

$$P\,(E') = C'\ \Omega\,(E') \tag{11.7}$$

Since entire system is isolated so the total energy of the system must remain constant, i.e. ,

$$E^0 = E + E'.$$

The probability of system A having the energy E and system B having energy near E′ is given by

$$P(E,E')=CC'\,\Omega(E)\Omega(E^0 - E) \tag{11.8}$$

For applying the condition for maximum probability ∂ P(E)/ ∂E =0,

Taking the logarithm on both sides

$$\ln P(E, E') =\ \ln C + \ln C' +\ \ln C\,\Omega\,(E) + \ln C'\,\Omega\,(E') \tag{11.9}$$

To locate the maximum position of P(E) at E

$$\frac{\partial \ln P(E)}{\partial E} = \frac{1}{P}\frac{\partial P}{\partial E}=0 \tag{11.10}$$

or $$\frac{\partial \ln P(E)}{\partial E} = \frac{\partial \ln \Omega(E)}{\partial E} + \frac{\partial \ln \Omega'(E')}{\partial E}=0 \tag{11.11}$$

where E^0=E+E′ which is dE=- dE′ then

$$\frac{\partial \ln \Omega(E)}{\partial E} - \frac{\partial \ln \Omega'(E')}{\partial E'}=0 \tag{11.12}$$

Let $\beta(E) =\frac{\partial ln\Omega}{\partial E} = \frac{d\Omega}{\Omega dE}$ and $\beta(E') =\frac{\partial ln\Omega'}{\partial E} = \frac{d\Omega'}{\Omega' dE}$ (11.13)

Hence $\beta(E)= \beta'(E')$

Where E and E′ denote the corresponding energies of A and A′ at the maximum.

It is the required condition of equilibrium when two systems are in thermal contact.
So two systems are in equilibrium when their functions (β parameter) are equal and it
has the following properties:
1. If two systems separately in equilibrium have the same value of β then the systems will
remain in equilibrium when brought into thermal contact with one another.
2. If two systems separately in equilibrium have different values of β then the systems will
not remain in equilibrium when brought into thermal contact with one another.
Instead, the system with the higher value of β will absorb heat from the other system until the
two β values are the same.

Thermodynamic temperature:

In terms of temperature, thermal equilibrium is specified by T= T'. Thus at thermal
equilibrium, temperature of the system attains maximum constant value.

Hence $\beta(E) = \beta'(E')$ implies that

$\beta(E) = \frac{\partial \ln \Omega}{\partial E}$, $\frac{1}{\beta} = kT \ and \ \frac{1}{\beta'} = kT'$. where k is some positive constant having the
dimension of energy and whose magnitude in some convenient arbitrary way. The dimension
of k is erg.deg^{-1} , identified as Boltzmann's constant k_B= R/N. The parameter T is termed the
thermodynamic temperature, and controls heat flow in much the same manner as a
conventional temperature. Thus, if two isolated systems in equilibrium possess the same
thermodynamic temperature then they will remain in equilibrium when brought into thermal
contact. However, if the two systems have different thermodynamic temperatures then heat
will flow from the system with the higher temperature (i.e., the "hotter" system) to the system
with the lower temperature until the temperatures of the two systems are the same. The
thermodynamic temperature of a macroscopic body depends only on the rate of change of the
number of accessible microstates with the total energy.

11.4 RELATION BETWEEN ENTROPY AND PROBABILITY

According to Second law of thermodynamics entropy S of a system is related with
temperature T by the relation dQ =T.dS can be written for a system having energy E as.

$$\frac{1}{T} = \frac{\partial S}{\partial E} \tag{11.14}$$

And statistically

$$\frac{1}{T} = k\beta = k\frac{\partial ln\Omega}{\partial E} \tag{11.15}$$

So, $\frac{\partial S}{\partial E} = k\frac{\partial ln\Omega}{\partial E}$, The integration gives

$$S = k.\ln \Omega \tag{11.16}$$

This is the famous relation between entropy and probability called Boltzmann's entropy
relation. Shows the entropy S of an equilibrium macrostate is related to the number of
accessible microstates Ω , it states that the entropy of a system is proportional to logarithm of
the thermodynamical probability of that system. We are assuming that the system is in a
particular macrostate which has fixed energy. Hence we have a microscopic meaning of
entropy. The system is perfectly ordered when Ω = 1 and S = k ln Ω = 0. When more
microstates are availiable Ω> 1 so S > 0.Since equilibrium state has maximumΩ, hence has
maximum entropy.The lesser the knowledge about a system, the more disordered it gets.

From the formula with which we obtained the relation of entropy with probability, we are unable to deduce the value of k. The value of k comes out from the ideal gas equation.

11.4.1 IDENTIFICATION OF K IN BOLTZMANN EQUATION

We can determine the value of k by applying the same conditions, as above considered, to a thermodynamical system. Let one mole ($N = 10^{23}$) of an ideal gas is contained in a chamber of volume V_1 and pressure p_1. Let this chamber is connected to an empty chamber of volume V_2 . So the final volume is V_1+V_2, let the final pressure is p_2. Assuming the process is isothermal i.e. temperature remains constant during the process.

After connecting two chambers, the probability of finding of one particle of gas in first

chamber of volume V_1 is $\left(\dfrac{V_1}{V_1 + V_2} \right)$

Since one mole of gas has N particles (atom or molecules), so the probability of finding of one mole of the gas in first chamber of volume V_1 is

$$\Omega_1 = \left(\frac{V_1}{V_1 + V_2} \right)^N$$

It is initial probability of the system.

The probability of finding of one mole of the gas in final volume $V_1 + V_2$ is

$$\Omega_2 = \left(\frac{V_1+V_2}{V_1 + V_2} \right)^N = 1$$

It is the final probability.

Now, since Ω_1 and Ω_2 are initial and final probability of the system.

So the change in entropy during the process IS

$\Delta S = S_2 - S_1 = k\ln\Omega_2 - k\ln\Omega_1 = k\ln\left(\dfrac{\Omega_2}{\Omega_1} \right)$

Substituting the values of Ω_1 and Ω_2,

We get

$$= k \ln \left(\frac{1}{V_1 \big/ V_1 + V_2} \right)^N$$

$$\Delta S = \ln \left(\frac{V_1+V_2}{V_1} \right)^{Nk} \tag{11.17}$$

Using thermodynamics principles for an isothermal process where the system changes its initial state $(p_1 v_1)$ to final state $(p_2, v_1 + V_2)$, the change in the entropy is

$$\Delta S = R \ln \left(\frac{V_1 + V_2}{V_1} \right)$$

or $\qquad \Delta S = \ln \left(\dfrac{V_1+V_2}{V_1} \right)^{R}$ $\tag{11.18}$

Comparing eq. (11.17) and (11.18) we have

$$\ln\left(\frac{V_1+V_2}{V_1}\right)^{Nk} = \ln\left(\frac{V_1+V_2}{V_1}\right)^{R}$$

Hence Nk = R or k = $\frac{R}{N}$, also since R is gas constant and N is Avogadro's number, the k is

certainly

Boltzmann's constant having value (k = 1.38x 10^{-23} J / K)

Example 2

Problem: For a system at constant temperature and fixed number of particles, by using the statistical

definition of entropy, calculate the entropy change between a state of final volume V_f and initial volume V_i .

Solution

Let a movable partition divides a closed chamber of volume V_f into two parts, one part having volume V_i and second part having volume V_f - V_i Fig. (11.4).
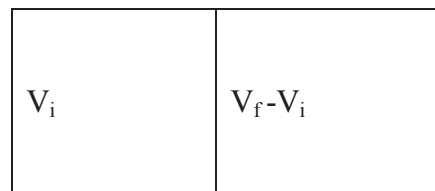

| V_i | V_f-V_i |

Fig. (11.4)

Suppose only one particle present in the chamber .the probability of finding that particle in

volume V_i will be $\frac{V_i}{V_f}$ .Similarly, if the chamber contains n particles, then the probability of

finding all the particles in volume V_i will be $\left\{\frac{V_i}{V_f}\right\}^{n}$

Let the chamber contains n gram moles of an ideal gas,then the probability of finding entire

gas in volume V_i will be $\left\{\frac{V_i}{V_f}\right\}^{nN}$

where N is Avogadro's number.

So the initial probability will be $\Omega_i = \left\{\frac{V_i}{V_f}\right\}^{nN}$ (11.19)

Now if we remove the partition, then the probability of finding all the particles in volume V_f

will be $\left\{\frac{V_f}{V_f}\right\}^{nN} = 1$.

So final probability Ω_f = 1.   (11.20)

Dividing eq. (11.19) by eq. (11.20)

we get

$$\frac{\Omega_i}{\Omega_f} = \left\{\frac{V_i}{V_f}\right\}^{nN}$$ (11.21)

Taking logarithm both sides of eq. (11.21)

we have $\ln\dfrac{\Omega_i}{\Omega_f} = nN\ln\left\{\dfrac{V_i}{V_f}\right\}$

Multiplying both sides by Boltzmann constant k, we have

$$k\ln\dfrac{\Omega_i}{\Omega_f} = nkN\ln\left\{\dfrac{V_i}{V_f}\right\}$$

Since, R = kN

so $k\ln\dfrac{\Omega_i}{\Omega_f} = nR\ln\left\{\dfrac{V_i}{V_f}\right\}$ (11.22)

If S and S are initial and final entropies respectively the change in entropy is

$$\Delta S = k\ln\Omega_f - k\ln\Omega_i$$

This can be written as $\Delta S = k\ln\dfrac{\Omega_f}{\Omega_i}$ (11.23)

Comparing eq. (11.22) with eq. (11.23), the change in entropy in terms of initial and final volume, when T and N are fixed is

$$\Delta S = nR\ln\dfrac{V_f}{V_i} \quad .$$ (11.24)

Example 3
Problem: How much heat (in eV) must be given to a system at room temperature $\sim 27^0$C for the number of accessible states to increase by a factor of 10^8 ?

Solution
By Boltzmann's entropy relation
        $\Delta S = k \ln(\Delta\,\Omega)$
But $\Delta S = \Delta Q/T$
or $\Delta Q = T\Delta S = kT\ln\Delta\,\Omega$
                $= (1.38 \times 10^{-23})(300)\ln10^8$
                $= 7.626 \times 10^{-20}$ joule
Since 1 eV = $1.6\text{x}10^{-16}$ J
So required amount of heat to increase number of microstates by a factor of 10^8 is,
$\Delta Q = 0.477$ eV

11.4.2 ENTROPY AND SECOND LAW OF THERMODYNAMICS

Entropy is a key concept in thermodynamics and statistical mechanics. An equilibrium macrostate of a system can be characterized by a quantity S (called entropy) which has the property
1. In any process in which a thermally isolated system goes from one macrostate to another, the entropy tends to increase $\Delta S \geq 0$
2. If the system is not isolated and undergoes a quasi-static infinitesimal process
    in which it absorbs heat dQ, then $dS = \dfrac{dQ}{T}$, dS is an exact differential.

It is an additive quantity. The entropy of a combined system is equals to the sum of entropies of
 individual systems.

Thermodynamical description of entropy depicts, it is a state function which depends on the present state of the system and no information we can draw about past state of the system. The exact physical picture of entropy in terms of physical condition of the system or thermodynamic properties cannot be established.

In classical statistical physics, if a system is in equilibrium, the statistical entropy of the system is defined as

$$\sigma = \log \Delta \Gamma$$

To make it additive it must be divided by h^{3N} and N! , (see earlier unit) i.e.

$$\sigma = \ln \frac{\Delta \Gamma}{h^{3N}.N!}$$

where $\Delta \Gamma$ are the phase space volume occupied by the system in the accessible range of energy E to E+ dE, h is Planck's constant and N is the number of particles.

11.4.3 ENTROPY AND THE THIRD LAW

The Third Law of Thermodynamics states that as the temperature $T \to 0$, the entropy $S \to 0$, it is approaching ground state as U(T) also approaches 0, so the disorder number tends to 1. When all the particles take the ground state, $\Omega(E_0) = 1$. From Boltzmann entropy relation

$$S_0 = k \log \Omega(E_0) = 0$$

From the third law, T=0 is a theoretically correct statement, but it is practically impossible. Why is this so? Because there exists very small interactions in the nucleus due to many type magnetic moments. In order to make T = 0, the magnetic moments are required to point in the same direction. Experimentally, this condition is not attainable. Some small interactions (e.g. nuclear paramagnetism) still remain in the ground state, i.e. $S_0 \neq 0$. Hence we can only say $S \to S_0$ as $T \to 0$ where S_0 is the entropy associated with the remaining small interactions.

11.5 CONDITION FOR EQUILIBRIUM

As we have discussed that the state of equilibrium is directly related with most probable state of the system. Therefore, we may state that equilibrium state of an isolated system has maximum entropy. At equilibrium the statistical entropy σ is a function of the energy of the system $U \equiv E$, the number of constituent particles n_i of particular group and some external parameter x_i that can affect the system like pressure, volume or some external field (electric or magnetic field).

11.5.1 THERMAL EQUILIBRIUM

If σ_1 and σ_2 are respective statistical entropies of two sub systems, by using the additive property of entropy, the entropy of entire system is
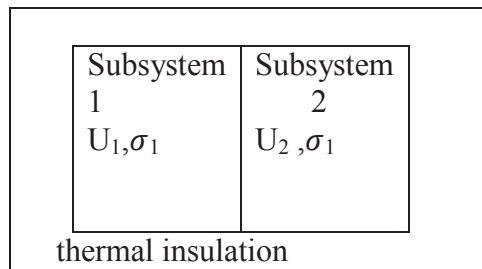
Fig (11.5)

$$\sigma(U_1, U_2) = \sigma_1 + \sigma_2 \tag{11.25}$$

And　　　　　$U = U_1 + U_2$ 　　　　　　　　　　　　　　　　　　　　(11.26)

If small heat transfer from one system to other takes place, then

$$d\,\sigma = d\sigma_1 + d\sigma_2$$

$$= (\frac{\partial \sigma 1}{\partial U1})dU_1 + (\frac{\partial \sigma 2}{\partial\ U2})dU_2 \tag{11.27}$$

With the condition $dU = dU_1 + dU_2 = 0$ at thermal equilibrium

So $dU_1 = -dU_2$

$$d\sigma = (\frac{\partial \sigma 1}{\partial U1})dU_1 + (\frac{\partial \sigma 2}{\partial\ U2})dU_2 \tag{11.28}$$

or　　　$d\,\sigma = (\frac{\partial \sigma 1}{\partial U1})dU_1 + (\frac{\partial \sigma 2}{\partial\ U2})dU_2 = 0$

So the substitution of relation $dU_1 = -dU_2$ gives

$$d\sigma = (\frac{\partial \sigma 1}{\partial U1} - \frac{\partial \sigma 2}{\partial\ U2})dU_1 = 0 \tag{11.29}$$

Since　　　　　$dU_1 \neq 0$

Therefore,　　$\frac{\partial \sigma 1}{\partial U1} = \frac{\partial \sigma 2}{\partial\ U2}$ 　　　　　　　　　　　　　　　　(11.30)

Defining a quantity τ as 　$\frac{1}{\tau} = \frac{\partial \sigma}{\partial U}$ 　　　　　　　　　　(11.31)

Where τ is called statistical temperature. Eq. (11.30) and (11.31) show that two subsystems of a system will be at thermal equilibrium if their temperature is equal. Therefore, two sub systems are said to be in **thermal equilibrium**, when the energy content and the temperatures of the sub systems will no longer be changing with time. **Statistical temperature τ** is related to absolute temperature by the relation

　　　　　$\tau = kT,$

Where k is Boltzmann constant having value 1.38×10^{-23} joule/K

11.5.2 MECHANICAL EQUILIBRIUM

Suppose that interface is movable, let it divides the two sub-systems into volume V_1 and V_2 so that total entropy gets maximum value. Then

$$\sigma(U_1, U_2, V_1, V_2) = \sigma_1 (U_1, V_1) + \sigma_2 (U_2, V_2) \tag{11.32}$$

At Mechanical equilibrium $d\,\sigma = 0$

i.e.,　　　　　$d\,\sigma = (\frac{\partial \sigma 1}{\partial U1})dU_1 + (\frac{\partial \sigma 1}{\partial V1})dV_1 + (\frac{\partial \sigma 2}{\partial\ U2})dU_2 + (\frac{\partial \sigma 2}{\partial\ V2})dV_2 = 0$　　(11.33)

As we have seen, at thermal equilibrium

$$(\frac{\partial \sigma 1}{\partial U1})dU_1 + (\frac{\partial \sigma 2}{\partial\ U2})dU_2 = 0 \tag{11.34}$$

so $\qquad (\frac{\partial\sigma1}{\partial V1})dV_1 \ + \ (\frac{\partial\sigma\ 2}{\partial\ V2})dV_2 \ = 0$ $\qquad\qquad\qquad\qquad$ (11.35)

And $V = V_1 +V_2 \ =$ constant, thus

$\qquad\qquad dV = dV_1 +dV_2 = 0$, hence $dV_1 = -dV_2$

Applying it in eq. (11.35)

$\qquad\qquad [(\frac{\partial\sigma1}{\partial V1}) \ - \ (\frac{\partial\sigma\ 2}{\partial\ V2})]dV_1 \ = 0$ $\qquad\qquad\qquad\qquad$ (11.36)

The above relation says that at mechanical equilibrium

$\qquad\qquad \frac{\partial\sigma1}{\partial V1}= \ \frac{\partial\sigma\ 2}{\partial\ V2}$ $\qquad\qquad\qquad\qquad\qquad\qquad$ (11.37)

Introducing a new quantity p such that

$\qquad\qquad \frac{p}{\tau}= \ (\frac{\partial\sigma}{\partial\ V})_{U,N}$ $\qquad\qquad\qquad\qquad\qquad\qquad$ (11.38)

If the microscopic expression for the entropy is known, this equation allows one to calculate the *equation of state* connecting *p, τ* and *V*.

Eq. (11.38) shows that for a system in thermal equilibrium, the condition for Mechanical equilibrium will be

$\qquad\qquad p_1 \ = p_2$

Suppose sub-systems are not initially in mechanical equilibrium but only in thermal equilibrium, and let initially $p_1> p_2$. The system will evolve so that $d \sigma >0$

From eq. (11.33) we have

$\qquad\qquad d \sigma = \ \frac{1}{\tau}(p_1 \ - p_2)dV_1> 0$ $\qquad\qquad\qquad\qquad$ (11.39)

We have assumed initially $p_1> p_2$,so dV_1 is positive. It shows p has characteristics of ordinary pressure.

From thermodynamics

$\qquad\qquad TdS= dU + PdV$

Substituting $S= k$ and $P = p$

$\qquad\qquad Td(k\sigma) = dU + pdV,$

$\qquad\qquad d\sigma = \ \frac{dU}{kT} + \ \frac{RdV\sigma}{k\ V}$ $\qquad\qquad\qquad\qquad\qquad$ (11.40)

$\qquad\qquad (\frac{\partial\sigma}{\partial\ V})_{E,N}= \ \frac{R}{k\ V} =\frac{N}{V}= \ \frac{p}{\tau}$ $\qquad\qquad\qquad\qquad$ (11.41)

The above relation gives $\qquad\qquad N\tau = pV$

Comparing it with perfect gas equation $PV = NkT$,

This gives $p = P$ which is named as **statistical pressure**.

11.5.3 DIFFUSIVE EQUILIBRIUM

Suppose diffusion of molecules of the gas is allowed through interface i.e. exchange of particles is allowed. Let at the equilibrium n_{i1} and ni_2, is number of molecule or particle of particular ith species of chemical system.

$\qquad\qquad \sigma(U_1, U_2, V_1 ,V_2,n_{i1}, n_{i2}) \ = \sigma_1(U_1, \ V_1 , n_{i1})+ \sigma_2 (\ U_2, V_2, n_{i2})$ $\qquad$ (11.42)

At equilibrium $d \sigma = 0$

Applying differentiation law

$d\sigma = (\frac{\partial\sigma1}{\partial U1})dU_1 + (\frac{\partial\sigma1}{\partial V1})dV_1+ (\frac{\partial\sigma\ 2}{\partial\ U2})dU_2+ (\frac{\partial\sigma\ 2}{\partial\ V2})dV_2+ (\frac{\partial\sigma1}{\partial ni1})dn_{i1}+ (\frac{\partial\sigma1}{\partial ni2})dn_{\ i2}= 0$ $\qquad$ (11.43)

When system has thermal equilibrium and mechanical equilibrium, from above, we have

$\qquad\qquad (\frac{\partial\sigma1}{\partial U1})dU_1 + \ (\frac{\partial\sigma\ 2}{\partial\ U2})dU_2=0$ $\qquad\qquad\qquad\qquad$ (11.44)

And so

$$(\frac{\partial \sigma 1}{\partial V1})dV_1 \ + \ (\frac{\partial \sigma\,2}{\partial\,V2})dV_2 \ = 0 \tag{11.45}$$

Thus we have, at particle equilibrium

$$d\,\sigma = \ \ (\frac{\partial \sigma 1}{\partial ni1})dn_{i1} \ + \ (\frac{\partial \sigma 1}{\partial ni2})dn_{i2}= 0 \tag{11.46}$$

$n_i = n_{i1} \ + \ n_{i2,}$ i.e., total number of molecules or particles of particular ith species of chemical system will remains constant.

Hence $dn_i = dn_{i1} \ + \ dn_{i2}= 0$, so $dn_{i1} \ = - \ dn_{i2}$

Thus, we have

$$(\frac{\partial \sigma 1}{\partial ni1} - \ \frac{\partial \sigma 1}{\partial ni2})dn_{i1}= 0$$

This implies $\frac{\partial \sigma 1}{\partial ni1} = \ \ \frac{\partial \sigma 1}{\partial ni2}$ 　　　　　　　　　　　　　　　(11.47)

By defining a new quantity μ_i,called chemical potential

$$-\frac{\mu i}{\tau} = (\frac{\partial \sigma}{\partial\,ni})_{U,V} \tag{11.48}$$

Obviously when a system is in thermal equilibrium and mechanical equilibrium, the required condition for particle or diffusive equilibrium will be

$$\mu_1 = \mu_2$$

i.e. Chemical potential of two sub systems should be equal.

11.6 RELATION BETWEEN STATISTICAL AND THERMODYNAMICAL QUANTITIES

Let there be a very small change in the system, so that under reversible process system remains in equilibrium, i.e. process should be slow and with slight deviation.

We have $\sigma \ = \sigma\,(U,n_i,\ x_j)$

$$d\,\sigma = \ (\frac{\partial \sigma}{\partial U})dU \ + \ \Sigma_i(\frac{\partial \sigma}{\partial ni})dn_i \ + \Sigma_j(\frac{\partial \sigma}{\partial\,xj})dx_j \tag{11.49}$$

From the relations

$$\frac{1}{\tau} = \ \frac{\partial \sigma}{\partial U} \quad \text{and} \quad -\frac{\mu i}{\tau} = \ \frac{\partial \sigma}{\partial\,ni}$$

and introducing $-\frac{Xj}{\tau} = \ \frac{\partial \sigma}{\partial\,xj}$, where X_j is some generalizing force related to coordinate x_j

This equation can be written as

$$d\,\sigma = \ \ \frac{1}{\tau}dU -\Sigma_i\frac{\mu i}{\tau} \ dn_i +\frac{1}{\tau}\Sigma_j \ X_j dxj \tag{11.50}$$

By arranging, we get

$$dU = \tau.\ d\,\sigma \ +\Sigma_i \ \mu_i \ dn_i \ - \Sigma_j \ X_j dxj \tag{11.51}$$

Suppose a simple system having only volume as an external parameter and number of particles is constant. So $dn_i = 0$, $x_j = V$ and generalizing force $X_j = p$ (statistical pressure) Applying these conditions in above equation

$$dU = \ \tau.\ d\,\sigma \ - \ pdV \tag{11.52}$$

It is obvious from equation (11.52) that the change in internal energy of the system takes place in two ways

When dV=0, external parameter remains constant, $\tau.d\sigma$ represents the change in internal energy U. It is a quantity of heat energy absorbed by the system in reversible process.

In case when d σ =0, the term -pdVwill represent the change in internal energy due to change in external parameter V, i.e. this term represents mechanical work. Thermodynamically the work done must be –PdV, comparing both we have p = P

Comparing eq. (11.52) with dU = TdS – PdV we have

$$TdS = \tau \cdot d\sigma \qquad (11.53)$$

So calculations show that S and σ, T and τ are equivalent quantities, related by a proportionality term known as Boltzmann constant k, as S = $k\sigma$, $\tau = kT$.

Now   U= U(σ, V)

$$dU = (\frac{\partial U}{\partial \sigma})d\sigma + (\frac{\partial U}{\partial V})dV \qquad (11.54)$$

Comparing Eq. (11.52) with Eq. (11.54), we get

$$\tau = (\frac{\partial U}{\partial \sigma})_V$$

and $p = -(\frac{\partial U}{\partial V})\ \sigma$ $\Big\}$ (11.55)

In practice, to study any physical process calculations in terms of the independent variables σ and V, are quite inconvenient. So more easily applicable relations can be established by using the auxiliary functions like Helmholtz free energy F which is a function of V and d τ , enthalpy H a function of σ and p, and Gibb's free energy G a function of τ and p.

11.6.1 HELMHOLTZ FREE ENERGY, F

By using the thermodynamic potential function, Helmholtz free energy F defined as

        F = U - TS

        = U – $\tau\sigma$

Differentiating above eq. both sides

        dF = dU - $\tau d\sigma$ - $\sigma d\tau$

By using eq. (11.52)

        dF = - pdV - $\sigma d\tau$ (11.53)

As F = F (V, τ)

        $dF = (\frac{\partial F}{\partial V})dV + (\frac{\partial F}{\partial \tau})d\tau$

Comparing above eq. with (11.53), we have

        $p = (\frac{\partial F}{\partial V})\ \tau$

and $\sigma = -(\frac{\partial F}{\partial \tau})_V$ $\Big\}$ (11.54)

11.6.2 THE ENTHALPY H

The enthalpy H is defined as

        H = U + pV

Differentiating it, dH = dU + pdV + Vdp, using dU = $\tau \cdot d\sigma$ - pdV

        dH = $\tau d\sigma$ + Vdp   (11.55)

Again H = H(σ, p), so

        $dH = (\frac{\partial H}{\partial \sigma})d\sigma + (\frac{\partial H}{\partial p})dp$ (11.56)

On comparing Eq. (11.55) with Eq. (11.56), gives

and
$$\tau = \left(\frac{\partial H}{\partial \sigma}\right)_p$$
$$V = \left(\frac{\partial H}{\partial p}\right) \sigma$$

(11.57)

11.6.3 GIBBS FREE ENERGY G

The Gibb's function G is defined as
$$G = U - TS + PV$$
$$= U - \tau\sigma - pV$$
On differentiating,
$$dG = dU - \tau d\sigma - \sigma\, d\tau + p\, dV + Vdp$$
$$= -\sigma d\tau + Vdp$$ (11.58)
As $G = G(\tau, p)$
$$dG = \left(\frac{\partial G}{\partial \tau}\right)d\tau + \left(\frac{\partial G}{\partial p}\right)dp$$ (11.59)
Comparing Eq. (11.58) with Eq. (11.59), we gt

$$\sigma = -\left(\frac{\partial G}{\partial \tau}\right)_p$$
and $$V = \left(\frac{\partial G}{\partial p}\right)\tau$$

(11.60)

Thus Gibbs free energy G is introduced if τ and p are independent variables.

11.7 STATISTICAL ANALYSIS OF A PERFECT GAS

Let us consider an isolated perfect monoatomic gas has constant energy E or U, constant numbers of particles N, having mass of each particle m and fixed volume V. The volume occupied by gas in phase space
$$\Delta\Gamma = \int dq_1......dq_f \int dp_1........dp_f$$ (11.61)
Here f = 3N for monoatomic gas
In an ideal gas, since all particles are non- interacting hence the energy of the system will be independent of position of the particles. So volume available for N particles is
$$\int dq_1......dq_f = V^N$$ (11.62)
So equation (11.61) becomes
$$\Delta\Gamma = V^N \int dp_1...........dp_f$$

(11.63)

The integration of the above equation will be evaluated in 3N dimensional momentum space in the energy range E – dE to E. So the radius of the hyper sphere of constant E in 3N dimensional momentum space will be $p = \sqrt{2mE}$ and similarly for hyper sphere of constant

E – dE is $\sqrt{2m(E-dE)}$, the thickness of spherical hyper shell is $\sqrt{\frac{m}{2E}}dE$

 Since the volume of 3-dimensonal sphere of radius R is

$$V_3 \frac{4}{3}\pi R^3 = \frac{\pi^{3/2}}{\Gamma(\frac{3+2}{2})} R^3 \qquad (11.64)$$

It can be generalized for the volume of f dimensional sphere, by replacing all 3 by f

Hence $V_f(R) = \frac{\pi^{f/2}}{\Gamma(\frac{f+2}{2})} R^f \qquad (11.65)$

Since f = 3N

The volume of 3N dimensional hypersphere of radius $p = \sqrt{2mE}$ is

$$V_{3N} = \frac{\pi^{3N/2}}{\Gamma(\frac{3N+2}{2})}(2mE)^{3N/2} \qquad (11.66)$$

Since $\qquad \Gamma\left\{\frac{3N+2}{2}\right\} = \frac{3N}{2}!$

we have

$$V_{3N} = \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!}(2mE)^{3N/2} \qquad (11.67)$$

The volume of spherical hyper shell is

$$\int dp_1.....dp_f = \frac{\pi^{3N/2}}{(\frac{3N}{2})!}[(2mE)^{3N/2} - \{2m(E-dE)^{3N/2}\}]$$

$$= \frac{\pi^{3N/2}}{(\frac{3N}{2})!}(2mE)^{3N/2}[1-(1-\frac{dE}{E})^{3N/2}]$$

$$= \frac{\pi^{3N/2}}{(\frac{3N}{2})!}(2mE)^{3N/2}[1-\exp(-\frac{3N}{2}\frac{dE}{E})] \qquad (11.68)$$

For a gaseous system 3N ~ 10^{23} (very large)

Hence $\frac{3N}{2}$ dE >> E, so the exponential term will be negligibly small, hence we drop it.

Hence Eq. (11.68) becomes

$$\int dp_1...........dp_f = \frac{\pi^{3N/2}}{(\frac{3N}{2})!}(2mE)^{3N/2} \qquad (11.69)$$

Substituting it in equation for $\Delta\Gamma$

$$\Delta\Gamma = V^N \frac{\pi^{3N/2}}{(\frac{3N}{2})!}(2mE)^{3N/2} \qquad (11.70)$$

Now the statistical entropy σ

$$\sigma = \ln\Delta\Gamma = \ln[V^N \frac{\pi^{3N/2}}{(\frac{3N}{2})!}(2mE)^{3N/2}]$$

can be written as

$$\sigma = N\ln[V \pi^{3/2}(2mE)^{3/2}] - \ln\left\{\frac{3N}{2}\right\}!$$ (11.71)

To simplify factorial term we have to use Stirlings's approximation $\ln n! = n\ln n - n$

$$\sigma = N\ln[V \pi^{3/2}(2mE)^{3/2}] - \left\{\frac{3N}{2}\right\}\ln\left\{\frac{3N}{2}\right\} + \frac{3N}{2}$$ (11.72)

Rearranging eq. (11.72)

$$\sigma = N\ln[\frac{V \pi^{3/2}(2mE)^{3/2}}{\left\{\frac{3N}{2}\right\}^{3/2}}] + \frac{3N}{2}$$

$$= N\ln[V\left\{\frac{4\pi m}{3}\right\}^{3/2}\left\{\frac{E}{N}\right\}^{3/2}] + \frac{3N}{2}$$ (11.73)

Since the entropy must be independent of the unit of hypervolume, to make the term inside ln dimensionless we divide it by h^{3N}, so the corrected relation between entropy and phase space hypervolume is

$$\sigma = \ln\frac{\Delta\Gamma}{h^{3N}}$$ (11.74)

or
$$\sigma = N\ln\left[\frac{V\left\{\frac{4\pi m}{3}\right\}^{3/2}\left\{\frac{E}{N}\right\}^{3/2}}{h^3}\right] + \frac{3N}{2}$$ (11.75)

Quantity such as E, V, N and σ etc. follows the additive rule and called extensive variables. On the other hand, the variables which arise from differentiating the entropy, such as temperature $1/T = \partial\sigma/\partial E$ and pressure $p = T\partial\sigma/\partial V$ and chemical potential $\mu = T\partial S\sigma/\partial N$ involves the ratio of two extensive quantities and so do not change as we divide or add the system: they are called intensive quantities. The eq. (11.75) do not follows additive law of entropy. To make it additive we have to divide it again by the factor N!.
Hence,

$$\sigma = \ln\frac{\Delta\Gamma}{h^{3N}.N!}$$ (11.76)

By Stirling's approximation $\ln N! = N\ln N - N = \ln(N/e)^N$, where e is the base natural logarithm ($\log_e e = 1$). So our equation modifies as

$$= N\ln\left[\frac{\frac{V}{N}\left\{\frac{4\pi m}{3}\right\}^{3/2}\left\{\frac{E}{N}\right\}^{3/2}e}{h^3}\right] + \frac{3N}{2}$$

or $\qquad \sigma = N \ln \left[\dfrac{\dfrac{V}{N} \left\{ \dfrac{4\pi m}{3} \right\}^{3/2} \left\{ \dfrac{E}{N} \right\}^{3/2}}{h^3} \right] + \dfrac{5N}{2}$ $\qquad$ (11.77)

In eq. (11.77) V and E both are divided by N, due to which these terms becomes volume per particle and energy per particle respectively .Thus, this relation will exactly follow the additive rule. By using this equation we can make the relation of statistical quantities with their corresponding thermodynamical quantities for an ideal gas. Let us make some relations.

11.7.1 INTERNAL ENERGY

In section 15.5.1 Eq. (7) we have established a relation for statistical temperature τ

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right) \qquad (11.76)$$

Here we have used total energy term E in place of U. so for an ideal gas

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial E} \right) \qquad (11.77)$$

Using equation (11.77)

$$\frac{1}{\tau} = \frac{\partial}{\partial E} \left[N \ln \left[\frac{\dfrac{V}{N} \left\{ \dfrac{4\pi m}{3} \right\}^{3/2} \left\{ \dfrac{E}{N} \right\}^{3/2}}{h^3} \right] + \frac{5N}{2} \right]$$

Applying log rule

$$\frac{1}{\tau} = \frac{\partial}{\partial E} \left[N \ln V - N \ln N + N \ln \left\{ \frac{4\pi m}{3} \right\}^{3/2} - \frac{3N}{2} \ln N + \frac{3N}{2} \ln E - N \ln h^3 + \frac{5N}{2} \right] \quad (11.78)$$

We get

$$\frac{1}{\tau} = \frac{\partial}{\partial E} \left[\frac{3N}{2} \ln E \right] = = \frac{3N}{2} \frac{1}{E} \qquad (11.79)$$

This gives

$\qquad$ E $= = \dfrac{3N\tau}{2}$, (since $\quad \tau$=kT)

Thus, E $= \dfrac{3NkT}{2}$ $\qquad$ (11.80)

This is the internal energy of an ideal monoatomic gas.

11.7.2 THERMODYNAMIC ENTROPY S OF IDEAL GAS

We have established a relation between statistical entropy σ with thermodynamic entropy S as

S = kσ using equation (11.77)

$$S = kN \ln \left[\frac{{}^V\!/_N \left\{ {}^{4\pi m}\!/_3 \right\}^{3/2} \left\{ {}^E\!/_N \right\}^{3/2}}{h^3} \right] + k \frac{5N}{2} \tag{11.81}$$

Since E $= \frac{3NkT}{2}$, Hence we have

$$S = Nk \ln \left[\frac{V}{N} \right] \left[\frac{2\pi mkT}{h^2} \right]^{3/2} + \frac{5}{2} Nk \tag{11.82}$$

(We will use this relation to resolve Gibbs paradox in forthcoming Unit)

$$S = Nk \ln \left[\frac{V(2\pi mkT)^{3/2}}{Nh^3} \right] + Nk \ln e^{5/2}$$

or $$S = Nk \ln \left[\frac{V(2\pi mkT)^{3/2}}{Nh^3} e^{5/2} \right] \tag{11.83}$$

This relation is known as Sacur -Tetrode formula for entropy of a perfect monoatomic gas. Since the thermal de-Broglie wavelength associated with a molecule at temperature T is

$$\lambda_T = \frac{h}{\sqrt{2\pi mkT}} \tag{11.84}$$

Hence S $= Nk \ln \left[\frac{V}{N\lambda^3} \right] + \frac{5}{2} Nk \tag{11.85}$

11.8 SUMMERY

1. A macrostate specifies a system in terms of quantities that "average" over the microscopic constituents of the system.
2. A microstate specifies a system in terms of the properties of each of the constituent particles. Many different microstates can correspond to a single macrostate
3. The *postulate of equal a priori probability* is: all accessible microstates corresponding to possible macrostate are equally probable.
4. The equilibrium state of a system corresponds to the macrostate of maximum thermo-dynamical probability.
5. Ergodic hypothesis is the time average for a thermodynamic variable which is equivalent to its
average over all possible microstates.
6. For a very large particles system $\ln\Omega \approx \ln\Omega_{mp} \approx \ln\overline{\Omega}$, that means in macroscopic systems almost all microstates are associated with the most probable macrostate. The knowledge of the most probable macrostate is sufficient for the systems at equilibrium.
7. The required condition of equilibrium when two systems are in thermal contact is

$$\frac{\partial \ln \Omega(E)}{\partial E} = \frac{\partial \ln \Omega'(E')}{\partial E'} \text{ , or } \beta(E) = \beta'(E') \text{ .where } \beta(E) = \frac{\partial \ln\Omega}{\partial E} = \frac{d\Omega}{\Omega dE}$$

8. Boltzmann's entropy relation is the statistical entropy of a system is defined as $S = k.\ln\Omega$
10. The statistical entropy of a system is, $\sigma = \ln \frac{\Delta\Gamma}{h^{3N}.N!}$
11. Two subsystems of a system will be at thermal equilibrium if their temperature are equal.
12. Statistical temperature τ is related to absolute temperature by the relation $\tau = kT$,

13. The condition for Mechanical equilibrium is $p_1 = p_2$ and $T_1 = T_2$, gives $\frac{p}{\tau} = (\frac{\partial \sigma}{\partial V})_{U,N}$

14. When a system is in thermal equilibrium and mechanical equilibrium, the required condition for particle or diffusive equilibrium will be $\mu_1 = \mu_2$, and $-\frac{\mu i}{\tau} = (\frac{\partial \sigma}{\partial n i})_{U,V}$

15. The relation between statistical entropy σ with thermodynamic entropy S is, $S = k\, \sigma$

16. Entropy of ideal gas is $S = Nk \ln \left[\dfrac{V}{N} \right] \left[\dfrac{2\pi mkT}{h^2} \right]^{3/2} + \dfrac{5}{2} Nk$

11.9 REFERENCES AND RELEVANT READINGS

1.   Reif, F. Fundamentals of Statistical and Thermal Physics. New York, NY: McGraw-Hill, June 1, 1965. ISBN: 0070518009.
2.   Hemne, P.S,Subrahmanyam N.,Brijlal .Heat and Thermodynamics. S Chand pub. New Delhi, 2014. ISBN 81-219-2813-3.
3.   Huang, Kerson, Statistical Mechanics, 2nd ed., John Wiley & Sons, Inc., 1987, ISBN 0-471-81518-7.
4.   L. D. Landau and E. M. Lifshitz, Statistical Physics, 3rd Edition, Part I (Butterworth-Heinemann, Oxford, 1980) ISBN 0-7506-3372-7.
5.   Wannier, Gregory H., Statistical Physics, Dover Publications, 1987, ISBN 048665401X.
6.   Satya Prakash, Statistical Mechanics. edition 2014 (Kedar Nath Ram Nath pub, Delhi).
7.   Beiser, A., Mahajan S., S.RaiChoudhary. Concepts of Modern Physics. 6th edition 2009 (Tata McGraw Hill, NewDelhi)ISBN: 978-0-07-015155-0.
8.   Laud, B.B. Fundamentals of Statistical Mechanics. 2nd edition 2012. ISBN 978-81-224-3278-7
9.   Pathria, R. K., Statistical Mechanics, 2nd ed., Butterworth-Heinemann, Burlington, MA, 1996, ISBN 0 -7506-2469-8.
10.   Zemansky, M., and R. Dittman. Heat and thermodynamics: an intermediate textbook. 7th Ed. New York, NY: McGraw-Hill Companies, 1997. ISBN: 0070170592

11.10 TERMINAL QUESTIONS

1. What are the fundamental postulates of statistical mechanics?
2. What is the theorem of a priori probability, explain with example.
3. What is Ergodic hypothesis? State and explain its significance.
4. Define the terms macrostate and microstate. What is accessible macrostate?
5. 4 particles are distributed in 2 cells; tabulate all possible macrostate and their corresponding microstate.
6. What is thermodynamical probability? When its value becomes maximum?
7. What is the most probable state? Give its connection with thermodynamical probability.
8. 9 classical particles are distributed in 3 cells of equal size. Calculate the thermodynamical probability for
    a. $n_1 = 0$, $n_2 = 0$, $n_3 = 9$
    b. $n_1 = 3$, $n_2 = 3$, $n_3 = 3$
    c. $n_1 = 4$, $n_2 = 2$, $n_3 = 3$
Which distribution is most probable, least probable? Calculate the number of microstate in

the macrostate (n_1 =4, n_2 = 2, n_3 = 3) and its probability.

(Ans. b, a, microstates: 1260, probability: 0.064)

9. Explain the significance of most probable state.

10. Define entropy; discuss second and third law of thermodynamics in terms of entropy.

11. Drive Boltzmann's entropy relation $S = k \ln \Omega$ and its importance.

12. State and prove the Boltzmann's relation between entropy and probability.

13. Prove that, when two systems are in thermal equilibrium $\beta(E) = \frac{\partial ln\Omega}{\partial E} = \frac{d\Omega}{\Omega dE} = \frac{1}{kT}$

14. Prove that when two subsystems of a system are at thermal equilibrium if their temperatures are equal.

15. How is Statistical temperature τ related to Thermodynamical temperature T?

16. What is Suckur-Tetrode equation? Explain its importance.

17. Discuss the condition for Mechanical equilibrium. Prove $\frac{p}{\tau} = (\frac{\partial \sigma}{\partial V})_{U,N}$

18. What is diffusive equilibrium .Prove that at diffusive equilibrium $-\frac{\mu i}{\tau} = (\frac{\partial \sigma}{\partial ni})_{U,V}$

19. Prove relation between statistical entropy σ with thermodynamic entropy S, $S = k \sigma$.

20. Prove the following relations:

a. $\tau = (\frac{\partial U}{\partial \sigma})_V$ and $p = -(\frac{\partial U}{\partial V}) \sigma$, where U is total internal energy.

b. $p = (\frac{\partial F}{\partial V}) \tau$ and $\sigma = -(\frac{\partial F}{\partial \tau})_V$, where F is Helmholtz free energy.

c. $\tau = (\frac{\partial H}{\partial \sigma})_p$ and $V = (\frac{\partial H}{\partial p}) \sigma$, where H isEnthalpy.

d. $\sigma = - (\frac{\partial G}{\partial \tau})_p$ and $V = (\frac{\partial G}{\partial p}) \tau$, where G is Gibbs free energy.

21.What are statistical temperature, statistical pressure and statistical entropy?

UNIT 12   CLASSICAL DISTRIBUTION FUNCTIONS

CONTENTS

12.1 OBJECTIVES

After going through this unit, you will be able to:
* Understand the behaviour of a system in thermal contact with heat bath
* Derive Boltzmann canonical distribution law and partition function
* Know the law of equipartition of energy
* Establish statistical definition of thermodynamic variables
* Understand Maxwell - Boltzmann statistics
* MB energy distribution function for ideal gas
* Define chemical potential
* Derive the relations of partition function with thermodynamic functions
* Give the relationships between energy and partition function.
* Understand Gibbs paradox and its resolution

12.2 SYSTEM IN THERMAL EQUILIBRIUM WITH A HEAT BATH

Let us consider a small sub system A′ in thermal contact with a large reservoir (heat bath) fig. (12.1) so that entire system is thermal equilibrium, i.e. temperature remains constant during the small exchange of energy between A and A′. Now our aim is to find general expression for the probability P_i of finding the system A′ in any one particular energy state i (microstate) of energy ϵ_i. Let $\Omega(\epsilon)$ be the number of accessible energy states when system lies between ϵ and $\epsilon + d\epsilon$, in a large reservoir A having energy ϵ.
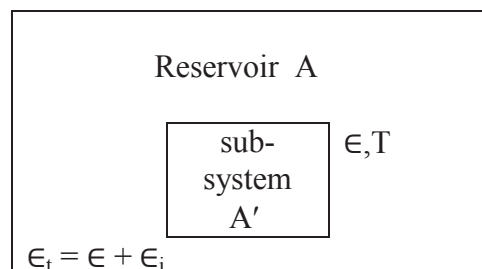
Fig (12.1)

When sub-system A is in its ith energy state by the law of energy conservation, the total energy of the whole system $A_t = A + A'$ will be $\epsilon_t = \epsilon + \epsilon_i$

So $\qquad \epsilon = \epsilon_t - \epsilon_i$ (12.1)

So the probability P_i of finding the system A' in any one particular energy state i of energy ϵ_i will be proportional to number of states accessible to energy range ϵ to $\epsilon + d\epsilon$, $d\epsilon$ is much less then

$\qquad P_i \propto \Omega(\epsilon_t - \epsilon_i)$ (12.2)

Since A′ is much smaller than A, obviously $\epsilon_t \gg \epsilon_i$. So

$$\in \approx \in_t \tag{12.3}$$

Expending $\ln\Omega\ (\in) = \ln\Omega(\in_t - \in_i)$ by Taylor's expansion

$$\ln\Omega(\in_t - \in_i) = \ln\Omega(\in_t) - \varepsilon_i \left(\frac{\partial \ln \Omega}{\partial \varepsilon}\right)_{\varepsilon=\varepsilon_T}$$

Since $\beta = \left(\frac{\partial \ln \Omega}{\partial \varepsilon}\right)$, so the above equation becomes

$$\ln\Omega(\in_t - \in_i) = \ln\Omega(\in_t) - \beta \varepsilon_i \tag{12.4}$$

where $\beta = \frac{1}{kT}$ is called β - parameter, hence

$$\ln\Omega(\in_t - \in_i) = \ln\Omega(\in_t) - \beta \varepsilon_i$$

$$= \Omega(\in_t)\, e^{-\beta\varepsilon_i}$$

From above equations, we get $P_i \propto \Omega(\in_t)\, e^{-\beta\varepsilon_i}$.

Since $\Omega(\in_t)$ is independent of $\ln\in_i$, this equation can be written as

$$P_i = C\, e^{-\beta\varepsilon_i} \tag{12.5}$$

This is Boltzmann canonical formula in which $e^{-\beta\varepsilon_i}$ is known as Boltzmann factor. Its plot at different temperature $(T_2 > T_1)$ is shown in Fig (12.2).The proportionality constant C can be evaluated by using the condition of normalization for probability distribution function P_i

as

$$\sum_i P_i = 1$$

$$= C\sum_i e^{-\beta\varepsilon_i} = 1 \tag{12.6}$$

This gives , $C = \dfrac{1}{\sum_i e^{-\beta\varepsilon_i}}$

Substituting the value of C in equation (12.5)

Finally, $P_i = \dfrac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}} \tag{12.7}$

The Boltzmann distribution gives the *relative* probability of a system in thermal equilibrium with a heat bath to be in a *single* microstate of given energy; it is *independent* of the internal structure of the system whether it is big, small, classical, quantum, fermion, boson, etc.
The quantity $\sum_i [e^{-\beta.\varepsilon i}]$ is the sum over all the states of the system or equivalently, the sum of the relative probabilities of each energy value, and known as **partition function** of the system, denoted by Z. By the knowledge of the partition function $Z(\beta)$ for all values of β, we can compute every thermodynamic parameter required to know about the system. That is, a system is fully characterized by its partition function. Since a system is also fully characterized by its energy density of states, therefore, knowledge of the partition function with that of the density of states are equivalent.
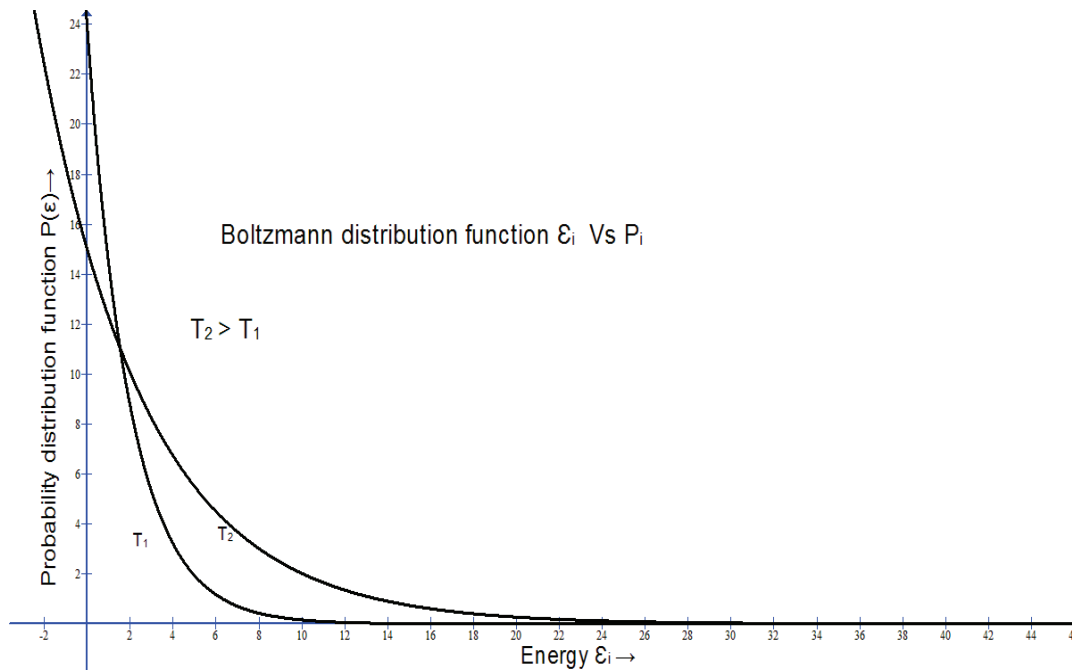
Fig (12.2)

Since P_i gives the probability of being a particle in ith energy state of energy ε_i, so the mean energy will be

$$\bar{E} = \sum_i P_i \varepsilon_i$$

$$= \frac{\sum_i \varepsilon_i e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}} \qquad (i)$$

Taking the numerator of eq. (i)

$$\sum_i \varepsilon_i e^{-\beta \varepsilon_i} = -\sum_i \frac{\partial}{\partial \beta} e^{-\beta \varepsilon_i}$$

$$= -\frac{\partial}{\partial \beta} \sum_i e^{-\beta \varepsilon_i} \qquad (ii)$$

We have $\quad \bar{E} = \sum_i P_i \varepsilon_i = \dfrac{-\dfrac{\partial}{\partial \beta} \sum_i e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}} \qquad (iii)$

Since $Z = \sum_i e^{-\beta\varepsilon_i}$ then the above equation becomes

$$\bar{E} = \frac{-\partial Z}{Z\partial\beta} \qquad\qquad\qquad \text{(iv)}$$

Or $$\bar{E} = \frac{-\partial\ln Z}{\partial\beta} \qquad\qquad\qquad \text{(v)}$$

It is clear from Eq. (v) that to calculate average energy we should have knowledge of partition Function Z.

Since $P_i = \dfrac{n_i}{N}$. where n_i is the number of particles in ε_i energy state and N is the total number of particles in the system.

Hence from eq. (12.7)

$$n_i = \frac{N}{Z} e^{-\beta\varepsilon_i} \qquad\qquad\qquad \text{(12.8)}$$

12.3 LAW OF EQUIPARTITION OF ENERGY

The mean energy of the system related to each degree of freedom is also known as law of equipartition of energy. A *degree of freedom* is essentially a variable whose value may change. In the case of a physical system, the positions of the particles that comprise the system are degrees of freedom. For a single particle in 3-dimensional space, there are three degrees of freedom because three coordinates are required to specify its location. Our main interest is in those variables that are related to the energy of the system, like the velocities gives the kinetic energy, the positions gives the potential energy, etc. In other words, we are supposed to associate some kinetic energy and some potential energy with each degree of freedom. So we treat the kinetic and potential energies as degrees of freedom. An isolated single point particle, which is free to move in three-dimensional space, has three mutually perpendicular components of its velocity, hence has three degrees of freedom which may have energy associated with them. We do not count particle's position coordinates as degrees of freedom because we assumed   it is not interacting with any other particle, On the other hand, a three-dimensional harmonic oscillator has potential energy as well as kinetic energy, so it has 6 degrees of freedom. The idea is that each degree of freedom, as it were, contains some energy. The total internal energy of a system is the sum of all the energies of all the degrees of freedom. Conversely, the amount of energy that may be transferred into a system is affected by how many degrees of freedom the system has.

Let us consider a monoatomic system having N particles. The total energy of the system will be function of f position coordinates $q_1, q_2, \ldots q_f$ and f momentum coordinates $p_1, p_1, \ldots p_f$.

Since, $$\varepsilon = \varepsilon(q_1, q_2, \ldots q_f, p_1, p_2, \ldots p_f) \qquad\qquad \text{(12.9)}$$

 Where number of degrees of freedom, $f = 3N$

The total energy of the system is $\varepsilon = \sum\limits_{i=1}^{3N} \dfrac{p_i^2}{2m}$ (12.10)

Equation (12.9) can be written as the sum of terms $\varepsilon_i = \varepsilon_i(p_i)$ and $\varepsilon' = \varepsilon'(q_1, q_2, \dots q_f, p_1, p_2, \dots p_{i-1}, p_{i+1} \cdot p_f)$ where $\varepsilon_i = \varepsilon_i(p_i)$ depends only on p_i so independent of rest of the system, and $\varepsilon' = \varepsilon'(q_1, q_2, \dots q_f, p_1, p_2, \dots p_{i-1}, p_{i+1} \cdot p_f)$ is not a function of p_i, hence represents rest of the system.

The mean energy $\varepsilon_i = \varepsilon_i(p_i)$

$$\varepsilon_i \left(\bar{p}_i \right)_i = \bar{\varepsilon}_i = \dfrac{\sum\limits_i \varepsilon_i e^{-\beta \varepsilon}}{\sum\limits_i e^{-\beta \varepsilon}}$$ (12.11)

Since, $\varepsilon = \varepsilon_i(p_i) + \varepsilon'(q_1, q_2, \dots q_f, p_1, p_2, \dots p_{i-1}, p_{i+1} \cdot p_f)$, we have

$$\bar{\varepsilon}_i = \dfrac{\int e^{-\beta(\varepsilon_i + \varepsilon')} \varepsilon_i dp_1, \dots dp_f}{\int e^{-\beta(\varepsilon_i + \varepsilon')} dp_1, \dots dp_f}$$ (vi)

This can be rearranged as

$$\bar{\varepsilon}_i = \dfrac{\int e^{-\beta \varepsilon_i} \varepsilon_i dp_i \int e^{-\beta \varepsilon'} dp_1, \dots dp_f}{\int e^{-\beta \varepsilon_i} dp_i \int e^{-\beta \varepsilon'} dp_1, \dots dp_f}$$

$$\bar{\varepsilon}_i = \dfrac{\int e^{-\beta \varepsilon_i} \varepsilon_i dp_i}{\int e^{-\beta \varepsilon_i} dp_i}$$

or, $\bar{\varepsilon}_i = -\dfrac{\partial}{\partial \beta} \ln \int e^{-\beta \frac{p_i^2}{2m_i}} dp_i$ (12.12)

Let $\varepsilon_i = \dfrac{p_i^2}{2m} = bp_i^2$ (vii)

$$\bar{\varepsilon}_i = -\dfrac{\partial}{\partial \beta} \ln \int e^{-\beta b p_i^2} dp_i$$ (12.13)

We are integrating eq. (12.13) in the limit $-\infty$ to ∞. Again let x= $p_i\sqrt{\beta}$ so dx = $\sqrt{\beta}.dp_i$, then eq. (12.13) becomes

$$\bar{\varepsilon}_i = -\frac{\partial}{\partial \beta} \ln(\frac{1}{\sqrt{\beta}} \int\limits_{-\infty}^{\infty} e^{-bx^2} dx) \tag{viii}$$

$$\bar{\varepsilon}_i = -\frac{\partial}{\partial \beta}(-\frac{1}{2}\ln \beta + \ln \int\limits_{-\infty}^{\infty} e^{-bx^2} dx) \tag{ix}$$

By using standard definite integral $\int e^{-\alpha x^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$ when limits are taken from 0 to ∞ . Since the second term of eq. (ix) does not contain β , hence its differentiation with respect to β will be zero.

Thus, we have

$$\bar{\varepsilon}_i = -\frac{\partial}{\partial \beta}(-\frac{1}{2}\ln \beta) \tag{12.14}$$

We get $\bar{\varepsilon}_i = \frac{1}{2\beta}$ (12.15)   As, $\beta = \frac{1}{kT}$

mean energy

$$\bar{\varepsilon}_i = \frac{kT}{2} \tag{12.16}$$

This is the law of equipartition of energy which state that "The average energy per degree of freedom, of a system at an equilibrium temperature T is $\bar{\varepsilon}_i = \frac{kT}{2}$, where k is Boltzmann constant". The modified statement of this theorem is "At thermal equilibrium T, the average energy per independent quadric term appearing in energy expression of a system is $\bar{\varepsilon}_i = \frac{kT}{2}$ ". So, each quadratic degree of freedom, at equilibrium, will have the same amount of energy. If all terms in the energy are quadratic then the mean energy is distributed equally over all degrees of freedom (hence the name "equipartition"). But, this equipartition of energy theorem is valid only in the classical limit and high temperature limits. That is, when the energy level spacing is small compared to kTi.e. $\Delta E < kT$.

12.4 STATISTICAL DEFINITION OF THERMODYNAMIC VARIABLES

In this section we will establish the relation between some thermodynamic variables like entropy, pressure, temperature etc. by the application of Boltzmann's canonical probability distribution function. We will see that statistical approach gives the same results as thermodynamical approach.

12.4.1 PRESSURE

If the system depends on the external parameter x, then $E_r = E_r(x)$ and from the definition of the generalized force X_r, we have

$$X_r = -\frac{\partial E_r}{\partial x} \tag{12.17}$$

So the average value of external parameter X is

$$\overline{X} = \frac{\sum_r e^{-\beta E_r}\left(-\dfrac{\partial E_r}{\partial x}\right)}{\sum_r e^{-\beta E_r}} \quad \ldots\ldots\ldots\ldots\ldots \tag{12.18}$$

Then

$$\overline{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x} \tag{12.19}$$

The average work done =average force x displacement, i.e.,

$$dW = \overline{X}\,dx$$

Where the external parameter is V, i.e. x = V

$$dW = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}dV \tag{12.20}$$

Therefore, the average pressure is

$$\overline{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} \tag{12.21}$$

12.4.2 ENTROPY

We can write thermodynamics functions in terms of partition function also. The partition function is given by $Z = e^{-\beta E_r(x)}$ so it can be represented in terms of β, x since $E_r = E_r(x)$

and   Z = Z (β , x), considering a small change

$$d\ln z = \frac{\partial \ln z}{dx}dx + \frac{\partial \ln Z}{\partial \beta}d\beta$$

or $d\ln Z = \beta dW - \overline{E}d\beta$ \tag{12.22}

The last term can be written in terms of the change in $\overline{E}$ rather than the change in β . Thus

$$d\ln Z = \beta dW - d\left(\overline{E}\beta\right) + \beta d\overline{E} \tag{12.23}$$

$$d\left(\ln Z + \beta \overline{E}\right) = \beta\left(dW + d\overline{E}\right) \equiv \beta dQ \tag{12.24}$$

Using mathematical form of second law of thermodynamics i.e. ,

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

we get, $S \equiv k\left(\ln Z + \beta \overline{E}\right)$

It is a relation between entropy S to partition function Z and the average energy $\overline{E}$

Now $\quad TS \equiv kT \ln Z + \overline{E}$

From Helmholtz free energy relation F= $\overline{E} - TS$, $\ln Z$ is very simply related to Helmholtz free energy F as F= $\overline{E} - TS$ = -kT lnZ

Thus, thermodynamic relations can also be obtained easily from the principles of statistical mechanics

12.5 MAXWELL-BOLTZMANN STATISTICS

Consider a closed system having N independent, identical and distinguishable particles, in other words a classical system. For an isolated system, the total numbers of particles and energy of the system must remain constant. Hence, we have two system constraints that can be expressed as

$$\sum_{i=1}^{k} n_i = N \tag{12.25}$$

$$\sum_{i=1}^{k} \epsilon_i n_i = E \tag{12.26}$$

Where k represents number of energy states from ε_1, ε_2... ε_i ...to ε_k. And n_i is the number of particles occupying the ith energy level with energy, εi . Expressing the total number of particles N, and the total energy E, in terms of summations over all possible energy levels inherently implies independent particles. We also note that the total system energy E, must, of course, be equivalent to the macroscopic internal energy U. Let the energy levels are again sub-divided into cells of equal volume. Let the ith energy level is divided into g_i cells. So g_i is the degeneracy of ith energy state. For classical particles there in no restriction on the number of particles in a cell.

Suppose in a particular distribution n_1 particles are distributed in 1st energy level, so the number of ways n_1 particles can be distributed in 1st energy level is $\dfrac{N!}{n_1!(N-n_1)!}$,since this energy level is further divided in g_1 cells, so number of ways n_i particles can be distributed in g_i cells is g_1 xg_2 xg_3 …..n_1 (times) = $(g_1)^{n1}$ .Hence the total number of ways n_1 particles can be distributed,from N particles, in 1st energy level is

$$C_{n1}^N \cdot (g_1)^{n1} = \frac{N!}{n_1!(N-n_1)!} \ (g_1)^{n1} \tag{12.27}$$

Let n_2 particles are distributed in 2nd energy state. The total number of ways n_2 particles can be distributed in 2nd energy level from the remaining $N-n_1$ particles

$$= \ C_{n2}^{N-n1} \cdot (g_2)^{n2} = \ \frac{(N-n_1)!}{n_2!(N-n_1-n_2)!} \cdot (g_2)^{n2} \tag{12.28}$$

and so on.

Fig. (12.3)

It is a composite event .So the total ways of possible distributions, i.e. the number of microstates corresponding to macrostate $(n_1, n_2 \ldots n_k)$

$$\Omega(n_1, n_2 \ldots n_k) = \ C_{n1}^N \cdot (g_1)^{n1} \cdot C_{n2}^{N-n1} \cdot (g_2)^{n2} \ldots \ldots C_{nk}^{N-n1-n2-\cdots-nk}(g_k)^{nk} \tag{12.29}$$

$$= \ \frac{N!}{n_1!(N-n_1)!} \ (g_1)^{n1} \cdot \frac{N-n_1!}{n_2!N-n_1-n_2!} \cdot (g_2)^{n2} \ldots \ldots \frac{N-n_1-n_2 \ldots n_{k-1}!}{n_k!N-n_1-n_2-\ldots n_k!} (g_k)^{nk}$$

$$= \frac{N!}{n_k!n_1!n_2! \ldots n_k!}(g_1)^{n1}(g_2)^{n2} \ldots (g_k)^{nk}$$

or, $$\Omega(n_1, n_2 \ldots n_k) = \ N! \cdot \prod_{i=1}^k \frac{(g_i)^{n_i}}{(n_i)} \tag{12.30}$$

Most probable macrostate: taking logarithm of eq. (12.30) and simplifying it

$$\ln\Omega(n_1, n_2 \ldots n_k) = \ \ln N! - \sum_i [\ln(g_i)^{ni} - \ln n_i! \ ]$$

$$= \ \ln N! \ - \ \sum_i [n_i \cdot \ln(g_i) - \ln n_i! \tag{12.31}$$

By applying Stirling's approximation, when N is a very large number

$$\ln N! \approx N \ln N - N$$

we have

$\ln\Omega(n_i) = N \ln N - N - \sum_i[n_i.\ln g_i - n_i.\ln n_i + n_i]$

Differentiating it with respect to n_i, we have

$d(\ln\Omega(n_i)) = \sum_i[\ln g_i - \ln n_i]dn_i$

$= \sum_i[\ln\left(\dfrac{g_i}{n_i}\right)]dn_i$

Since the condition for most probable macrostate is $d(\ln\Omega(n_i)) = 0$

Therefore,

$$\sum_i[\ln\left(\dfrac{g_i}{n_i}\right)]dn_i = 0 \qquad\qquad (12.32)$$

Since the system is closed (N and E is constant), using the constraints as stated earlier

$$\sum_{i=1}^{k} dn_i = dN = 0 \qquad\qquad (12.33)$$

$$\sum_{i=1}^{k} \in_i dn_i = dE = 0 \qquad\qquad (12.34)$$

To evaluate Eq. (12.32), applying Lagrange's method of undetermined multipliers, let Eq. (12.33) be multiplied by $-\alpha$ and Eq. (12.34) by $-\beta$, adding to Eq. (12.32). We have

$$\sum_i[\ln\left(\dfrac{g_i}{n_i}\right) - \alpha - \beta.\varepsilon i]dni = 0 \qquad\qquad (12.35)$$

From the above equation

$\ln\left(\dfrac{g_i}{n_i}\right) - \alpha - \beta.\varepsilon_i = 0$

which gives,

$$n_i = g_i. e^{-\alpha - \beta.\varepsilon i} \qquad\qquad (12.36)$$

This is Maxwell-Boltzmann distribution law, gives the count of particles in i^{th} energy state when system is in equilibrium state (most probable). Assuming $A = e^{-\alpha}$, Eq. (12.36) becomes

$$n_i = g_i A e^{-\beta.\varepsilon i} \qquad\qquad (12.37)$$

In this equation A and β are dependent parameters of thermodynamical state of the system. Eq. (12.37) shows that the number of particles in a cell decreases exponentially with the increase in energy ε_i corresponding to that cell. From the graph, fig (12.2), we conclude that low energy cells will contain more particles in comparison to high energy cells; the number of particles being maximum in zero-energy cell.it does not mean that the number of particles having zero energy is greater than any other energy because there are more cells corresponding to high energy. The quantity $e^{-\beta.\varepsilon i}$ in this expression is called Boltzmann factor and gi is priori probability for the energy zone ε_i.

12.5.1 EVALUATION OF THE CONSTANT A

By putting Eq. (12.37) into Eq.(12.25)

$$\sum_i(n_i) = \sum_i[g_i.A. e^{-\beta.\varepsilon i}] = N$$

or $N = A . \sum_i [g_i . e^{-\beta.\varepsilon i}]$ (13.38)

The quantity $\sum_i [g_i . e^{-\beta.\varepsilon i}]$ is the sum over all the states of the system or sum of relative probabilities of all the microstates, or equivalently, the sum of the relative probabilities of each energy value, and known as partition function of the system, denoted by Z. By the knowledge of   the partition function $Z(\beta)$ for all values of β, we can compute every thermodynamic parameter there as to know about the system. Thus, a system is fully characterized by its partition function. Since a system is also fully characterized by its energy density of states, therefore,

$$Z = \frac{N}{A} = \sum_i [g_i . e^{-\beta.\varepsilon i}] \; ,$$

From this we get,

$$A = \frac{N}{Z} = \frac{N}{\sum_i g_i e^{-\beta \varepsilon_i}}$$

Now

$$n_i = \frac{N.e^{-\beta.\varepsilon i}}{\sum_i [e^{-\beta.\varepsilon i}]}$$

The probability of finding a particle in energy state ε_i is, therefore

$$P(\varepsilon_i) = \frac{ni}{N} = \frac{e^{-\beta.\varepsilon i}}{\sum_i [e^{-\beta.\varepsilon i}]}$$ (12.39)

Hence $P(\varepsilon_i)$ is also known as probability distribution function.

12.5.2 EVALUATION OF THE CONSTANT β

Second law of thermodynamics states that the increase in internal energy of an isolated system at constant volume is related with entropy by
          $dE = dQ = TdS$
Let a small amount of heat dQ is given to the system due to which some particles of the system jump from lower to higher energy states. During this process, due to particle fluctuation let $dn_1, dn_2, \dots dn_k$ be the change in the number of particles in energy cell1, cell2, ……cellk, respectively.
So the change in the energy of the system
          $dE = \varepsilon_1 . dn_1 + \varepsilon_2 . dn_2 + \dots . \varepsilon_k . dn_k$
             $= \sum_i \varepsilon_i . dn_i$ (12.40)

By Boltzmann's entropy relation
          $S = k \ln\Omega$
or $dS = kd(\ln\Omega)$

Using the relation for expansion of $\ln \Omega(n_i)$ as given earlier and assuming all energy states are of equal size, i.e. $g_i = 1$,
          $dS = -k\sum_i \ln n_i dn_i$ (12.41)
From eq. (12.37)
          $dS = -k\sum_i \ln A . e^{-\beta.\varepsilon i} dn_i$

$$= -k\sum_i [ln\ A - \beta\varepsilon_i]dn_i$$

$$= -k\ lnA \sum_i dn_I + k\beta \sum_i \varepsilon_i dn_i \tag{12.41}$$

Applying eq. (12.40) and constraint (12.33)

$$dS = k\beta \sum_i \varepsilon_i dn_i = k\beta dE$$

So $\qquad dE = \dfrac{dS}{k\beta}$ \hfill (12.42)

Comparing eq. (12.42) with relation dE = TdS, we have

$$T = \frac{1}{k\beta} \quad \text{or,} \quad \beta = \frac{1}{kT} \tag{12.43}$$

Substituting these values in expression for n_i, we get

$$n_i = \frac{N.e^{-\frac{1}{kT}.\varepsilon i}}{\sum_i [e^{-\frac{1}{kT}.\varepsilon i}]} \tag{12.44}$$

It is another form of M-B distribution law.

12.5.3 M-B ENERGY DISTRIBUTION FUNCTION FOR IDEAL GAS

First we have to evaluate the term α for which let us take the relations

$$A = e^{-\alpha} \quad \text{and} \quad A = \frac{N}{Z}$$

We have

$$e^{-\alpha} = A = \frac{N}{Z} = \frac{N}{\sum_i g_i e^{-\varepsilon_i/kT}} \tag{12.45}$$

$$= \frac{N}{\int_0^\infty g(\varepsilon)e^{-\varepsilon/kT}d\varepsilon} \tag{12.46}$$

Since the variation of energy states can be assumed continuous, we can replace summation by integration, ε_i by ε and g_i by $g(\varepsilon)d\varepsilon$.

$$g(\varepsilon)d\varepsilon = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\varepsilon^{1/2}d\varepsilon \tag{12.47}$$

and $\qquad e^{-\alpha} = \dfrac{N}{\int_0^\infty 2\pi V\left(\dfrac{2m}{h^2}\right)^{3/2}\varepsilon^{1/2}e^{-\varepsilon/kT}d\varepsilon}$

or $\qquad e^{-\alpha} = \dfrac{N}{2\pi V\left(\dfrac{2m}{h^2}\right)^{3/2}\int_0^\infty \varepsilon^{1/2}e^{-\varepsilon/kT}d\varepsilon}$ \hfill (12.48)

Since $\qquad \int_0^\infty \varepsilon^{1/2}e^{-\varepsilon/kT}d\varepsilon = \left(kT\right)^{3/2}\dfrac{\sqrt{\pi}}{2}$ \hfill (12.49)

Therefore,
$$e^{-\alpha} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} \tag{12.50}$$

Taking logarithm both sides

$$\alpha = \ln\left\{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} \tag{12.51}$$

Since, the partition function $Z = \dfrac{N}{e^{-\alpha}}$, so

$$Z = \frac{V}{h^3}(2\pi mkT)^{3/2} \tag{12.52}$$

It is the expression of the partition function of an ideal monoatomic system.

The function which gives the number of particles per degenerate state is called energy distribution function

$$f(\varepsilon_i) = \frac{n_i}{g_i} = e^{-\alpha - \beta.\varepsilon i} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} e^{-\frac{1}{kT}.\varepsilon i} \tag{12.53}$$

In an ideal monoatomic system the number of particles having energy range between ε to
$\varepsilon + d\varepsilon$ is $n(\varepsilon)d\varepsilon = f(\varepsilon)g(\varepsilon)d\varepsilon$.
Substituting the value of $f(\varepsilon)$ and $g(\varepsilon)$, we get

$$n(\varepsilon)d\varepsilon = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} e^{-\varepsilon/kT} 2\pi V\left(\frac{2m}{h^2}\right)\varepsilon^{1/2}d\varepsilon$$

Rearranging it we get

$$n(\varepsilon)d\varepsilon = \frac{2N}{\sqrt{\pi}}\left(\frac{1}{kT}\right)^{3/2} \varepsilon^{1/2}.e^{-\varepsilon/kT}.d\varepsilon \tag{12.54}$$

It is clear from the relation that $n(\varepsilon)$ depends on $\varepsilon^{1/2}.e^{-\varepsilon/kT}$, so at $\varepsilon=0$, $n(\varepsilon)=0$. In low energy region the term $\varepsilon^{1/2}$ dominant over exponential term $e^{-\varepsilon/kT}$ and in high energy region $e^{-\varepsilon/kT}$
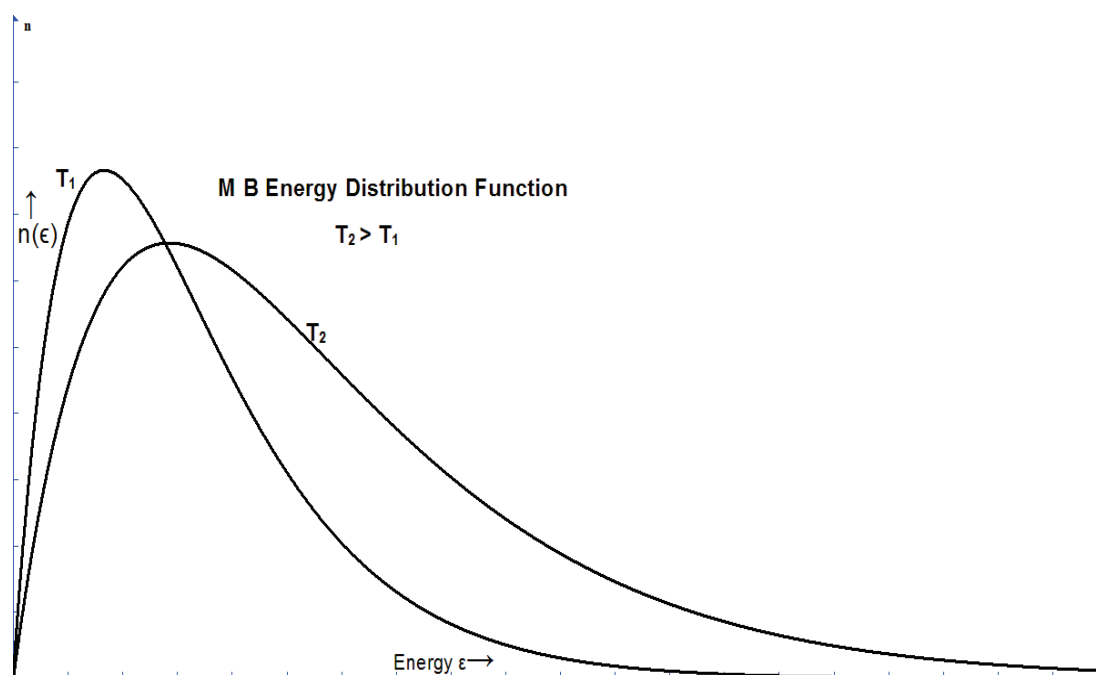
Fig (12.4)

dominates $\varepsilon^{1/2}$. So if we plot n(ε) Vs. ε at   different temperatures T_1 and T_2 Fig(12.4) , the energy distribution curve increases in low energy region ,then reaches maximum at particular value of ε ,then falls exponentially. From the graph we conclude that higher the temperature, peak of curve shifts toward high energy i.e. higher are the energy possessed by the most number of gas particles .but the area under all these curves should remain same.

12.6 CHEMICAL POTENTIAL

The chemical potential plays a role analogous to that of temperature and pressure. Understanding the nature of the chemical potential is more difficult. We know that if two systems are at different temperatures and are then placed in thermal contact, there will be a net transfer of energy from one system to the other until the temperatures of the two systems become equal.

If there is a movable wall between two systems at different pressures, then the wall will move so as to change the volume of each system to make the pressures equal. Similarly, if two systems are initially at different chemical potentials and are then allowed to exchange particles, there will be a net transfer of particles from the system at the higher chemical potential to the one at the lower chemical potential until the chemical potentials become equal.

The chemical potential μ of a particle in a system is the amount of change in the internal energy of that system due to adding one particle. In other words, the chemical potential of a particle in a system is the free energy cost of adding the particle. Thus the combined equation of the first and second laws of thermodynamics expressed by dU = TdS – PdV, must be modified in the case of changing numbers of particles, and the modified equation should contain an extra term μdN, so

dU = TdS –PdV + μdN   (12.55)

where N is the number of particles in the system.

It is clear from equation (12.55) that we can write an expression for μ as a partial differential of U with respect to N, keeping S and V constant, i.e.,

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} \tag{12.56}$$

But keeping S and V constant is practically difficult. So equation (12.55) combined with the thermodynamic potentials $F = U - TS$ and $G = U + pV - TS$ can be written as

$$dF = -PdV - SdT + \mu dN \tag{12.57}$$
$$dG = VdP - SdT + \mu dN \tag{12.58}$$

Differentiating eq. (12.57) and eq. (12.58) with respect to N, keeping V, T and P, T constant respectively, we get

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} \tag{12.59}$$

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P} \tag{12.60}$$

It is easy to keep p and T constant for a chemical systems.   So Eq. (12.60) is practically useful.

What drives a system to form a particular equilibrium state? As we know that it is the second law of thermodynamics which states that entropy always increases, the entropy of a system can be considered to be a function of U, V and N, so that $S = S(U, V, N)$.
Therefore, we can write

$$dS = \left(\frac{\partial S}{\partial U} \right) dU + \left(\frac{\partial S}{\partial V} \right) dV + \left(\frac{\partial S}{\partial N} \right) dN \tag{12.61}$$

From Eq. (12.55)

$$dS = \left(\frac{dU}{T} \right) + \left(\frac{PdV}{T} \right) - \left(\frac{\mu dN}{T} \right) \tag{12.62}$$

Comparing both equations, we get

$$\left(\frac{\partial S}{\partial U} \right)_{N,V} = \frac{1}{T} \ , \ \left(\frac{\partial S}{\partial V} \right)_{N,U} = \frac{P}{T} \ , \ \left(\frac{\partial S}{\partial N} \right)_{U,V} = -\frac{\mu}{T} \tag{12.63}$$

Since $S = k\ln\Omega(U,N)$, therefore

$$dS = k \left(\frac{\partial \ln \Omega}{\partial U} dU + \frac{\partial \ln \Omega}{\partial N} dN \right) \tag{12.64}$$

$$\therefore \left(\frac{\partial S}{\partial U} \right)_{V,N} = k \frac{\partial \ln \Omega}{\partial U} = \frac{1}{T} = k\beta \tag{12.65}$$

And

$$\left(\frac{\partial S}{\partial U} \right)_{V,U} = k \frac{\partial \ln \Omega}{\partial N} = -\frac{\mu}{T} = k\alpha \tag{12.66}$$

$$\therefore \alpha = -\frac{\mu}{kT} \tag{12.67}$$

Now consider two systems which are able to exchange heat or particles between them. If we write an expression for dS, then we can use the second law of thermodynamics in the form $dS \geq 0$ to determine the equilibrium state. We repeat this analysis for two cases as follows:

• The case of heat flow:

Consider two systems which are able to exchange heat with each other while remaining thermally isolated from their surroundings Fig. (12.5). If system 1 loses internal energy dU, system 2 must gain internal energy dU. Thus the change in entropy is

$$dS = \left(\frac{\partial S_1}{\partial U_1} \right)_{N,V} dU_1 + \left(\frac{\partial S_2}{\partial U_2} \right)_{N,V} dU_2$$

$$dS = \left(\frac{\partial S_1}{\partial U_1} \right)_{N,V} (-dU) + \left(\frac{\partial S_2}{\partial U_2} \right)_{N,V} dU$$

$$= \left(-\frac{1}{T_1} + \frac{1}{T_2} \right) dU \geq 0$$
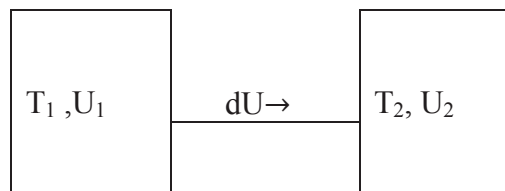
Fig (12.5)

So dU >0, i.e. energy flows from 1 to 2, when $T_1 > T_2$. As expected, equilibrium is found when $T_1 = T_2$, i.e. when the temperatures of the two systems are equal.

• The case of particle exchange

Now consider two systems which are able to exchange particles with each other, but remain isolated from their surroundings (see Fig. 12.6). If system 1 loses dN particles, system 2 must gain dN particles. Thus the change in entropy is

Fig (12.6)

$$dS = \left(\frac{\partial S_1}{\partial N_1}\right)_{U,V}(-dN_1) + \left(\frac{\partial S_2}{\partial N_2}\right)_{U,V} dN_2$$

$$dS = \left(\frac{\partial S_1}{\partial N_1}\right)_{U,V}(-dN) + \left(\frac{\partial S_2}{\partial N_2}\right)_{U,V} dN$$

$$dS = \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)dN \geq 0$$
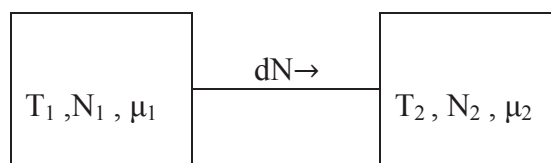
Assuming that $T_1 = T_2$, we find that $dN > 0$ (so that particles flow from 1 to 2) when $\mu_1 > \mu_2$. Similarly, if $\mu_1 < \mu_2$, then $dN < 0$. Hence equilibrium is found when $\mu_1 = \mu_2$, i.e. when the chemical potentials are the same for each system. This demonstrates that chemical potential plays a similar role in particle exchange as temperature does in heat exchange.

12.7 RELATIONS OF PARTITION FUNCTION WITH THERMODYNAMIC FUNCTIONS

All of the macroscopic thermodynamic quantities are obtainable from the microscopic statistics of the single particle energy states. For instance,

12.7.1 ENTROPY

The entropy of an isolated system related to thermodynamical probability is given by the relation

$$S = k \ln \Omega \tag{i}$$

where

$$\Omega(n_i) = N! . \prod_{i=1}^{k} \frac{(g_i)^{n_i}}{(n_i)} \tag{ii}$$

and $\quad \ln\Omega(n_i) = N.\ln N - N - \sum_i [n_i.\ln g_i - n_i.\ln n_i + n_i] \tag{iii}$

Substituting

$$n_i = g_i A . e^{-\beta.\varepsilon i} \quad \text{in Eq. (iii)}$$

$$\ln\Omega(n_i) = N \ln N - N - \sum_i [n_i.\ln g_i - n_i.\ln g_i.A. e^{-\beta.\varepsilon i} + n_i] \tag{iv}$$

Applying the constraints $\sum_{i=1}^{k} n_i = N$ and $\sum_{i=1}^{k} \epsilon_i n_i = E$ on Eq. (iv), and after rearranging we get

$$\ln\Omega(n_i) = N.\ln N - N.\ln A + \beta E$$

or $\quad \ln\Omega(n_i) = N.\ln \frac{N}{A} + \beta E \tag{12.68}$

Applying eq. (12.68) in eq. (i)

$$S = k \ln \Omega = kN.\ln \frac{N}{A} + \beta E \quad \text{, on putting } \beta = \frac{1}{kT} \text{ , and } Z = \frac{N}{A}$$

$$= kN.\ln Z + \frac{E}{T} \tag{12.69}$$

Since the total energy of an ideal gas

$$E = \frac{3}{2}NkT \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(v)}$$

So $\qquad\qquad S = kN \ln Z + \frac{3}{2}Nk \qquad\qquad\qquad\qquad\qquad\qquad$ (12.70)

It is entropy S in terms of partition function Z for an ideal gas.

12.7.2 HELMHOLTZ FREE ENERGY F

Since F = E –TS
Using eq. (12.70)
$\qquad\qquad\qquad F = - NkTlnZ \qquad\qquad\qquad\qquad\qquad\qquad$ (12.71)
It is Helmholtz free energy F in terms of partition function Z.

12.7.3 PRESSURE

From the laws of thermodynamics

$$TdS = dU + PdV$$

or, $\quad P = -\dfrac{dU}{dV} + T\dfrac{dS}{dV} = -\left(\dfrac{\partial}{\partial V}(E - TS)\right)_T = -\left(\dfrac{\partial}{\partial V}F\right)_T$

Using eq. (12.71)

$$P = NkT\left[\frac{\partial \ln Z}{\partial V}\right]_T \qquad\qquad\qquad\qquad\qquad\qquad (12.72)$$

12.7.4 INTERNAL ENERGY E

The mean energy $\bar{E}$ of entire system is

$$\bar{E} = \frac{E}{N} = \frac{\sum_i n_i \varepsilon_i}{\sum_i n_i} \qquad \text{Substituting the value of } n_i \text{ from eq. (iii)}$$

$$= \frac{\sum_i gi.A.e^{-\beta \varepsilon_i}\varepsilon_i}{\sum_i gi.A.e^{-\beta \varepsilon_i}}$$

$$\bar{E} = \frac{\sum_i g_i \varepsilon_i e^{-\beta \varepsilon_i}}{Z} \qquad\qquad\qquad\qquad\qquad\qquad (12.73)$$

Where $Z = \sum_i g_i e^{-\varepsilon_i/kT}$, Differentiating it with respect to T at constant volume V

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

or
$$\left(\frac{\partial Z}{\partial T}\right)_V = \frac{1}{kT^2} \sum_i g_i \varepsilon_i e^{-\varepsilon_i/kT}$$

Rearranging it, we get

$$kT^2 \left(\frac{\partial Z}{\partial T}\right)_V = \sum_i g_i \varepsilon_i e^{-\varepsilon_i/kT} \tag{12.74}$$

Now from Eq. (12.73)

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

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

Since total energy

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

or $E = NkT^2 \left(\dfrac{\partial \ln Z}{\partial T}\right)_V \tag{12.75}$

12.8 PARTITION FUNCTION OF IDEAL MONOATOMIC GAS

Taking a gas consisting of N identical monoatomic molecules of mass m enclosed in a contain- ner of volume V. The position vector of the ith molecule denoted by r_i , its momentum by p_i the total energy given by

$$E = \sum_{i=1}^{N} \frac{P_i^2}{2m} + U(r_1, r_2, \dots r_N) \tag{i}$$

We have to establish the partition function in phase space and calculate (i) the value for the mean pressure (ii) the mean energy (ii) the heat capacity and (iv) the entropy.
Let us divide phase-space occupied by gas into cells of equal volume h^f. Here, f = 3N is the number of degrees of freedom and h is a small constant with dimensions of angular momentum which limits the precision to which the positions and momenta of molecules are determined. Each cell in phase-space corresponds to a different state. The partition function is the sum of the Boltzmann factor $e^{-\beta.\varepsilon i}$ over all possiblestates, where Er is the energy of state r. Thus, since for non-interacting monoatomic ideal gas U=0 therefore, the partition function in phase space can be given as follows

$$Z = \int .. \int \exp\left\{-\beta\left[\frac{1}{2m}\left(p_1{}^2 + ... + p_N{}^2\right) + \right]\right\}\frac{d^3r_1...d^3r_N dp_1{}^3...dp^3{}_N}{h^{3N}}$$

(ii)

$$Z = \frac{1}{h^{3N}}\int .. \int \exp\left\{-\beta\left[\frac{1}{2m}\left(p_1{}^2 + ... + p_N{}^2\right)\right]\right\}dp_1{}^3...dp_N{}^3 \cdot \int ... \int d^3{}_1...d^3{}_N$$

(iii)

Since

$$\int .. \int d^3{}_1...d^3{}_N = V^N$$

(iv)

Substituting eq. (iv) in eq. (iii), we get

$$Z = \frac{V^N}{h^{3N}}\int .. \int \exp\left\{-\left[\frac{\beta p^2{}_1}{2m}\right]\right\}dp_1{}^3 ..... \exp\left\{-\left[\frac{\beta p^2{}_N}{2m}\right]\right\}dp_N{}^3$$

(12.76)

Where $p^2{}_1 = p_{1x}{}^2 + p_{1y}{}^2 + p_{1z}{}^2$, $dp_1{}^3 = dp_{1x}dp_{1y}dp_{1z}$ so for the ith particle .Note that the integral over the coordinates of a given molecule simply gives the volume of the container, V. Since the energy E is independent of the locations of the molecules in an ideal gas. There are N such integrals, so we obtain the factor V^N in the above expression. Note, also, that each of the integrals over the molecular momenta in Eq. (12.76) is identical. It follows that the partition function Z of the gas is made up of the product of such N identical factors: i.e.

$$Z = z^N$$

Where z is given by

$$z = \frac{V}{h^3}\int \exp\left\{-\beta\left[\frac{p^2}{2m}\right]\right\}dp$$

(12.77)

Since

$$\int_{-\infty}^{\infty} e^{\frac{-\beta p_{1x}{}^2}{2m}}dp_{1x} = \sqrt{\frac{2m\pi}{\beta}} \text{ ,using standard definite integral } \int_0^{\infty} e^{-\alpha x^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

Hence $$\int_{-\infty}^{\infty} e^{\frac{-\beta p^2}{2m}}dp = \left(\frac{2m\pi}{\beta}\right)^{3/2}$$

Eq. (12.77) becomes

$$z = \frac{V}{h^3}\left(\frac{2m\pi}{\beta}\right)^{3/2} = V\left(\frac{2m\pi}{\beta h^2}\right)^{3/2}$$

(12.78)

$$Z = z^N = \left[V \left(\frac{2m\pi}{\beta h^2} \right)^{3\!/\!2} \right]^N$$

(12.79)

It is the required partition function expression for perfect monoatomic gas.

Taking the logarithm of Eq. (12.79)

$$\ln Z = N[\ln V + \frac{3}{2}\ln\left(\frac{2m\pi}{h^2}\right) - \frac{3}{2}\ln\beta]$$

12.8.1 THE MEAN PRESSURE

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{NkT}{V}$$

(i)

or
$$\bar{p}V = NkT$$

(ii)

12.8.2 THE TOTAL MEAN ENERGY

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\bar{E} = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}NkT$$

(i)

Now, as

$$\bar{\varepsilon} = \frac{3}{2}kT$$

(ii)

So,
$$\bar{E} = N\bar{\varepsilon}$$

(iii)

12.8.3 ENTROPY

The entropy is given by the relation

$$S \equiv k\left(\ln Z + \beta\bar{E}\right), \text{ where } \quad \beta\bar{E} = \frac{3}{2}N$$

Since
$$\ln Z = N[\ln V + \frac{3}{2}\ln\left(\frac{2m\pi}{h^2}\right) - \frac{3}{2}\ln\beta]$$

(i)

Applying it in expression for S, we have

$$S = Nk[\ln V + \frac{3}{2}\ln\left(\frac{2m\pi}{h^2}\right) - \frac{3}{2}\ln\beta + \frac{3}{2}]$$

(ii)

Since $\beta = \frac{1}{kT}$, therefore,

$$S = Nk[\ln V + \frac{3}{2}\ln T + \frac{3}{2}\{\ln\left(\frac{2m\pi k}{h^2}\right) + 1\}]$$ (12.80)

whence, $$\delta = \frac{3}{2}\left\{\ln\left(\frac{2m\pi k}{h^2}\right) + 1\right\}$$
(iii)

$$S = Nk\left\{\ln V + \frac{3}{2}\ln T + \delta\right\}$$
(12.81)

But it is an incorrect relation for entropy, why? Let's read next article 12.9.

12.9 ENTROPY OF AN IDEAL GAS: GIBBS PARADOX

The Gibbs paradoxis a thought (imaginary) experiment, related to what happens when the two similar gases having identical particles with same particle density, are initially on the two sides of the partition are allowed to mix by removing the partition wall. Since removing or inserting the partition does not change the state of the system, there should be no entropy of mixing; i.e., the change in entropy of the system after removing or reinserting the partition should be zero. While, if we calculate the change in entropy, by using Eq. (12.81) of Section 12.8.3, we get such a change. Let's see the reason of the paradoxical condition and its resolution.
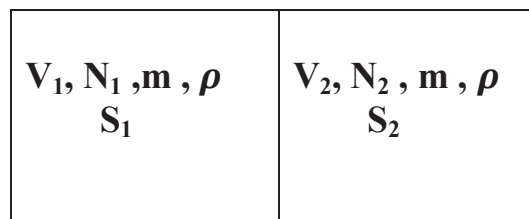

V₁, N₁ ,m , ρ **S₁**	**V₂, N₂ , m , ρ** **S₂**

Fig (12.7)

Consider an ideal gas consists of N particles in a container with volume V, assuming that the density of gas is the same throughout the system. A partition separates the container into two sections with volumes V_1 and V_2 respectively, and let there are N_1 particles in the volume V_1 and N_2 particles in the volume V_2 Fig. (12.7). Since we have assumed the density remains constant, hence

$V_1 + V_2 = V$ (i)

$N_1 + N_2 = N$ (ii)

And density $\rho = \dfrac{N_1}{V_1} = \dfrac{N_2}{V_2} = \dfrac{N}{V}$ (iii)

What should be the total entropy, if we remove the partition? The total entropy should not increase, because all the particles of the gas are identical, as the partition is removed, the two states cannot be differentiated due to the indistinguishability of the particles. Let use the expression for entropy we have derived above in section 12.7.1. That is

$$S = kN.\ln Z + \frac{3}{2} Nk \qquad \text{(iv)}$$

By substituting the partition function Z of a perfect monoatomic gas in Eq. (iv), we get same expression as (section 12.8.3)

$$S = Nk\left\{\ln V + \frac{3}{2}\ln T + \delta\right\} \qquad \text{(v)}$$

So the entropies S_1 and S_2, before the partition is removed, are

$$S_1 = N_1 k \ln V_1 + \frac{3}{2} N_1 k \ln T + \delta \qquad \text{(vi)}$$

and

$$S_2 = N_2 k \ln V_2 + \frac{3}{2} N_2 k \ln T + \delta \qquad \text{(vii)}$$

For a given system δ and T are constants, So S_1 can be written approximately

$$S_1 \quad N_1 k \ln V_1 + \frac{3}{2} N_1 k \qquad \text{(viii)}$$

Similarly

$$S_2 \quad N_2 k \ln V_2 + \frac{3}{2} N_2 k \qquad \text{(ix)}$$

And the total entropy before the partition removed is $S_i = S_1 + S_2$

$$S_i = N_1 k \ln V_1 + \frac{3}{2} N_1 k + N_2 k \ln V_2 + \frac{3}{2} N_2 k \qquad \text{(12.82)}$$

Now we removed the partition, the total entropy will be,

$$S_f = (N_1 + N_2)k \ln(V_1 + V_2) + \frac{3}{2}(N_1 + N_2)k \qquad \text{(12.83)}$$

Thus, the difference of entropies is $\Delta S = S_f - S_i$

$$\Delta S = (N_1 + N_2)k \ln(V_1 + V_2) - N_1 k \ln V_1 - N_2 k \ln V_2 \qquad \text{(12.84)}$$

Rearranging it

$$\Delta S \ = N_1 k \ln \frac{(V_1 + V_2)}{V_1} + N_2 k \ln \frac{(V_1 + V_2)}{V_2} \tag{x}$$

Since V = V$_1$+ V$_2$

$$\Delta S \ = N_1 k \ln \frac{(V)}{V_1} + N_2 k \ln \frac{(V)}{V_2} > 0 \tag{12.85}$$

This contradicts our predicted result that dS = 0. Therefore, the expression for entropy given by equation (12.81) is not quite correct.

12.9.1 RESOLUTION OF THE PARADOX

For the resolution of this paradox, note that while after removing and reinserting the partition, the macroscopic system does return to its initial configuration, the actual particles that occupy the two partitions are not the same. But as the particles are by assumption *identical*, these configurations cannot be distinguished. For example, in a two distinguishable particles system exchange of particles leads to two distinct (2! = 2) configurations Fig (12.8):
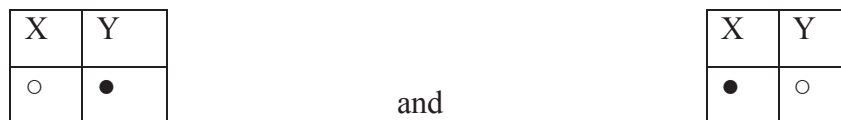
X	Y
○	●

and

X	Y
●	○

Fig. (12.8)

But a similar exchange has no effect on indistinguishable and identical particles, as in Fig. (12.9)

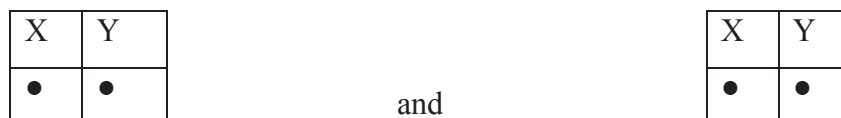| X	Y
●	●

and

X	Y
●	●

Fig (12.9)

Therefore, we have over-counted the phase space associated with N identical particles by the number of possible permutations. As there are N! permutations leading to indistinguishable microstates.

The correct expression for thermodynamical entropy S is, since statistical entropy $\sigma = Sk$.

$$S = Nk \ln \left[\frac{V}{N} \right] \left[\frac{2\pi mkT}{h^2} \right]^{3/2} + \frac{5}{2} Nk \tag{12.86}$$

This is known as the Sackur-Tetrode equation. This expression is obtained by introducing a correction term 1/$N!$, to make entropy S additive. Using this expression for the entropy, the difference now becomes

$$\Delta S = (N_1 + N_2)k\ln\frac{(V_1 + V_2)}{(N_1 + N_2)} - N_1 k\ln\frac{V_1}{N_1} - N_2 k\ln\frac{V_2}{N_2} \qquad \text{(xi)}$$

Using relations (i) and (ii), we get

$$\Delta S = N_1 k\ln\frac{V}{V_1} + N_2 k\ln\frac{V}{V_2} - N_1 k\ln\frac{N}{N_1} - N_2 k\ln\frac{N}{N_2} \qquad \text{(12.87)}$$

$$= N_1 k\ln\left(\frac{V}{N}\frac{N_1}{V_1}\right) + N_2 k\ln\left(\frac{V}{N}\frac{N_2}{V_2}\right) = 0 \qquad \text{(12.88)}$$

by applying the relation (iii), and since $\log_e(1) = 0$

Hence, the change in entropy, $\Delta S = 0$, as expected. Thus, the $1/N!$ term is necessary to resolve the paradox. This means that only a correct quantum mechanical treatment of the ideal gas gives the consistent entropy.

12.10 SUMMRY

1. Boltzmann canonical formula is $P_i = C e^{-\beta\varepsilon_i}$, in which $e^{-\beta\varepsilon_i}$ is known as Boltzmann factor.

2. Probability distribution function, $P_i = \dfrac{e^{-\beta\varepsilon_i}}{\sum\limits_i e^{-\beta\varepsilon_i}}$, the quantity $Z = \sum_i [e^{-\beta.\varepsilon_i}]$ is the

sum over all the states of the system and is known as partition function of the system,

3. Law of equipartition of energy says that at thermal equilibrium T, the average energy per independent quadratic term appearing in energy expression of a system is $\bar{\varepsilon_i} = \dfrac{kT}{2}$

4. Average pressure is $\bar{p} = \dfrac{1}{\beta}\dfrac{\partial \ln Z}{\partial V}$

5. Helmholtz free energy $F = -kT\ln Z$

6. The number of microstates corresponding to macrostate $(n_1, n_2 \ldots n_k)$ is

$$\Omega(n_1, n_2 \ldots n_k) = N! . \prod_{i=1}^{k}\frac{(g_i)^{n_i}}{(n_i)}$$

7. The probability of finding a particle in energy state ε_i is $P(\varepsilon_i) = \dfrac{ni}{N} = \dfrac{e^{-\beta.\varepsilon i}}{\Sigma_i[e^{-\beta.\varepsilon i}]}$, $P(\varepsilon_i)$ is also

known as probability distribution function.

8. The partition function of an ideal monoatomic system $Z = \dfrac{V}{h^3}(2\pi mkT)^{3/2}$

9. The energy distribution function of ideal gas is n(ε) = $\dfrac{2N}{\sqrt{\pi}}\left(\dfrac{1}{kT}\right)^{3/2}\varepsilon^{1/2}.e^{-\varepsilon/kT}$

10 .The chemical potential μ of a particle in a system is the amount of change in the internal energy of that system due to adding one particle

11. The chemical potential μ in terms of U, F, and G is:

$$\mu = \left(\dfrac{\partial U}{\partial N}\right)_{S,V}, \quad \mu = \left(\dfrac{\partial F}{\partial N}\right)_{T,V}, \quad \mu = \left(\dfrac{\partial G}{\partial N}\right)_{T,P}$$

12. Entropy S in terms of partition function Z for an ideal gas, S = kN.lnZ + $\dfrac{3}{2}Nk$

13. Pressure in terms of partition function Z,   P = $NkT\left[\dfrac{\partial \ln Z}{\partial V}\right]_{T}$

14. Total energy terms of partition function Z,   E = $NkT^2\left(\dfrac{\partial \ln Z}{\partial T}\right)_{V}$

15. Partition function of monoatomic ideal gas, $Z=\left[V\left(\dfrac{2m\pi}{\beta h^2}\right)^{3\!/\!2}\right]^{N}$

12. 11 REFERENCES AND SUGGESTED READINGS

1.   Reif, F. Fundamentals of Statistical and Thermal Physics. New York, NY: McGraw-Hill, June 1, 1965. ISBN: 0070518009.
2.   Hemne, P.S,Subrahmanyam N.,Brijlal .Heat and Thermodynamics. S Chand pub. New Delhi, 2014. ISBN 81-219-2813-3.
3.   Laud, B.B. Fundamentals of Statistical Mechanics. 2nd edition 2012. ISBN 978-81-224-3278-7
4.   Satya Prakash, Statistical Mechanics. edition 2014 (Kedar Nath Ram Nath pub, Delhi).
5.   Wannier, Gregory H., Statistical Physics, Dover Publications, 1987, ISBN 048665401X.
6.   Murugeshan, R., and K. Sivaprasath. Modern Physics .edition 2015 (S.Chand pub, New Delhi),ISBN: 978-81-219-2801-4.
7.   Beiser, A., Mahajan S., S.RaiChoudhary. Concepts of Modern Physics. 6th edition 2009 (Tata McGraw Hill, NewDelhi)ISBN: 978-0-07-015155-0.
8.   Huang, Kerson, Statistical Mechanics, 2nd ed., John Wiley & Sons, Inc., 1987, ISBN 0-471-81518-7.
9.   L. D. Landau and E. M. Lifshitz, Statistical Physics, 3rd Edition, Part I (Butterworth-Heinemann, Oxford, 1980) ISBN 0-7506-3372-7.
10.   Pathria, R. K., Statistical Mechanics, 2nd ed., Butterworth-Heinemann, Burlington, MA, 1996, ISBN 0 -7506-2469-8.
11.   Zemansky, M., and R. Dittman. Heat and thermodynamics: an intermediate textbook. 7th Ed. New York, NY: McGraw-Hill Companies, 1997. ISBN: 0070170592

12.   Carter, Ashley, Classical and Statistical Thermodynamics, Prentice-Hall, Upper
       Saddle River, NJ, 2001, ISBN 0-13-779208-5.

12.12 TERMINAL QUESTIONS

1. Derive Boltzmann canonical distribution law and partition function for a system in thermal
   contact with a large heat bath.

2. What is partition function? Explain its significance in statistical mechanics.

3. Using the relation $P_i = \dfrac{e^{-\beta\varepsilon_i}}{\sum\limits_i e^{-\beta\varepsilon_i}}$ and $Z = \sum\limits_i e^{-\beta\varepsilon_i}$, prove that the mean energy

$$\bar{E} = \frac{-\partial \ln Z}{\partial \beta}.$$

4. What are the degrees of freedom? Explain with example.

5. State and prove law of the equipartition of energy.

6. What is Maxwell - Boltzmann statistics? Derive Maxwell-Boltzmann distribution law and
its partition function.

7. Prove that, the partition function of an ideal monoatomic system is $Z = \dfrac{V}{h^3}(2\pi m k T)^{3/2}$

8. The energy distribution function of ideal gas is $n(\varepsilon) = \dfrac{2N}{\sqrt{\pi}}\left(\dfrac{1}{kT}\right)^{3/2} \varepsilon^{1/2}.e^{-\varepsilon/kT}$

   Plot $n(\varepsilon)$ Vs. ε at different temperature.

9. What is chemical potential? Explain its importance in large particle system. Establish the
   following relations :

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}, \quad \text{and} \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

Which relation is most applicable and why?

10. Show that the pressure of an ideal gas in terms of partition function Z is

$$P = NkT\left[\frac{\partial \ln Z}{\partial V}\right]_T$$

11. Prove that, the total energy is terms of partition function Z, $E = NkT^2\left(\dfrac{\partial \ln Z}{\partial T}\right)_V$

12. Prove that, the partition function of monoatomic ideal gas, $Z = \left[V\left(\dfrac{2m\pi}{\beta h^2}\right)^{3/2}\right]^N$

13. What is Gibbs paradox and how it was resolved?
14. Classical Maxwell–Boltzmann statistics considers particles to be distinguishable with no
limit on the number of particles in each energy state. A physical example is a solid composed

of localized atoms at distinguishable lattice sites. The thermodynamic probability in this case is given by

$$\Omega(n_i) = N! \prod_{i=1}^{k} \frac{(g_i)^{n_i}}{(n_i)}$$

Where n_i is the number of particles and g_i is the degeneracy of the ith energy level.
(a) Using the methods of statistical thermodynamics, show that the equilibrium particle distribution is

$n_i = g_i. \, e^{-\alpha - \beta.\varepsilon i}$

(b) Defining the molecular partition function $Z = \sum_i [\, g_i. \, e^{-\beta.\varepsilon i}\,]$,
show that $S \equiv k(\ln Z + \beta \overline{E})$, where $\quad \beta \overline{E} = \frac{3}{2} N$

(c) Using classical thermodynamics, verify that $\beta = 1/kT$. Hence, show that the Helmholtz free
energy for classical Maxwell–Boltzmann statistics becomes $F = -NkT \ln Z$.
(d) Beginning with the equation for Helmholtz free energy derived in part (c), show that the chemical potential and pressure for a classical gas can be expressed as

$\mu = -kT \ln Z \qquad and \qquad P = NkT \left[\dfrac{\partial \ln Z}{\partial V}\right]_T$

(e) Show that the probability of a particle being in the ith energy *state* is given by

$P(\varepsilon_i) = \dfrac{ni}{N} = \dfrac{e^{-\beta.\varepsilon i}}{Z}$. Where the partition function $Z = \sum_i [\, e^{-\beta.\varepsilon i/kT}\,]$

(f) Demonstrate that the entropy can be directly related to the probabilities Pi of the various energy states accessible to the system, i.e., $S = -kN\sum_i [\, Pi \ln Pi \,]$ .Discuss the significance of this result.

UNIT 13   QUANTUM STATISTICS

CONTENTS

13.1 OBJECTIVES

After going through this unit, you will be able to:
- Explain the principles of quantum statistical mechanics.
- Understand identical particles and indistinguishability.
- Understand the symmetry requirements in quantum statistics.
- Construction of symmetric and anti-symmetric wave functions.
- Differentiate pure and mixed states.
- Know density operator and its properties.
- Derive F - D and B - E distribution functions.
- Compare all the three statistical distribution laws.

13.2 INTRODUCTION TO QUANTUM STATISTICS

Classically, the complete description of a physical system is given by the phase space $\Gamma(q, p)$: and the Hamilton's equations of motion.

$$\dot{q}_i = \frac{\partial H}{\partial pi} \ , \quad \dot{p}_i = -\frac{\partial H}{\partial qi}$$

The solution of these equations of motion defines a trajectory in the phase space. One has to employ statistical methods in order to describe the macroscopic state out of the incomplete microscopic information. By saying "incomplete", we mean that we don't necessarily know the initial conditions for the trajectory of each particle of the system. That's why we treat the system statistically. In quantum mechanics the state of the system can be specified by calculating its wavefunction Ψ $(q_1, \cdot \cdot \cdot, q_f, s_1, \cdot \cdot \cdot, s_g, t)$ at time t, where f is the number of translational degrees of freedom, and g the number of internal (e.g., spin) degrees of freedom. For instance, if the system consists of N spin-one-half particles then there will be 3N translational degrees of freedom, and N spin degrees of freedom (i.e., the spin of each particle can either point up or down along the z-axis). In another way, if the system is in a stationary state (i.e., an eigen state of the Hamiltonian) then we can just specify (f+g) quantum numbers. Either way, the future time evolution of the wave-function is fully determined by Schrodinger equation.

$$\widehat{H}. \Psi(r, t) = i\hbar \frac{\partial \Psi(r,t)}{\partial t}$$

In practice, this approach does not work because the Hamiltonian of the real physical systems is not exactly known, so taken approximately. Typically, we are dealing with a system consisting of many weakly interacting particles. We usually know the Hamiltonian for completely non-interacting particles, but the component of the Hamiltonian associated with particle interactions is not very well known. We can define approximate stationary eigenstates using the Hamiltonian for non-interacting particles. The state of the system is then specified by the quantum numbers identifying these eigenstates. In the absence of particle interactions, if the system starts off in a stationary state then it stays in that state forever, so its quantum numbers never change. The interactions allow the system to make transitions

between different "stationary" states, causing its quantum numbers to change in time. We apply classical mechanics to deal with the translational degrees of freedom of the constituent particles, and quantum mechanics to deal with the non-translational degrees of freedom.

13.3 QUANTUM MECHANICAL SYSTEMS

Suppose we have a N particle quantum mechanical system. The quantum statistics is the statistical method of quantum mechanical study of an *N*-particle system. Suppose the corresponding *N*-particle classical system has Cartesian coordinates q_1 , q_2 , ….. ,q_f , and momenta p_1 , p_2 …… , p_f , where f = 3N for a monoatomic system and Hamiltonian H = T + V, T is kinetic and V is potential energy term.

$$H = \sum_{i=1}^{f} \frac{p^2_i}{2m} + V(q_1, q_2..q_f) \tag{13.1}$$

As we have discussed earlier for every quantum mechanical system, the state vector $\Psi(r,t) \equiv$ $|\Psi(t) >$ is a solution of $\widehat{H}.|\Psi(t) >= i\hbar\frac{\partial|\Psi(t)>}{\partial t}$ $\qquad$ (13.2)

Where r $\equiv q_1, q_2..q_f$.

And the operators $Q_1, Q_2...Q_f$, $P_1, P_2...P_f$ corresponding to the dynamical variables q_1 , q_2 , ….. ,q_f , and p_1 , p_2 …… , p_f follow these commutation relations

$$\left[Q_i, P_j \right] = i\hbar\delta_{ij} \tag{13.3}$$

$\delta_{ij} = 1$ for i = j, and $\delta_{ij} = 0$ for i $\neq$ j and

$$\left[Q_i, Q_j \right] = \left[P_i, P_j \right] = 0 \tag{13.4}$$

The state function of $|q_1 q_2...q_f >$ of N particle system can be written as a tensor product of the individual eigenstate $|q_1 >, |q_2 >,..., and |q_f >$

So $\qquad |q_1 q_2...q_f >= |q_1 >. |q_2 >... |q_f > \tag{13.5}$

The Schrodinger eq. (2) by multiplying the eigen bra of state vector $|q_1 q_2...q_f >$, which is is denoted as $< q_1, q_2,...q_f |$

gives $< q_1, q_2,...q_f | H | \psi(t) >= i\hbar \frac{\partial}{\partial t} < q_1, q_2,...q_f | \psi(t) > \tag{13.6}$

or $\left(-\sum_{i=1}^{f} \frac{\hbar^2}{2m}\nabla^2 + V(q_1, q_2..q_f) \right)\Psi(r,t) = i\hbar\frac{\partial\Psi(r,t)}{\partial t} \tag{13.7}$

where $\Psi(r,t) = < q_1, q_2,...q_f | \psi(t) >$

The expectation value of an operator A = A ($Q_1, Q_2 ... Q_f, P_1, P_2 ... P_f$) associated with one of the observables of the system can be calculated by the knowledge of state vector.

13.3.1 IDENTICAL PARTICLES AND INDISTINGUISHABILITY

Identical particles in a system are regarded as those particles which when interchanged in the system will not make any change in it. These particles can be distinguished from one another by their some intrinsic (inbuilt) properties like spin. The component of spin in the direction of some reference axis, of subatomic particles remains unchanged during elastic collisions. So we can easily identify same kind of particles by their different spin values in particular direction. If we consider a gas of atoms or molecules at temperature T, the thermal de-Broglie wavelength of a 'wave packet' associated with each gas particle (atom or molecule) of mass m is given by

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$$

Which is inversely dependent on temperature.

13.3.2 CLASSICAL DOMAIN

At high temperatures, λ_T is very small i.e. the size of 'wave packet' associated with each gas particle is much smaller than the inter-particle distance. So the constituents of the system are distinguishable, M-B statistics is well applicable on such systems. As the temperature is lowered, the particles associated thermal wavelength increases. When the wave packets of the particles begin to overlap with each other, it is impossible to identify individual particles in overlapping wavepacket. So the constituents of the system are called indistinguishable, M-B statistics not hold valid on such systems. So quantum effects must be taken into account. .For a system to be in the classical regime, λ_T should be much smaller than the average inter - particle distance r_0, if n being the density of the particles, i.e.,

$$r_0 \sim \left\{\frac{1}{n}\right\}^{1/3}$$

So condition for applicability of classical statistics is

$$r_0 \gg \lambda_T \quad \text{or} \quad \left(\frac{1}{n}\right)^{1/3} \gg \lambda_T$$

Hence $n\lambda_T^3 \ll 1$, this condition is fulfilled when particle density n is low and temperature T is high. Systems at low density have a tendency to act as ideal classical gases two distinct reasons: (i) Low density implies the particles are far apart, and so their Coulomb potential is low and so it behaves like a non-interacting or ideal gas.

(ii) Low density implies low fractional occupancy of quantum states, so the fermion or boson quantum interactions are negligible.

13.3.3 QUANTUM DOMAIN

The quantum effects become important when

$$n\lambda_T^3 \approx 1$$

When this condition is fulfilled, the wave functions of different particles begin to overlap, so becomes indistinguishable and the system has to be treated according to quantum statistics. The condition

$$n\lambda_T^3 = 1$$

or $\qquad n\left(\dfrac{h^2}{2\pi mk_B T}\right)^{3/2} = 1$ gives

$$n \propto T^{3/2}$$

that defines a line in the $T - n$ plane Fig. (13.1) and that sets the division between the classical and the quantum regions.
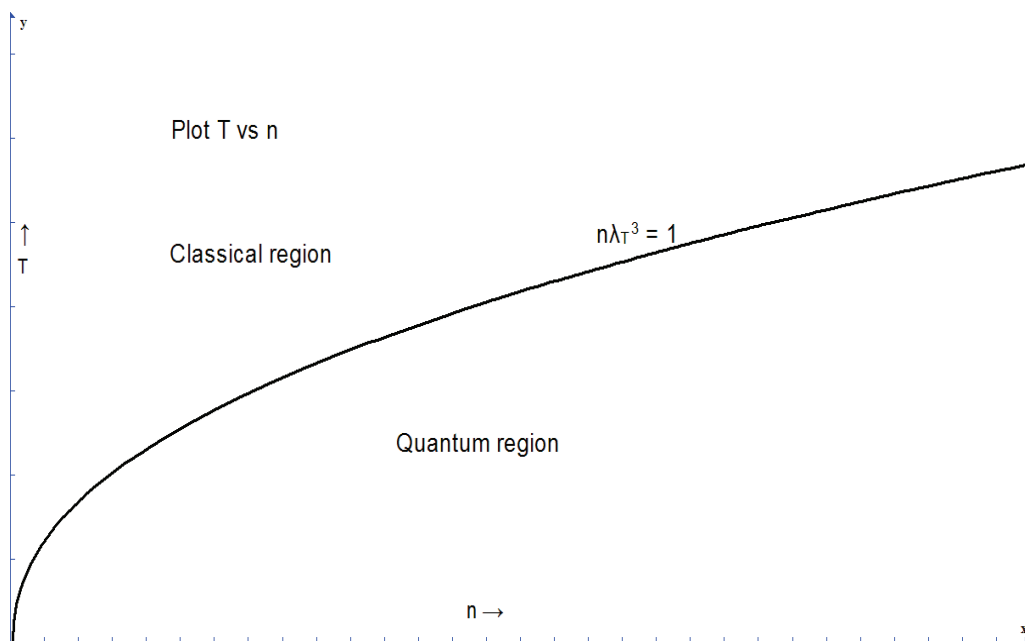

Fig (13.1)

We define the critical or quantum degeneracy temperature T_0, below this temperature systems become degenerate or of quantum nature.

$$T_0 = \left(\frac{h^2}{2\pi mk_B}\right) n^{2/3}$$

T_0 can have very different values, depending on the physical system under study. Examples of quantum degeneracy temperatures are:

System	Density n (per c.m.^{3})	Critical Temperature T_0 (K)
H_2 gas	$2x\ 10^{19}$	0.05
Liquid He	$2x\ 10^{22}$	2.0
Electrons in metal	10^{22}	10000

Table (13.1)

From above table it is clear that, a gas can be treated classically at room temperature, whereas free electrons in a metal are in the extreme quantum region. Liquid helium has a degeneracy temperature 2.17 K; it makes a transition from He I to He II below this temperature He II exhibits the properties of superfluid.

13.4 SYMMETRY REQUIRMENTS IN QUANTUM STATISTICS

Consider a gas consisting of N identical, non-interacting, structureless particles enclosed within a container of volume V. Let Qi denote collectively all the coordinates of the ith particle: i.e., the three Cartesian coordinates which determine its space position, as well as the spin coordinate which determines its internal state. Let s_i be the possible quantum states of the ith particle: i.e., each possible value of s_i corresponds to a specification of the three momentum components of the particle, as well as the direction of its spin orientation.
According to quantum mechanics, the entire or complete state of the system when the ith particle is in state s_i can be determined by the wave-function

$\Psi\ s_1,\cdots,s_N(Q1,Q2,\cdots,QN)$ (13.8)

In particular, the probability of an observation of the system finding the ith particle with coordinates in the range Qi to Qi + dQi, etc., is simply

$|\ \Psi\ s_1,\cdots,s_N\ (Q1,Q2,\cdots,QN)|^2\ dQ1\ dQ2\cdots dQN.$ (13.9)

One of the fundamental postulates of quantum mechanics is the essential indistinguishability of particles of the same kinds. i.e., a proton is just a proton we cannot label, it is proton number 1 and it is proton number 2, etc. No such restriction arises in classical mechanics. Therefore, in classical mechanics particles of the same species are regarded as being distinguishable, and can, therefore, be labeled.
Suppose that we interchange the ith and jth particles: i.e.

$Qi \leftrightarrow Qj$ (i)

$s_i \leftrightarrow s_j$ (ii)

If the particles are truly indistinguishable then nothing has changed: i.e., we have a particle in quantum state s_i and a particle in quantum state s_j both before and after the particles are exchanged. Thus, the probability of observing the system in a given state also cannot have changed: i.e.

$|\psi(Q_1 \cdots Qi \cdots Qj \cdots Q_N)|^2 = |\psi\ (Q_1 \cdots Qj \cdots Qi \cdots\ Q_N)|^2$ (13.10)

Note that it does not mean the wave-function is unaffected when the particles are exchanged, because it cannot be observed experimentally. Only the probability density $|\psi|^2$ is observable. Equation (5) implies that

$\psi(Q_1 \cdots Qi \cdots Qj \cdots Q_N) =\ A\psi\ (Q_1 \cdots Qj \cdots Qi \cdots Q_N)$ (13.11)

Where A is a complex constant of modulus unity: i.e., $|A|^2 = 1$.
Suppose that we interchange the ith and jth particles a second time.   Exchanging the ith and jth particles twice leaves the system completely unchanged: i.e., it is equivalent to doing

nothing to the system. Thus,the wave-functions before and after this process must be identical. It follows from Eq. (13.11) that

$$A^2 = 1 \qquad (13.12)$$

Thus possible solutions to the above equation are $A = \pm 1$.

The conclusion from the above discussionis that the wave-function is either completely symmetric under the interchange of particles, or it is completely anti-symmetric.

In other words, either

$$\Psi (Q_1 \cdots Q_i \cdots Q_j \cdots Q_N) = +\psi (Q_1 \cdots Q_j \cdots Q_i \cdots Q_N) \qquad (13.13)$$

or

$$\Psi (Q_1 \cdots Q_i \cdots Q_j \cdots Q_N) = -\psi (Q_1 \cdots Q_j \cdots Q_i \cdots Q_N). \qquad (13.14)$$

In 1940 physicist W Pauli, by using the idea of relativistic invariance, established that the wave-function associated with a collection of identical integer-spin (i.e., spin 0, 1, 2, etc.) particles satisfies eq. (13.13), whereas the wave-function associated with a collection of identical half-integer-spin (i.e., spin ½, 3/2, 5/2, etc.) particles satisfies Eq. (13.14). The former type of particles is known as Bosons [after the Indian physicist S.N. Bose, who first put forward eq. (13.13) on empirical grounds]. The latter type of particles is called Fermions (after the Italian physicists E Fermi, who first studied the properties of Fermion gases). Common examples of bosons are photons, α particle and He^4 atoms. Common examples of Fermions are protons, neutrons, and electrons.

Consider a gas made up of identical bosons. Equation (13.13) implies that the interchange of any two particles does not give a new state of the system. Bosons must, therefore, be considered as indistinguishable when counting the different possible states of the gas. Note that eq. (13.13) imposes no restriction on how many particles can occupy a given single-particle quantum states. Consider a gas made up of identical fermions. Equation (13.14) implies that the interchange of any two particles does not lead to a new physical state of the system (since $| \psi |^2$ is invariant). Hence, Fermions must also be considered indistinguishable when counting the different possible states of the gas. Consider the special case where particles i and j lie in the same quantum state. In this case, the act of exchanging the two particles is equivalent to leaving the system unchanged, so

$$\Psi (Q_1 \cdots Q_i \cdots Q_j \cdots Q_N) = \psi (Q_1 \cdots Q_j \cdots Q_i \cdots Q_N). \qquad (13.15)$$

However, eq. (13.14) is also applicable, since the two particles are fermions. The only way in which eqs.(13.14) and (13.15) can be reconciled is if

$$\psi = 0 \qquad (13.16)$$

wherever particles i and j lie in the same quantum state. This is another way of saying that it is impossible for any two particles in a gas of Fermions to lie in the same single-particle quantum state. This concept is known as the Pauli exclusion principle.

How to differentiate it with classical system, a gas made up of identical classical particles. In this case, the particles must be considered distinguishable when counting the different possible states of the gas. Furthermore, there are no constraints on how many particles can occupy a given quantum state.

According to the above discussion, there are three different sets of rules which can be used to compute the states of a gas made up of identical particles. For a boson gas, the particles must be treated as being indistinguishable, and there is no limit to how many particles can occupy a given quantum state. This set of rules is called Bose-Einstein statistics. For a Fermion gas, the particles must be treated as being indistinguishable, and there can never be more than one particle in any given quantum state. This set of rules is called Fermi-Dirac statistics. Finally, for a classical gas, the particles must be treated as being distinguishable, and there is no limit to how many particles can occupy a given quantum state. This set of rules is called Maxwell-Boltzmann statistics.

13.4.1 SYMMERIC AND ANTISYMMERRIC WAVE FUNCTIONS

Let us consider a system of two particles, 1 and 2. One of them is in state a and the other in state b. If the particles are distinguishable, then the pair in states a and b and the pair in state b and a are also distinguishable. The two possibilities are:

$$\psi_I = \psi_a(1). \psi_b(2) \tag{13.17}$$

And $$\psi_{II} = \psi_a(2). \psi_b(1) \tag{13.18}$$

Both of these state functions are equally possible for distinguishable particles. Therefore, the linear combination of ψ_I and ψ_{II} is also a valid wave function for the system. We can construct two kinds of linear combination.A symmetric wave function that remains unaffected by the exchange of two particles between the two states can be written as follows:

$$\psi_B = (1/\sqrt{2})[\psi_a(1). \psi_b(2) + \psi_a(2). \psi_b(1)] \tag{13.19}$$

The factor $(1/\sqrt{2})$ has been used for normalization so that the total probability of finding the particle over the entire volume is Unity.**As we know that a symmetric** wave function represents the Bosons having integral angular momentum $= n\hbar$ where n=0,1,2,3…. . So it is a wave function for the Bosons. The other one an anti-symmetric wave function that changes sign on interchange of state. can be written as follows:

$$\psi_F = (1/\sqrt{2})[\psi_a(1). \psi_b(2) - \psi_a(2). \psi_b(1)] \tag{13.20}$$

This is the wave function describing Fermions having spin angular momentum $= (1/2 + n) \hbar$ where n=0, 1, 2, 3…which obeys Pauli Exclusion Principle.

Now what is the possibility that both particles are in the same quantum state (a).For distinguishable particles,this new state of overlap of wave function is

$$\psi_M = \psi_a(2). \psi_a(1) \tag{13.21}$$

For bosons the wave function is

$$\psi_B = (1/\sqrt{2})[\psi_a(1). \psi_a(2) + \psi_a(2). \psi_a(1)] \tag{13.22}$$

$$=(1/\sqrt{2})[2\psi_a(1). \psi_a(2)] = \sqrt{2} \psi_a(1). \psi_a(2) \tag{13.23}$$

Probability density of Bosons in same state:

$$\psi_B. \psi_B^* = \sqrt{2} \psi_a(1). \psi_a(2). \sqrt{2} \psi_a^*(1).\psi_a^*(2) \tag{13.24}$$

$$\psi_B. \psi_B^* = 2. \psi_M. \psi_M^* \tag{13.25}$$

Thus the probability that two bosons are in the same state is twice the probability that two distinguishable particles will be in the same state.

For Fermions, the wave function, when both particles are in the same quantum state (a), will be

$$\psi_{F} = (1/\sqrt{2})[\psi_a(1) \cdot \psi_a(2) - \psi_a(2) \cdot \psi_a(1)] = 0 \qquad (13.26)$$

Therefore fermions can never be in the same quantum state because fermions always follow Pauli's Exclusion Principle. We can generalize these results for many particle systems.
1. In a bosonic system, the presence of a particle in a particular energy state increases the probability of presence of other particles in the same state.
2. In a system of fermions, the presence of a particle in a particular energy state prevents the probability of presence of any other particles in that state.

13.5 DENSITY OPERATOR

In quantum systems due to the incomplete information of the microscopic data of the system it is almost impossible to predict exact characteristics of the system. In some special cases when we have complete knowledge of the microscopic data about the system, we can establish exact state vector of that system. Such state is called pure state. But we still cannot calculate the result of an experimental measurement since any measurement will also disturbs the system. This lack of information manifests itself in the statistical interpretation of the wave function and in the uncertainty relation between qi and pi, which cannot be accurately measured at the same time. It is similar condition to that which occurs in classical statistics, where without the knowledge of initial conditions of all particles of a system we cannot calculate an exact mechanical description of its behavior, the analogy is also inadequate.
To describe the state of a macroscopic body by quantum mechanical wave function is impractical, because the available data related to the state of such a body are not sufficient to establish its complete wave function and the concepts of phase space and phase trajectory have no meaning for quantum systems.
For quantum mechanical systems,the states of a system are classified as pure state and mixed states.

13.5.1 PURE STATE

If we have a complete set of commuting observables of a system. We can make a state vector |Ψ(t) >through measuring these observables .It is a pure state vector in the Hilbert space.
Now, if A is an operator associated with one of the observables in this complete set, with state vector | ψ>in Hilbert space. We will write it in terms of the eigenstates of the Hamiltonian of the system H, the so-called energy eigenstates, given by H| ψ_n> = E_n| ψ_n>. By introducing an orthonormal set of vectors | ϕ_n > such that< ϕ_n | ϕ_n >= $\delta_{nm} \phi_n \phi_n$ and expanding the state vector, the state of the system can now be written as

$$|\psi> = \sum_n c_n |\phi_n> \quad , \quad \text{where} \quad c_n = <\phi_n|\psi> \qquad (13.27)$$

$$\hat{A}|\phi_n> = a_n|\phi_n> \qquad (13.28)$$

With the condition $< \phi_n|\phi_n >= \delta_{nm}$ (13.29)
The expectation value of $\hat{A}$, $<\hat{A}>$, can be as the averaged result of
1 – Repeated measurements of A done on the same system or

2 - Measurements of A done simultaneously on similar copies of the system.

$$<\hat{A}> = <\Psi|\hat{A}|\Psi> = \sum_n < \Psi|\hat{B}|\phi_n > < \phi_n|\Psi > \qquad (13.30)$$

$$<\hat{A}> = \sum_n a_n |c_n|^2 \qquad (13.31)$$

13.5.2 MIXED STATE

The quantum-mechanical description based on an incomplete set of data concerning the system can be reformulated in term of density matrix or density operator, instead of quantum states. By the knowledge of density matrix we are capable to calculate the mean value or the probabilities of various values of such quantities describing the system. The incompleteness of the description lies in the fact that the results of various kinds of measurement which can be predicted with a certain probability from knowledge of the density matrix might be predictable with greater or even complete certainty from a complete set of data for the system, from which its wave function could be derived.

A quantum system in a state $|\psi>$ can be described by a density operator given by

$$\hat{\rho} = |\psi><\psi| \qquad (13.32)$$

provided that vector $|\psi>$is normalized. The expectation value of an observable can then be written as

$$<A> = \mathrm{Tr}\,[\_\hat{\rho}\hat{A}\,] \qquad (13.33)$$

If one uses the energy eigenstates of the system to take the trace over states of the system, one gets

$$<A> = \sum_{n,m}' < \phi_n|\hat{\rho}|\phi_m > < \phi_m|\hat{A}|\phi_n >$$
$$= \sum \rho_{nm} < \phi_n|\hat{A}|\phi_m > \qquad (13.34)$$

Where ρ_{nm} is the called the density matrix. For a pure state, described by a single wave function, this density matrix is always non-diagonal; it can be diagonal only when the system is in one of its energy eigenstates.

The density matrix may be non-diagonal if another set of states, different from the energy eigenstates, are used to take the trace (trace is invariant under change of representation).

The average value of an observable can now be written as

$$<A> = \sum \rho_{nn} < \phi_n|\hat{A}|\phi_n > \qquad (13.35)$$

The above relation represents an average of the observable A over an ensemble which consists of similar copies of the system, in different quantum states $|\emptyset_1>$, $|\emptyset_2>$ $|\emptyset_3>$ etc. The microstate (quantum state) $|\emptyset_k>$occurs with a probability ρ_{kk}. Here ρ_{nm} is an example of a mixed-state density matrix. Such a density matrix cannot represent a single system in a particular quantum state. It represents a mixture, or an ensemble of systems in different microstates, occurring with different probability.

13.5.3 PROPERTIES OF DENSITY MATRIX

1.The density matrix must be Hermitian i.e.,

$$\rho_{nm} = \rho_{nm}{}^{*} \tag{i}$$

so that its eigenvectors form a complete orthonormal set of vectors that span the Hilbert space.

2. If we have a unit operator I having expectation value 1it required that

$$Tr(\rho I) = Tr\{\rho. 1\} = \sum \rho_{nn} = 1 \tag{ii}$$

3. Since every operator has non-negative mean value, so ρ must be always positive.

$$\rho_{nm} \geq 0 \tag{iii}$$

4. Under the unitary transformation ρ_{nm} can be reduced to diagonal

$$\rho_{j}\delta_{jj'} = \sum_{n,m} U_{jn}\rho_{nm} U^{-1}{}_{mj'} \tag{iv}$$

By conditions

$$\sum'_{j} \rho^{2}{}_{j} \leq (\sum \rho_{j})^{2} = (Tr\rho)^{2} = 1 \tag{v}$$

So we have $Tr(\rho^{2}) \leq 1$ $\tag{vi}$

13.6 Quantum Statistical Distribution Functions

When the system is at low density and temperature is high, a system has a large number of accessible energy states such as translational, rotational, electronic etc. The number of available states is much more than the number of particles. At high temperatures, a large number of states become accessible, especially the translational states. In such a case, the possibility of multiple occupancy of a state will be greatly reduced. *Thus the occupied energy levels are mostly non-degenerate*. Thus, the occupation due to quantum statistics is not important and classical Boltzmann statistics works well. We have already discussed that Maxwell-Boltzmann statistics holds good in the thermodynamic limit, $n\lambda_{T}^{3} \ll 1$ (where n is

the number density, λ_{T} is the thermal de-Broglie wavelength, $\lambda_{T} = \left(\dfrac{h^{2}}{2\pi m k_{B} T}\right)^{\frac{1}{2}}$) because

$m \gg 1$, $T \gg 1$ and $n \ll 1$. This is the classical regime where indistinguishability can be exactly accounted for. But as we go on to *low temperatures and high densities* multiple occupancy (degeneracy) of states increases. Under the conditions, when $n\lambda^{3}{}_{T} \approx 1$, the indistinguishability of particles becomes much more significant. This is where the quantum nature of system dominates over classical nature. It is the quantum regime studies under quantum statistics. In the previous parts of this course, we derived the Boltzmann distribution, which described how the number of distinguishable particles in different energy states varied with the energy of those states, at different temperatures:

$$n_{i} = g_{i}. \, e^{-\alpha - \varepsilon i/kT} \tag{i}$$

However, in systems consisting of collections of identical fermions or identical bosons, the wave function of the system has to be either anti-symmetric (for fermions) or symmetric (for

bosons) under interchange of any two particles. With the allowed wave functions, it is no longer possible to identify a particular particle with a particular energy state. Instead, all the particles are shared between the occupied states. The particles are said to be indistinguishable.

Consider a closed system having N independent, identical and indistinguishable particles. For an isolated system, the total number of particles and energy of the system must remain constant. Hence, we have two system constraints that can be expressed as

$$\sum_i n_i = N \qquad \qquad \text{(ii)}$$

$$\sum_i n_i \varepsilon_i = E \qquad \qquad \text{(iii)}$$

These constraints become very important when there is degenerate/multiple occupancy of energy   levels.   .

To understand the effects of these statistics on the distribution of energy levels, we first group the energy levels with energy within a small interval together and assign a degeneracy factor to each group according to the number of energy levels in each group. Let us denote the energy and degeneracy of ith group by ε_i and g_i, respectively Fig. (13.2).

$n_k,\ \varepsilon_k$	$g_{k=2}$	
$n_i,\ \varepsilon_i$	$g_{i=3}$	
$n_1,\ \varepsilon_1$	$g_{1=4}$	quantized cell of phase volume $\sim h^3$

Fig (13.2)

13.6.1 FERMI - DIRAC DISTRIBUTION LAW

The particles must be treated as being indistinguishable, and there can never be more than one particle in any given quantum state. Fermions obey this condition on the occupation of a state, a state can have 1 particle or 0 particle in it, but never two or more. So, n_i is always less than or equal to g_i. This is because they obey the Pauli exclusion principle.

$n_i = 1$ or 0

Let n_i be the number of particles occupying an energy level ε_i in a particular configuration.

If g_i is the degeneracy of ε_i , (such that the degeneracy of that energy is $g_i \geq n_i$ the number of particles occupying that energy level), then the number of possible arrangements amongst the degenerate levels of ε_i is

$$\Omega_i = \frac{g_i!}{n_i!(g_i - n_i)!} \tag{i}$$

The total number of arrangements possible for a particular configuration for F-D distribution. This is over all the energy levels of a particular configuration given as

$$\Omega\{n_1, n_2, n_3, ..n_k\} = \prod_i \Omega_i$$

or

$$\ln\Omega\{n_1, n_2, n_3, ..n_k\} = \ln\prod_{i-1}^{k}\Omega i = \sum_i \ln\Omega_i \tag{ii}$$

So

$$d\ln\Omega = \sum_i d\ln\Omega_1$$

Now since

$$\Omega_i = \frac{g_i!}{n_i!(g_i - n_i)!}$$

$$\ln\Omega_i = \ln g_i! - \ln n_i! - \ln(g_i - n_i)!$$

Applying Stirling's approximation

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

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

$$= g_i \ln\left(\frac{g_i}{g_i - n_i}\right) + n_i\left(\frac{g_i - n_i}{n_i}\right)$$

$$= -g_i \ln\left(\frac{g_i - n_i}{g_i}\right) + n_i\left(\frac{g_i - n_i}{n_i}\right)$$

$$= -g_i \ln\left(1 - \frac{n_i}{g_i}\right) + n_i \ln\left(\frac{g_i}{n_i} - 1\right)$$

$$\ln \Omega_i = n_i \ln \left(\frac{g_i}{n_i} - 1 \right) - g_i \ln \left(1 - \frac{n_i}{g_i} \right)$$

$$d \ln \Omega_i = \left[\ln \left(\frac{g_i}{n_i} - 1 \right) + n_i \frac{\left(\frac{-g_i}{n_i^2} \right)}{\left(\frac{g_i}{n_i} - 1 \right)} - g_i \left(\frac{\frac{-1}{g_i}}{1 - \frac{n_i}{g_i}} \right) \right] dn_i$$

$$= \left[\ln \left(\frac{g_i}{n_i} - 1 \right) - \frac{g_i}{n_i} \left(\frac{1}{\frac{g_i}{n_i} - 1} \right) + \left(\frac{1}{1 - \frac{n_i}{g_i}} \right) \right] dn_i$$

$$d \ln \Omega_i = \left[\ln \left(\frac{g_i}{n_i} - 1 \right) \right] dn_i \tag{iii}$$

Since

$$\sum_i n_i = N \text{ and } \sum_i \varepsilon_i n_i = E \tag{iv}$$

Hence, $\sum_i dn_i = 0$ and $\sum_i \varepsilon_i dn_i = 0$ (v)

To solve it completely we shall apply the Lagrange's method of undetermined multipliers and applying the condition for maximum probability $d \ln \Omega = \sum_i d \ln \Omega_1 = 0$.

$$d \ln \Omega - \left[\alpha \sum_i dn_i - \beta \sum_i \varepsilon_i dn_i \right] = 0 \tag{13.36}$$

Thus,

$$\sum_i \left[\ln \left(\frac{g_i}{n_i} - 1 \right) - \alpha - \beta \varepsilon_i \right] dn_i = 0$$

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

$$n_i = \frac{g_i}{\left[e^{\alpha + \beta \varepsilon_i} + 1 \right]} \tag{13.37}$$

This is the equation for most probable distribution of particles among different quantized energy levels for fermions . in 1926 Enrico Fermi and Paul Dirac idependently showed that all half spin particles like electrons , protons and neutrons etc.   follow new statistical distrbution function , equation, hence named as Fermi-Dirac distribution law .

As we know that $\alpha = -\dfrac{\mu}{kT}$ where μ is the chemical potential. Two systems at thermodynamic equilibrium have the same temperature T. The systems at chemical (particle number) equilibrium have the same μ.
Note that:
1) The positive sign in Fermi-Dirac distribution implies that $n_i \leq 1$ which is Pauli
Exclusion principle (which states that no two fermions can share the same quantum state).
2) For open systems, $\sum_{i=1}^{k} n_i = N$ is not a constraint, μ is zero, but isolated systems have fixed number of particles, N, so μ has a value.

13.6.2 F-D ENERGY DISTRIBUTION FUNCTION

The energy distribution function f (ε_i)is the average number of fermions per quantum state in the energy level ε_i . Since the degenracy of ith state is g_i and number of particles in that state is n_i , hence by the definition , energy distribution function will be

$$f(\varepsilon_i) = \frac{n_i}{g_i} = \frac{1}{\left(e^{\alpha + \beta \varepsilon_i} + 1\right)} \qquad \text{since, } \beta = \frac{1}{kT}$$

$$f(\varepsilon_i) = \frac{n_i}{g_i} = \frac{1}{\left(e^{\alpha + \varepsilon_i \cdot 1/kT} + 1\right)} \tag{13.38}$$

The variation of energy distribution function at different temperatures ($T_3 > T_2 > T_1$) shown in fig.(13.3) gives the probability of occupation of a single state so also called occupational probability. In the case when energy levels are very close ,then the descrete distribution of energy levels may be considerd as continous, and then the number of particles having energy range from ε to (ε+ dε) is given by
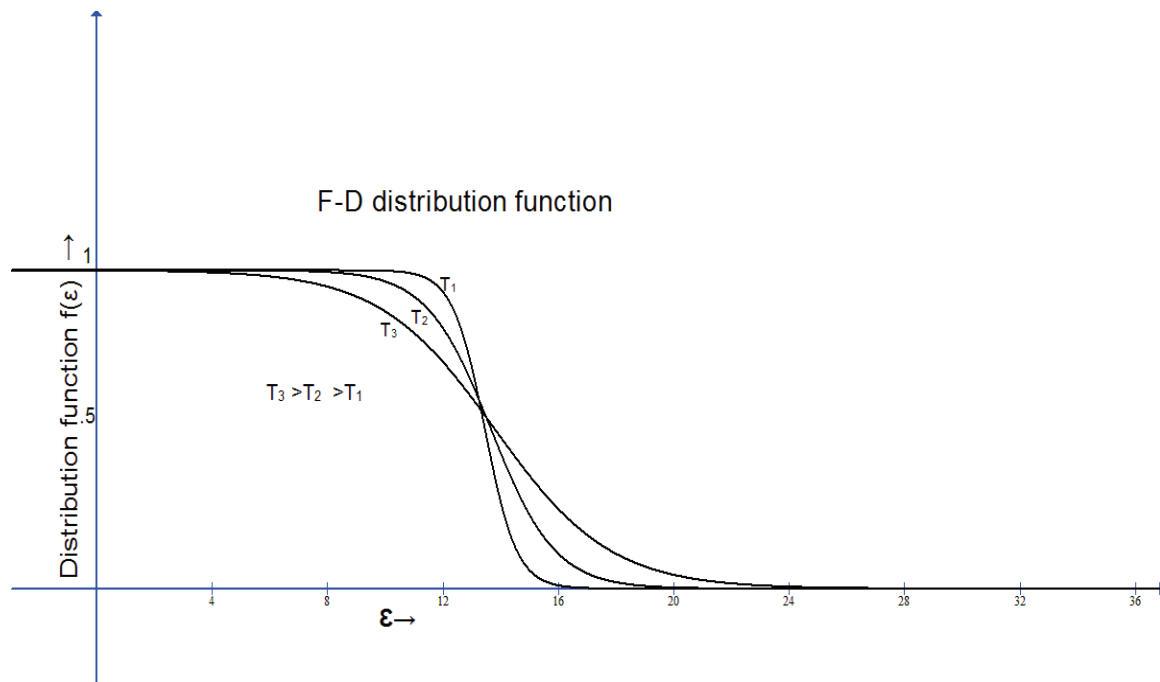
Fig (13.3)

$$n(\varepsilon)d\varepsilon \; = \; f(\varepsilon)g(\varepsilon)d\varepsilon$$

where $g(\varepsilon)$ is density of states. Thus $g(\varepsilon)d\varepsilon$ is number of accesseible states in energy range from ε to $(\varepsilon + d\varepsilon)$.

Therfore, eq. (13.38) modified as

$$n(\varepsilon)d\varepsilon = \frac{g(\varepsilon)d\varepsilon}{\left(e^{\alpha + \varepsilon. \frac{1}{kT}} + 1\right)} \tag{13.39}$$

for fermions like electrons $g(\varepsilon)d\varepsilon$ is given by

$$g(\varepsilon)d\varepsilon = \frac{2 \times 2\pi V(2m)}{\left(h^2\right)} d\varepsilon \tag{13.40}$$

In the expression the term 2 comes due to spin degenracy of electrons . So the F-D energy distrbution function for continuous system is given by

$$n(\varepsilon)d\varepsilon = \frac{2 \times 2\pi V(2m)}{\left(h^2\right)} \frac{\varepsilon^{1/2}d\varepsilon}{\left(e^{\alpha + \varepsilon. \frac{1}{kT}} + 1\right)} \tag{13.41}$$

13.6.3 BOSE-EINSTEIN DISTRIBUTION LAW

Consider a system of N identical and indistinguishable bosons. There is no constraint on the occupation of a particular state in an energy level because these particles do not obey the Pauli's principle. Any number of particles can occupy a state in an energy level.

$n_i =$0, 1, 2, 3,…… $n_i^{max} =\infty$. Let n_i be the number of particles occupying an energy level ε_i in a particular configuration. If g_i is the degeneracy of energy state ε_i ,then the number of possible arrangements amongst the degenerate levels of ε_i are

$$\Omega_i = \frac{(n_i + g_i -1)!}{n_i !(g_i -1)!} \tag{i}$$

Therefore, the total number of distinct ways of arranging N bosons into all possible energy states

$$\Omega \{n_1 ,n_2 ,n_3 ,..n_k \} = \prod_i \Omega_i \tag{ii}$$

Taking logarithm of both side of eq. (i)

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

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

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

$$= \ln\Omega_i = n_i \ln \frac{(n_i +g_i -1)}{n_i} +(g_i -1)\ln \frac{(n_i +g_i -1)}{(g_i -1)} \tag{iii}$$

As n_i and g_i both are much greater in comparison to 1. So we can drop all 1 in eq. (3), then we have

$$\ln\Omega_i = n_i \ln \left(1+ \frac{g_i}{n_i} \right)+ g_i \ln \left(1+ \frac{n_i}{g_i} \right) \tag{iv}$$

Differentiating eq. (iv) with respect to n_i we have

$$d \ln \Omega_i = \left[\ln \left(\frac{g_i}{n_i} +1 \right) + n_i \frac{\left(-g_i / n_i^2 \right)}{\left(\frac{g_i}{n_i} +1 \right)} + g_i \frac{\left(1/g_i \right)}{1+ \frac{n_i}{g_i}} \right] dn_i$$

By rearranging it

$$= \left[\ln\left(\frac{g_i}{n_i}+1\right) - \frac{g_i}{n_i}\left(\frac{1}{\frac{g_i}{n_i}+1}\right) + \left(\frac{1}{1+\frac{n_i}{g_i}}\right) \right] dn_i$$

Again rearranging the last two terms, we get

$$= \left[\ln\left(\frac{g_i}{n_i}+1\right) - \left(\frac{1}{1+\frac{n_i}{g_i}}\right) + \left(\frac{1}{1+\frac{n_i}{g_i}}\right) \right] dn_i$$

So we have

$$d \ln \Omega_i = \left[\ln\left(\frac{g_i}{n_i}+1\right) \right] dn_i \qquad\qquad (v)$$

Since

$$\ln \Omega\{n_1, n_2, n_3, ..n_k\} = \ln \prod_{i-1}^{k} \Omega i$$

$$= \sum_i \ln \Omega_i$$

$$d \ln \Omega = \sum_i d \ln \Omega_1$$

$$= \sum_i d \ln \Omega_i = \sum_i \left[\ln\left(\frac{g_i}{n_i}+1\right) \right] dn_i$$

To solve it completely we shall apply the Lagrange's method of undetermined multipliers.

$$d \ln \Omega - \left[\alpha \sum_i dn_i - \beta \sum_i \varepsilon_i dn_i \right] = 0$$

Thus,

$$\sum_i \left[\ln\left(\frac{g_i}{n_i} + 1 \right) - \alpha - \beta\varepsilon_i \right] dn_i = 0$$

$$= \ln\left(\frac{g_i}{n_i} + 1 \right) - \alpha - \beta\varepsilon_i = 0$$

or $$n_i = \frac{g_i}{\left(e^{\alpha + \beta\varepsilon_i} - 1 \right)} \qquad\qquad (13.42)$$

This is the equation for most probable distributinon of particles among different quantized energy levels for bosons. It gives the population of an energy level that has energy ε and degenracy g. the constant α and β are determined from the constraints related to the total number of particles and the total energy .S.N Bose in 1924 derived Planck's radiation formula on the basis of Planck's hypothisis of quntization of energy in light photons whose number is not conserved . Later on Einstein extended the same idea for subatomic particles having integral spin, whose number is conserved . Hence the particle distribution function , eq. (13.42) was named as Bose – Einstein distribution law .

13.6.4 B-E ENERGY DISTRIBUTION FUNCTION

The energy distribution function f (ε$_i$) is the average number of bosons per quantum state in the energy level ε$_i$. Since the degeneracy of ith state is g$_i$ and number of particles in that state is n$_i$, hence by the definition, energy distribution function will be

$$f(\varepsilon_i) = \frac{n_i}{g_i} = \frac{1}{\left(e^{\alpha + \beta\varepsilon_i} - 1 \right)}, \qquad\qquad \text{since, } \beta = \frac{1}{kT}$$

$$f(\varepsilon_i) = \frac{n_i}{g_i} = \frac{1}{\left(e^{\alpha + \varepsilon_i \cdot 1/kT} - 1 \right)} \qquad\qquad (13.43)$$

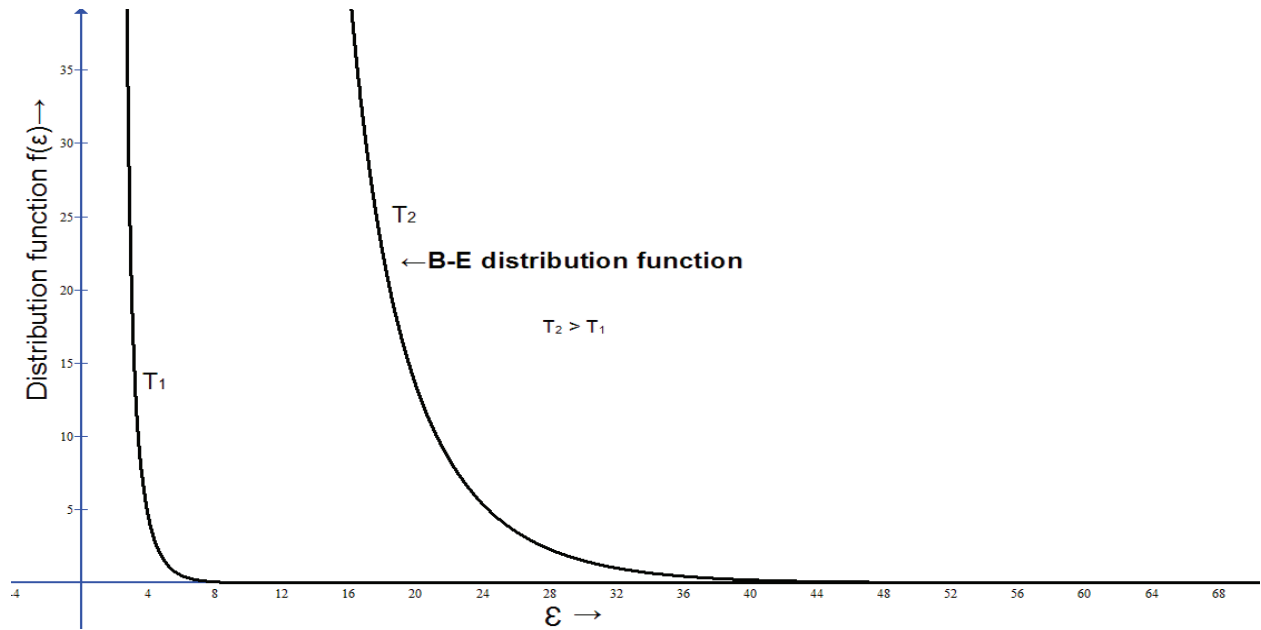The variation of energy distribution function at different temperatures (T$_2$> T$_1$) shown in fig.(13.4)

Fig.(13.4)

In the case when energy levels are very close ,then the descrete distribution of energy levels may be considerd as continous and then the number of particles having energy range from ε to (ε+ dε) is given by

$$n(\varepsilon)d\varepsilon \ = \ f(\varepsilon)g(\varepsilon)d\varepsilon$$

where g(ε)dε is number of accessible states in energy range from ε to (ε+ dε) .

Hence the equation is modified as

$$n(\varepsilon)d\varepsilon = \frac{g(\varepsilon)d\varepsilon}{\left(e^{\alpha+\varepsilon.\frac{1}{kT}}-1\right)} \qquad (13.44)$$

for bosons like He gas g(ε)dε is given by

$$g(\varepsilon)d\varepsilon = \frac{2\times 2\pi V(2m)}{\left(h^2\right)}d\varepsilon \qquad (13.45)$$

the term 2 comes due to spin degenracy of bosons . So the F-D energy distrbution function for continuous system is given by

$$n(\varepsilon)d\varepsilon = \frac{2\times 2\pi V(2m)}{\left(h^2\right)}\frac{\varepsilon^{1/2}d\varepsilon}{\left(e^{\alpha+\varepsilon.\frac{1}{kT}}-1\right)} \qquad (13.46)$$

13.7 COMPARISION OF THREE DISTRIBUTION LAWS

The energy distrbution functions $f(\varepsilon_i)$ for all three statistics combindly can be written as

$$f(\varepsilon_i) = \frac{n_i}{g_i} = \frac{1}{\left(e^{\alpha + \varepsilon_i \cdot 1/kT} + \delta\right)}$$

(13.47)

$f(\varepsilon_i)$ is also known as occupation index. The term $\delta = 0$ for M-B statistics, $\delta = +1$ for F-D statistics and $\delta = -1$ for B-E statistics . other term e^{α} called degenracy parameter, which is a function of temperature , mass and density of the system . Since $\delta = 0$ for M-B distribution , so distribution function is purely exponential . In case of photon gas $\alpha = 0$, since rest mass of photons are zero . The $\delta = -1$ comes in B-E distribution because of any number of particles can occupy a single energy state . The $+ 1$ term comes in F-D distribution due to Pauli 's exclusion principle . whetver be the value of T ,εor α, f (ε) for fermions can never be greater than 1.
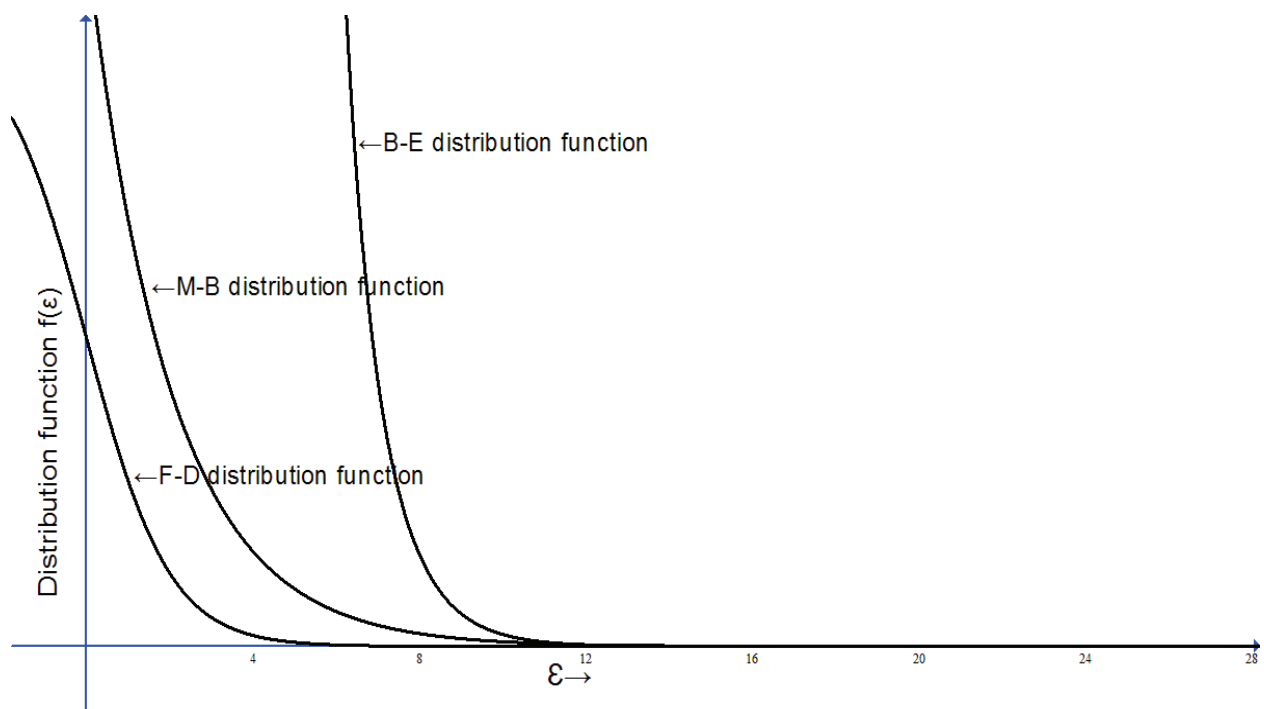

Fig (13.5)

Hence if we plot all distrbution function under the same condition i.e., taking α same for all fig. (13.5) , the B-E function is always higher then M-B function ,and F-D function is always lower . When $\varepsilon \gg kT$ the exponential term $e^{\alpha + \varepsilon_i \cdot 1/kT} \gg 1$ so the effect of $+ 1$ or -1 is

negligible in F-D and B-E distributions. In such conditions F-D and B-E distribution laws

reduce to M-B distibution .

Example 1
In Maxwell-Boltzmann statistics valid for hydrogen gas at standard temperature and pressure (STP), 273 K, and 1 atmosphere?

Solution

Under STP 1 mol H_2 gas = 6.02 x10^{23} molecules occupies 22.4 liter
Mass of H_2 molecule m = 3.34 x 10^{-27} kg,

$$n = \frac{6.02 \times 10^{23}}{22.4 \times 10^{-3}} = 0.269 \times 10^{26}$$

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

$k = 1.381 \times 10^{-23}$ J/K   , substituting these values in equation

$$n \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} = 1$$

$$\eta = 0.269 \times 10^{26} \left(\frac{\left(6.626.10^{-34}\right)^2}{2 \times 3.14 \times 3.34 \times 10^{-27} \times 1.381 \times 10^{-23} \times 273} \right)^{\frac{3}{2}}$$

= 8.83x 10^{-8}<< 1 so H_2 behaves like a classical gas at STP, for it M.B. statistics is applicable.

Example 2
Is the Maxwell-Boltzmann statistics valid for electrons in Silver?

Solution
Silver has a density of 10.5 g/cm^{-3} and molar weight 197.9 g. assuming one free electron per silver atom, density n of free electrons is

$$\frac{10.5}{197.9} 6.02 \cdot 10^{23} \, electrons \, / \, m^3 = 5.86 \cdot 10^{28} \, electrons \, / \, m^3$$

Mass of electron is 9.109 10^{-31} kg

Assuming 'room temperature' T = 300 K, substituting in equation

$n \left(\dfrac{h^2}{2\pi m k_B T} \right)^{3/2}$ gives 4.46. As it is greater than 1, the Maxwell-Boltzmann statistic is not

applicable for silver.

This is because of the two reasons, small mass of electron, density of electrons in silver about 2000 times higher than density of H_2 at STP. Since electrons are fermions, so Fermi-Dirac statistics is applicable here.

Example 3

Eight particles are distributed in ten energy cells of equal size .Calculate all possible ways of this distribution when particles are (i) Classical particles (ii) Bosons (iii) Fermions

Solution

(i) Since classical particles are distinguishable. They obey M-B statistics.
Given N = 8 and number of cells k = 10

Total possible distribution or total number of microstates $\Omega_{MB} = (k)^N = (10)^8 = 10^8$

(ii) Number of possible distribution for bosons, $\Omega_i = \dfrac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$

$n_i = 8$ and $g_i = 10$
So the number of possible ways of this distribution when the particles are bosons

$$\Omega_{BE} = \frac{(8+10-1)!}{8!(10-1)!} = \frac{17!}{8!9!} = \frac{17 \times 16 \times 15 \times 14 \times 13 \times 12 \times 11 \times 10}{8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1} = 24310$$

(iii) Number of possible distribution for fermions, $\Omega_i = \dfrac{g_i!}{n_i!(g_i - n_i)!}$

$n_i = 8$ and $g_i = 10$,
So the number of possible ways of this distribution when particles are fermions

$$\Omega_{FD} = \frac{10!}{8!(10-8)!} = \frac{10!}{8!2!} = 45$$

It is clear from the above calculations that $\Omega_{MB} > \Omega_{BE} > \Omega_{FD}$

13.8 SUMMARY

1. The thermal de –Broglie wavelength of a "wave packet" associated with each gas particle

of mass m is given by, $\lambda_T = \dfrac{h}{\sqrt{2\pi m k_B T}}$

2. In quantum mechanics the state of the system can be specified by calculating its wave-function Ψ ($q_1, \cdots, q_f, s_1, \cdots, s_g$, t), the future time evolution of the wave-function is

fully determined by Schrodinger equation. $\widehat{H}.\Psi(r, t) = i\hbar\dfrac{\partial\Psi(r,t)}{\partial t}$

3. Identical particles in a system are those particles which when interchanged in the system

   will not make any change in it.

4. The condition for applicability of classical statistics is $r_o \gg \lambda_T$ or $(\frac{1}{n})^{1/3} \gg \lambda_T$ or

$n \lambda_T^3 \ll 1$, this condition is fulfilled when particle density 'n' is low and temperature T is high.

The M-B distribution is given by $n_i = g_i e^{-\alpha - \epsilon_i / kT}$

5. The quantum statistics is applicable when the condition $n \lambda_T^3 \approx 1$ is fulfilled. Then wave functions of different particles begin to overlap, so becomes indistinguishable and the system has to be treated according to quantum statistics.

6. Symmetric wave function represents the Bosons having integral angular momentum $= n\hbar$ where n = 0, 1, 2, 3…. . So it is a wave function for the Bosons.

7. Anti-symmetric wave functions describing Fermions having spin angular momentum $= (1/2 + n) \hbar$ where n=0, 1, 2, 3… which obeys Pauli Exclusion Principle.

8. The probability that two bosons are in the same state is twice the probability that two distinguishable particles will be in the same state.

9. Fermions can never be in the same quantum state. Because, fermions always follow Pauli's Exclusion Principle.

10. Fermi-Dirac distributions are $n_i = \dfrac{g_i}{\left[e^{\alpha + \beta \varepsilon_i} + 1 \right]}$ and Bose-Einstein distribution function is

$n_i = \dfrac{g_i}{\left(e^{\alpha + \beta \varepsilon_i} - 1 \right)}$ respectively.

11. When $\varepsilon \gg kT$ the exponential term $e^{\alpha + \varepsilon_i \cdot 1/kT} \gg 1$ so the effect of $+ 1$ or -1 is negligible

in F-D and B-E distributions , in such conditions F-D and B-E distribution laws reduce

to M-B distibution .

13.9 TERMINAL QUESTIONS

1. Explain the principles of quantum statistical mechanics and discuss the significance of wave function in quantum statistics.
2. Explain the need of quantum statistics.
3. What do you understand by the terms identical particles and indistinguishability.
4. What is de-Broglie thermal wavelength?
5. What are the classical and quantum domains of statistical mechanics?
6. What are the symmetry requirements in quantum statistics?
7. Construct symmetric and anti-symmetric wave functions for 3 particle system having two states.
8. Differentiate pure and mixed states.
9. What is density operator? Write its properties.
10. Explain Pauli's exclusion principle. What type of particles follow this principle?
11. Derive Fermi – Dirac distribution law.
12. What is energy distribution function?
13. Using Fermi – Dirac distribution law, establish F-D energy distribution function.

14. What will be the number of arrangements of distributing 2 indistinguishable particles in 4 cells when only one particle can occupy one cell?   (Ans. 6)
15. What are bosons ?Which statistics is used to study bosonic system
16. Derive Bose – Einstein distribution functions.
17. Using Bose– Einstein distribution law , establish Bose– Einstein energy distribution Function.
18. In how many ways can 2 particles be distributed in 5 states, if particles are:
(i) distinguishable (ii) indistinguishable and follows Bose-Einstein statistics.
(Ans. (i) 25 (ii) 15)
19. Compare all the three statistical distribution laws.
20. Classify the particles as Bosons and Fermions: α, β , and γ particles , H_2 molecule, H atom,He atom, He^+ ion, O_2.

13.10 REFERENCES AND SUGGESTED READINGS

1.   Reif, F. Fundamentals of Statistical and Thermal Physics. New York, NY: McGraw-Hill, June 1, 1965. ISBN: 0070518009.
2.   Beiser, A., Mahajan S., S.RaiChoudhary. Concepts of Modern Physics. 6th edition 2009 (Tata McGraw Hill, NewDelhi)ISBN: 978-0-07-015155-0.
3.   Huang, Kerson, Statistical Mechanics, 2nd ed., John Wiley & Sons, Inc., 1987, ISBN 0-471-81518-7.
4.   Pathria, R. K., Statistical Mechanics, 2nd ed., Butterworth-Heinemann, Burlington, MA, 1996, ISBN 0 -7506-2469-8.
5.   Zemansky, M., and R. Dittman. Heat and thermodynamics: an intermediate textbook. 7th Ed. New York, NY: McGraw-Hill Companies, 1997. ISBN: 0070170592
6.   Hemne, P.S,Subrahmanyam N.,Brijlal .Heat and Thermodynamics. S Chand pub. New Delhi, 2014. ISBN 81-219-2813-3.
7.   Laud, B.B. Fundamentals of Statistical Mechanics. 2nd edition 2012. ISBN 978-81-224-3278-7
8.   Satya Prakash, Statistical Mechanics. edition 2014 (Kedar Nath Ram Nath pub, Delhi).
9.   Introduction to quantum theory: D. Park, 3rd Edition (McGraw-Hill, New York NY, 1992).
10.   Sinha, H.P. Kinetic Theory Thermodynamics & Statistical Physics. ed 2004, pub. Ram Nath and Sons, Agra India.
11.   Kumar A. and Taneja, S.P. Thermal Physics and Statistical Mechanics, R. Chand & Co. Pub., New Delhi (2017).